2020

Zientzia eta Teknologia Fakultateko VII. Ikerkuntza Jardunaldiak

VII Jornadas de Investigación de la Facultad de Ciencia y Tecnología

www.ztf-fct.org

Klima-aldaketa

Cambio Climático

Leioan, 2020ko irailaren 30a

Lankide agurgarriak,

2020ko martxoaren 16, 17 eta 18an Zientzia eta Teknologia Fakultatean “VII. Ikerketa Jardunaldiak” egin behar ziren, **Klima Aldaketa** lelopean.

COVID19 pandemia zela eta, Jardunaldiak irailaren amaierara atzeratu ziren. Zoritxarrez, pandemiak aurrera jarraitzen du eta ezin izango dugu jardunaldietan, Nazioarteko Ingurumen-politikako Aholkulari eta Kontsultorea eta Klima Aldaketari buruzko Nazio Batuen Konbentzioko Idazkari Exekutibo ohia, Yvo de Boer jauna, gure artean eduki. Horregatik erabaki dugu Fakultateko VII. Ikerketa Jardunaldien lehen egunean egingo zen Klima Aldaketari buruzko egunaren ospakizuna pandemia gainditu arte itxarotea.

Gaur egun bizi dugun egoera kezkagarria izan arren, gure ustez komenigarria da Fakultateko VII. Ikerketa Jardunaldiak egitea, modu birtualean bada ere, egoerak eskatzen duen bezala, eta bertan jarduera hauek aurkeztuko dira:

1) Jardunaldiak EHUko Ikerketako errektoreordearen eta Fakultateko dekanoaren ongietorriarekin hasiko dira. Ongietorria irailaren 30ean jarriko da ZTF-FCTren webgunean.
2) Zentroko ikerketa-taldeek irailaren 30etik urriaren 7ra bitartean beren ikerketa poster moduan aurkeztuko dute, kasu honetan modu birtualean, eta Fakultatearen webgunean ikusi ahal izango dira. Era berean, ohi bezala, aurkeztutako poster onena sarituko da.
3) Programatu ziren doktorego aurreko ikertzaileen ahozko komunikazioak bideo moduan aurkeztuko dira web-orrian.
4) Aurreko Ikerketa Jardunaldietan bezala, "Abstracts" liburuak Fakultateko taldeen ikerketa argitaratuko du, eta aurten aurkeztutako posterrak ere jasoko ditu.

Zientzia eta Teknologia Fakultateko VII. Ikerketa Jardunaldiak birtualki jarraitzea animatzen zaituztet,

Jaso agur bero bat,

Fernando Plazaola

Leioa, 30 de septiembre de 2020

Estimadas compañeras, estimados compañeros,

Los días 16, 17 y 18 de marzo de 2020 se iban a celebrar en la Facultad de Ciencia y Tecnología las "VII Jornadas de Investigación", con el lema: **Cambio Climático.**

Sin embargo, con motivo de la pandemia las Jornadas se retrasaron a finales de septiembre. Desgraciadamente, la pandemia continúa y no podremos contar en las mismas con D. Yvo de Boer, asesor y consultor en política ambiental internacional y ex Secretario Ejecutivo de la Convención Marco de las Naciones Unidas sobre el Cambio Climático. Razón por la cual hemos decidido esperar a la superación de la pandemia para celebrar el día relativo al Cambio Climático que iba a tener lugar el primer día de las VII Jornadas de Investigación de la Facultad.

A pesar de la situación en la que nos encontramos, hemos creido conveniente celebrar las VII Jornadas de Investigación de la Facultad, aunque sea de manera virtual, como la situación lo exige, y en la misma se presentarán las siguientes actividades:

1) Las Jornadas comenzarán con la bienvenida del Vicerrector de Investigación de la UPV/EHU y el Decano de la Facultad que se colgará el 30 de septiembre en la página web de la ZTF-FCT.
2) Los grupos de investigación del Centro presentarán su investigación en forma de póster, en este caso de manera virtual, y durante los días 30 de septiembre al 7 de octubre, los posters podrán ser visualizados en la página web de la Facultad. Así mismo, como es habitual se premiará al mejor poster presentado.
3) Las comunicaciones orales de los investigadores predoctorales que se habían programado se presentarán en forma de video en la página web.
4) Como en Jornadas de Investigación anteriores se publicará el libro de "abstracts" con la investigación de los diferentes grupos de la Facultad, que este año también incluirá los posters presentados.

Animándoos a que sigáis virtualmente las VII Jornadas de Investigación de la Facultad de Ciencia y Tecnología,

Recibid un cordial saludo,

Fernando Plazaola

ABSTRACTS

IDATZIZKO KOMUNIKAZIOAK

COMUNICACIONES ESCRITAS

Klima-aldaketa
Cambio Climático

BIOZIENTZIAK

BIOCIENCIAS

Klima-aldaketa
Cambio Climático

How to adapt the agro-pastoral systems to global change: experimental approaches for designing suitable alternatives

Agirresarobe, A.[1], Aiartzaguena, L.[1], Aldezabal, A.[1], Andonegi, A.[1], Del Canto-Romero, A.[2], García-Baquero, G.[1], Herrero, A.[1], Lacuesta, M.[2], Laskurain, N.A.[2], Martínez-Goñi, X.S.[1], Mena-Petite, A.[1], Miranda-Apodaca, J.[1], Muñoz-Rueda, A.[1], Odriozola, I.[1], Pardo, I.[1], Pérez-López, U.[1], Sanz-Sáez, A.[2], Sarrionandía-Areitio, E.[2], Yoldi-Achalanbaso, A.[1]

Dpto. Biología Vegetal y Ecología, [1]FCyT y [2]Fac. Farmacia, UPV/EHU

KEY WORDS: Biodiversity, cereals, climate change (drought, salinity, elevated CO2 and high temperature), ecosystem multifunctionality, legume-rhizobium symbiosis, soil-plant-herbivore interaction.

The global change, which includes climate change (warming, drought, etc.) and land use change, has been defined as the most change driver governing the planet future. These changes modify plant growth and productivity, food quality, and productive systems' sustainability and resilience. In fact, global change is transforming food production systems, such as agricultural crops and extensive grazing in mountain areas, altering species distribution, production practices and land use. In this context, basic and applied research is needed to understand, not only the impact of climate change on plant production and quality, but also the adaptation capacity of agricultural crops and grassland resources to climate change, seeking new strategies to minimize its negative impact and to favour production sustainability under the future climatic conditions. Specifically, in our research group (IT1022-16), the following three experimental approaches are been performed currently:

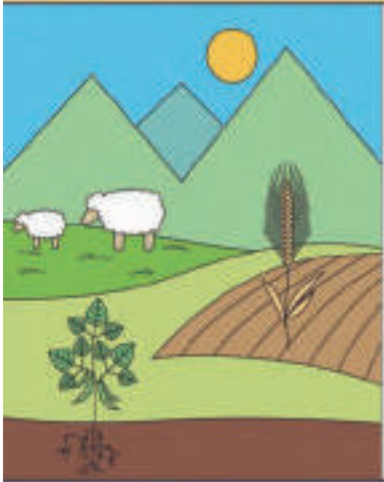
- Experiment 1: The objective is to look for strategies for increasing legumes' productivity under climate change, selecting cultivars and *Rhizobium* strains of high symbiotic efficiency under controlled and field conditions either in organic or conventional farming.

- Experiment 2: The objective is to understand how climate change affects barley production and quality, and to select which are the most important physiological traits that determine these impacts. The studies are done in environmental controlled growth chambers where more than one climatic variable can be simulated. Physiological and metabolic measurements on growth, water relations, photosynthetic, nitrogen, and antioxidant metabolism are done. Experiment 1 and 2 will give relevant information to breeders in order to advice on which plant parameters should they take into account to maintain or maximize productivity and quality with future increases of CO_2 and temperature, and transfer this information to politicians and farmers.

- Experiment 3: The aim is to analyze the environmental impacts of dairy sheep farms using the LCA methodology (Life Cycle Assessment). To do so, the data of 30 sheep farms of the Latxa breed have been collected (24 conventional farms and 6 organic farms). We expect worse results in the case of organic farms due to the lack of local and specific data and the "productivity-based" view of the methodology. Therefore, it would be necessary to consider other aspects that could balance the comparison between typologies, such as carbon sequestration, biodiversity and ecotoxicity, among others.

Acknowledgements: IT1022-16, EHUA16/17, AGL2013-48361-C2-1-R and Project 32-2016-00043 from Departamento de Desarrollo Económico e Infraestructuras del Gobierno Vasco.

HOW TO ADAPT THE AGRO-PASTORAL SYSTEMS TO GLOBAL CHANGE: EXPERIMENTAL APPROACHES FOR DESIGNING SUITABLE ALTERNATIVES



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EXPERIMENT 1

EXPERIMENT 2

EXPERIMENT 3

Acknowledgements and colaborators

IT1022-16, EHUA16/17, AGL2013-48361-C2-1-R and Project 32-2016-00043 from Departamento de Desarrollo Económico e Infraestructuras del Gobierno Vasco.

Marine and estuarine plankton ecology

Villate, F.[1,3], Iriarte, A.[2,3], Uriarte, I.[2,3], Seoane, S.[1,3], Laza-Martínez, A.[1,3], Madariaga, I.[1], Blanco, E.[1,3], Barroeta, Z.[1,3], Txurruka, E.[1], Bilbao, J.[1,3], Llorente A.[1,4]

[1]Landare-Biologia eta Ekologia Saila, Zientzia eta Teknologia Fakultatea, UPV/EHU; [2]Landare-Biologia eta Ekologia Saila, Farmazia Fakultatea, UPV/EHU; [3]Itsas Biologia eta Bioteknologia Esperimentalen Ikerketa Zentroa PIE, UPV/EHU; [4]AMBIOTEK S.L., Erandio Etorbidea 11 B bajo, Altzaga

KEY WORDS: Planktona, Itsaso, Estuarioak, Bioindikatzaileak.

Abstract

"Marine and estuarine plankton ecology" group of the Department of Plant Biology and Ecology is made up of eleven researchers: six lecturers, a Ph.D. researcher, and four doctoral researchers. The activity of the group focuses on the monitoring of the plankton ecosystem, especially, on the influence of natural and anthropic factors on the zooplankton. In addition, another aim of our study is the use of plankton as bioindicators of environmental change, among others, the influence of harmful algae and the occurrence of invasive zooplankton. For this purpose, since 1997 monthly samplings have been carried out in the estuaries of Bilbao and Urdaibai, which include both measurements of abiotic parameters and biological community organisms. The analyses of these organisms are carried out using different methods, both traditional and microscopy, as well as more recent methods, such as genetic analysis. In our estuaries, the main group of phytoplankton is that of diatoms and metagenetic analyses have greatly facilitated their identification. Regarding zooplankton, phenology changes are associated to latitude gradient, thus, the zooplankton of our coast is much earlier if we compare it with the zooplankton of the North Sea. On the other hand, replacement processes have been detected at different steps in our estuaries. At these phases, copepod species like *Acartia tonsa*, *Oithona davisae*, *Pseudodiaptomus marinus*, have appeared, colonized and dominated our estuaries. Thanks to our research, we are part of various international organizations, such as ICES/CIEM (International Council for the Exploration of the Sea), and our data/results can be found in global databases.

ITSASO ETA ESTUARIOEN PLANKTON EKOLOGIA

TALDEARI BURUZKO INFORMAZIOA

Nor gara?

TALDEKIDEAK:
FERNANDO VILLATE
ARANTZA IRIARTE
IBON URIARTE
SERGIO SEOANE
AITOR LAZA-MARTINEZ
IOSU MADARIAGA
ESTHER BLANCO
ZIORTZA BARROETA
ESTIBALITZ TXURRUKA
JONE BILBAO
ALFREDO LLORENTE

SAILA: **LANDAREEN BIOLOGIA ETA EKOLOGIA**
FAKULTATEA: **ZIENTZIA ETA TEKNOLOGIA, ETA FARMAZIA**
ERAKUNDEA: **UPV/EHU. PIE – UPV/EHU**

Zer ikertzen dugu?

IKERKETA-LERROAK:
- Kutsaduraren eta klima-aldaketaren inpaktua plankton-ekosistemetan
- Alga kaltegarrien eragina
- Zooplankton inbaditzailearen eragina
- Iktioplankton/arrainen erantzuna inguruneko aldaketei

Zertan jarduten dugu?

Plankton-ekosistemaren monitorizazioa
Ekosistemak: Bilbo eta Urdaibaiko estuarioak
Noiztik: 1997tik aurrera
Inguruneko neurketak: gazitasuna, tenperatura, oxigeno disolbatua, uhertasuna
Komunitate-deskriptoreak: zooplankton abundantzia eta konposizioa eta fitoplanton biomasa





Fitoplankton eta zooplaktonaren taxonomia
Teknikak: mikroskopia optikoa, elektronikoa eta epifluorestzentziakoa, HPLC eta teknika molekularrak

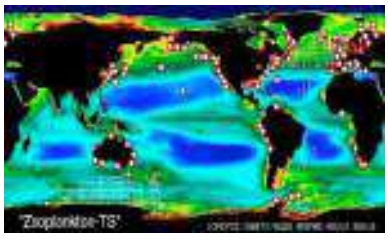

Fitoplankton eta zooplakton kultiboak eta esperimentazioa


Zein da gure nazioarteko proiekzioa?

ICESeko lan-taldeetan partaidetza
(International Council for the Exploration of the Sea)
- *Working Group on Zooplankton Ecology (WGZE)*
- *Working Group on Phytoplankton and Microbial Eology (WGPME)*
- *WGEUROBUS* (Working Group "Towards a EURopean OBservatory of the non-indigenous calanoid copepod Pseudodiaptomus marinUS"

Mundu-mailako datu basetan aritzea
NOAA, COPEPODITE zooplankton time series report and photo gallery
IGMETS (International Group of Marine Ecological Time Series)
Bilbao: https://www.st.nmfs.noaa.gov/copepod/time-series/es-30101/
Urdaibai: https://www.st.nmfs.noaa.gov/copepod/time-series/es-30102/

WG125 Zooplankton Time Series Collection (SCOR, 2016)

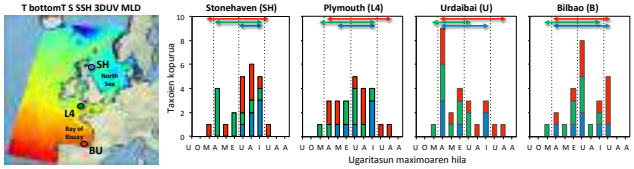


AZKEN URTEETAKO ZENBAIT EMAITZA

Zooplanktonaren ezberdintasun fenologikoa latitude eta egoera trofikoaren arabera

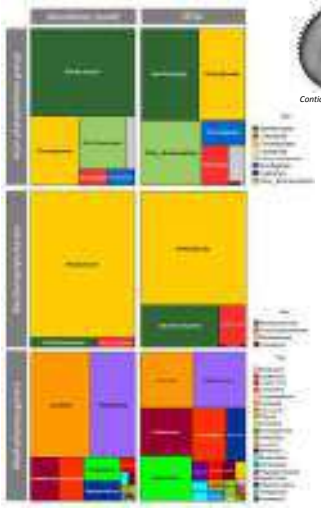
Latitudearen eragina: Taxoi gehienen urteko maximo berantiarrenak Ipar itsasoko Stonehavenen eta goiztiarrenak Bizkaiko Golkoko Urdaibain

Egoera trofikoaren eragina : Taxoi gehienen urteko maximo berantiarrenak Bilboko sistema mesotrofikoan eta goiztiarrenak Urdaibaiko sistema oligotrofikoan

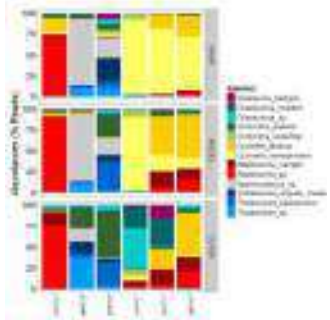


Fitoplanktonaren azterketa Bilboko estuarioan

2000. urteaz geroztik Bilboko estuarioko fitoplankton komunitatearen egitura aztertu dugu teknika ezberdinak erabiliz: argi zein elektroi mikroskopia, HPLC bidezko pigmentu analisia, analisi metagenetikoak. Fitoplankton talde zehatzetan jarri dugu arreta: espezie toxikoak dituztenak edota hazkuntza masiboak sortzen dituztenak. Azken hauen adibide, **diatomeoak:**

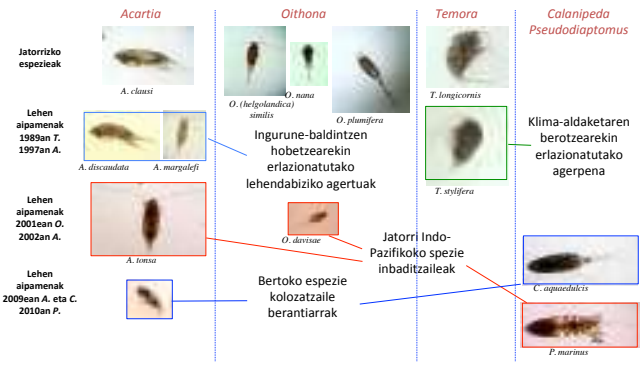


Ugarien diren **diatomeo** espezieak nekez identifikatu daitezke argi mikroskopioan eta elektroi-mikroskopia nekeza da. Alternatiba: analisi metagenetikoa

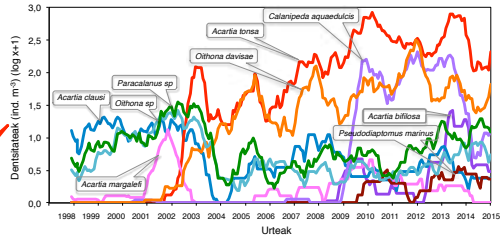


Bilboko itsasadarraren zooplankton bilakaera: 1980-2015

Copepodo espezie berriak 1980tik
Hiru txandatan ailegatu ziren: 1996an baino lehen, 2001-2002 urteetan eta 2009-2010 urteetan



Kopepodo espezieen bilakaera barnealdean: Espezie inbaditzaile gazikarek ordezkatu dituzte bertako espezie neritikoak berreskuratze prozesuan



Ecophysiology of plant stress and soil contamination (EKOFISKO)

José Mª Becerril[1] *(I.P.), José I. García Plazaola*[1]*, Antonio Hernández*[1]*, Raquel Esteban*[1]*, Mª Teresa Gómez*[2]
RESEARCHERS: Unai Artetxe[1]*, Aritz Burges*[1]*, Rafael Gómez*[1]*, Irati Arzak*[1]*, Juan Vilela*[1], Manuel Encinas[3]
[1]Department of Plant Biology and Ecology; [2] Department of Biochemistry and Molecular Biology; [3]Basque Centre for Climate Change

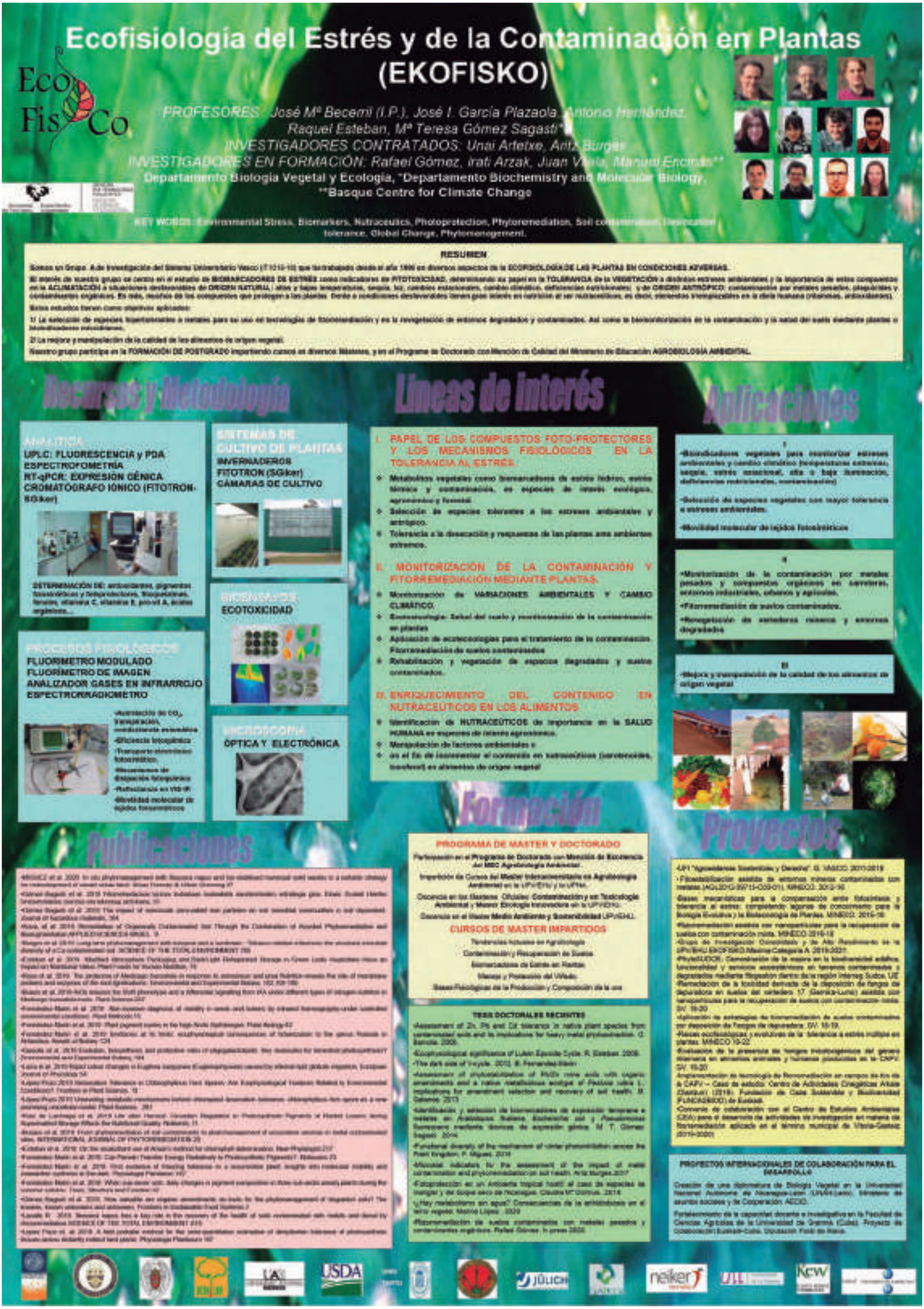
KEY WORDS: Environmental Stress, Biomarkers, Nutraceutics, Photoprotection, Phytoremediation, Soil contamination, Desiccation tolerance, Global Change, Phytomanagement.

Since 1990, the EKOFISKO group has developed research and teaching activities on physiological and ecophysiological aspects of natural and anthropic agents causing stress in plants. Our group is a consolidated research group distinguished with the highest grade of the Basque Government classification for Scientific Groups and it is composed of 7 PhD and 4 PhD students.

Our group has developed a variety of novel methodological tools: (i) determination of plant stress biomarkers, in particular those related to photoprotection and oxidative stress, (ii) set up of plant toxicity bioassays to determine the ecotoxicological effects of pollutants in contaminated soils, and (iii) implementation of physiological parameters to evaluate phytotoxicity or damage caused by natural stress conditions as extreme temperatures, drought, light intensity, nutritional disorders, etc. In collaboration with other groups, we have incorporated genomic methodologies with emphasis in differential gene expression and in the application of DNA microarrays to assess and monitor soil health in a multidisciplinary approach; and developed a procedure to study molecular mobility of photosynthetic tissues, which is relevant to understand the mechanisms that underpin tolerance to desiccation. These methodologies have been implemented in several more applied research areas:

- Determination of the role of photoprotective compounds and tolerance to stress conditions (natural or anthropic) with particular emphasis on the acclimation to extreme environmental conditions, such as those prevailing at high altitudes, forest understory or historically polluted sites.
- Use of plant biomarkers to monitor environmental and global change and genotype plant selection for tolerance to adverse climatic agents and to the soil ecotoxicology.
- Identification of environmental agents to enhance nutraceutical compounds (carotenoids and tocopherols) in plant foods.
- Use of plants for ecological restoration of degraded environments, specially polluted soils through ecotechnologies as phytomanagement and bio- and phytoremediation (phytostabilization, phytoextraction and rhizodegradation).
- Assessment and monitoring soil health with biological indicators during remediation processes.

The research indicated above is currently carried out in a multidisciplinary approach in collaboration with relevant national and international scientists from universities (Complutense de Madrid, Autónoma de Barcelona, La Laguna, Helsinki, La Frontera, Tartu, Australian National, Innsbruck, St. Thomas, Florence, etc) and institutions (Neiker, Gaiker, Ayto. Vitoria-Gasteiz, Phytosphere Institute, Royal Kew Gardens, USDA, NASA, etc), and supported regularly by competitive projects (EU, Spanish Ministries). The quality of group's achievements is supported by regular publications in international journals. We also have a compromise on the cooperation for development, with several projects in Latin American universities (Chile, Nicaragua, Puerto Rico and Cuba). Besides, we participate in four Master Programs: "Agrobiología Ambiental", "Environmental Contamination and Toxicology", "Enología Innovadora" and "Medio Ambiente, Sostenibilidad y ODS"; and in the Doctorate Program "Agrobiología Ambiental".


Ecofisiología del Estrés y de la Contaminación en Plantas
(EKOFISKO)
Eco Fis Co
PROFESORES: José Mª Becerril (I.P.), José I. García Plazaola, Antonio Hernández, Raquel Esteban, Mª Teresa Gómez Sagasti*
INVESTIGADORES CONTRATADOS: Unai Artetxe, Aritz Burges
INVESTIGADORES EN FORMACIÓN: Rafael Gómez, Irati Arzak, Juan Vilela, Manuel Encinas**
Departamento Biología Vegetal y Ecología, *Departamento Biochemistry and Molecular Biology,
**Basque Centre for Climate Change
KEY WORDS: Environmental Stress, Biomarkers, Nutraceutics, Photoprotection, Phytoremediation, Soil contamination, Desiccation tolerance, Global Change, Phytomanagement.
RESUMEN
Recursos y Metodología
Líneas de interés
Aplicaciones
ANALÍTICA
UPLC: FLUORESCENCIA y PDA
ESPECTROFOTOMETRÍA
RT-qPCR: EXPRESIÓN GÉNICA
CROMATÓGRAFO IÓNICO (FITOTRON-SGIker)
SISTEMAS DE CULTIVO DE PLANTAS
INVERNADEROS
FITOTRON (SGIker)
CÁMARAS DE CULTIVO
BIOENSAYOS
ECOTOXICIDAD
PROCESOS FISIOLÓGICOS
FLUORÍMETRO MODULADO
FLUORÍMETRO DE IMAGEN
ANALIZADOR GASES EN INFRARROJO
ESPECTRORRADIÓMETRO
MICROSCOPÍA
ÓPTICA Y ELECTRÓNICA
I. PAPEL DE LOS COMPUESTOS FOTO-PROTECTORES Y LOS MECANISMOS FISIOLÓGICOS EN LA TOLERANCIA AL ESTRÉS.
II. MONITORIZACIÓN DE LA CONTAMINACIÓN Y FITORREMEDIACIÓN MEDIANTE PLANTAS.
III. ENRIQUECIMIENTO DEL CONTENIDO EN NUTRACEÚTICOS EN LOS ALIMENTOS
Formación
PROGRAMA DE MASTER Y DOCTORADO
CURSOS DE MASTER IMPARTIDOS
TESIS DOCTORALES RECIENTES
Publicaciones
Proyectos
PROYECTOS INTERNACIONALES DE COLABORACIÓN PARA EL DESARROLLO
USDA
JÜLICH
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Kew

Terrestrial plant diversity group: research for understanding plant communities and populations, and their evolution and conservation during climate change

Juan A. Campos[1], Itziar García-Mijangos.[1], Idoia Biurrun[1], Diego Liendo[1], Daniel García-Magro[1,4], Pablo Arufat[1,4], Adrián Fuente[1,4], Víctor García-Riaño[1,4], Camila Subieta[1,4], Irati Díaz[1,4], Maialen Martínez[1,4], Elena Goñi[1,4], Sara Sánchez[1,4], Ander Cocó[1,4], Unai Zorrozua[1,4], Jon Larrinaga[1,4], Gorka Melgar[1,4], Peter B. Pearman[1,2,3], Javier Loidi[1]
1. Dept. of Plant Biology and Ecology UPV/EHU; 2. IKERBASQUE; 3. BC3; 4. UPV student researcher

KEY WORDS: climate change, community classification, human impact, functional and phylogenetic diversity, invasive species, molecular ecology, phylogeny, evolution, molecular biology, threatened species, survey, vegetation structure

Our group has evolved over 30 years, from a focus on the diversity, mapping and classification of plant communities to include taxonomic, functional, and phylogenetic diversity of communities, monitoring and ecological modelling of plant populations in the face of climate change, and studying genetic variation that characterizes plant populations. We use a range of botanical, analytical/statistical and laboratory techniques, as well as in-house and global databases of plant communities, species occurrences, climate data and models. Students and professional researchers in our group conduct field, laboratory, and computational research to further community classification and mapping, ecological analysis and modelling, and population genetic and evolutionary analyses. Student researchers contribute to field studies to understand plant diversity as a basis for management, and conduct basic research into plant community ecology, evolution, and adaptation.

Plant Community Diversity and Ecology
We analyse vegetation plot data to classify vegetation, using phytosociological typology and EUNIS habitat types. These types are essential for understanding plant diversity patterns and the impact of alien invasive species, and for management, restoration and conservation.

Coastal Habitats Management and Conservation
Coastal habitats are threatened by over-use and development. We study plant diversity in dune and marshes habitats to assist in forming management goals.

Forest Diversity and Management
We study effects of environment and forest management on plant diversity in a variety of forests. The combined analysis of physical factors, climate, forest structure and management type and intensity help us to understand and predict potential climate impacts on forest habitats.

Mire Restauration and Monitoring
We use permanent plots to assess changes in species composition and diversity of mire habitats after restoration actions, with control plots to track baseline changes due to climate trends.

Multiscale Grassland Diversity
Natural and semi-natural grasslands are highly threatened by agricultural expansion and climate change. We focus on how land-use and climate influence grassland diversity. This research uses field sampling, plot data and GIS to describe the distribution of grassland diversity at multiple scales for conservation and management.

Models of Climate Impacts on Plant Diversity
We study how plants were impacted by previous climate change and will be in the future. We model climate impacts, taking data from global species data bases and climate predictions from global circulation models.

Adaptive Diversification and Plant Population Genomic Diversity
We discover and analyse genetic diversity that allows plant species to respond to climate change and soil variability. We develop and use genomic resources, bioinformatics, molecular techniques, and phylogenies.

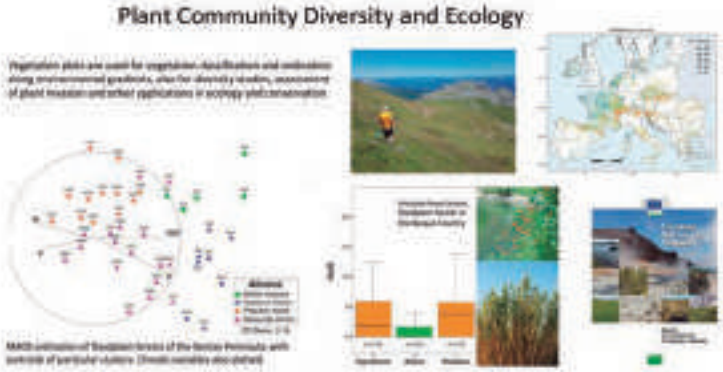
Looking forward, student and professional researchers in our group will continue to use field work, molecular laboratory techniques and analytical approaches to understand vegetation patterns, evolutionary processes, and to inform species conservation and habitat management. Student research plays a vital role in this effort.

Terrestrial Plant Diversity Group: Research for Understanding Plant Communities and Populations, and Their Evolution and Conservation During Climate Change

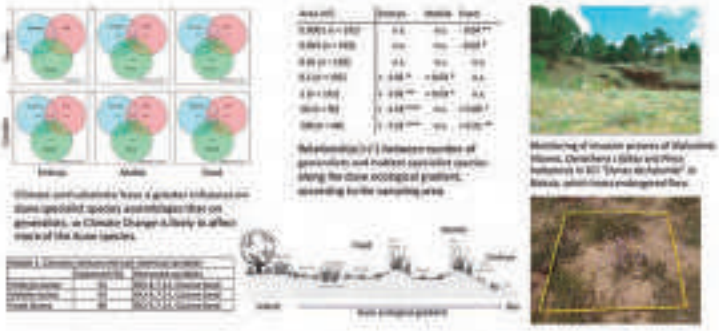
Juan A. Campos[1], Itziar García-Mijangos.[1], Idoia Biurrun[1], Diego Liendo[1], Daniel García[1,4], Pablo Arufat[1,4], Adrián Fuente[1,4], Víctor García[1,4], Camila Subieta[1,4], Irati Díaz[1,4], Maialen Martínez[1,4], Ángel García[1,4], Elena Goñi[1,4], Sara Sánchez[1,4], Ander Cocó[1,4], Unai Zorrozua[1,4], Jon Larrinaga[1,4], Gorka Melgar[1,4], Peter B. Pearman[1,2,3], Javier Loidi[1]

1. Dept. of Plant Biology and Ecology UPV/EHU; 2. IKERBASQUE; 3. BC3; 4. UPV student researcher

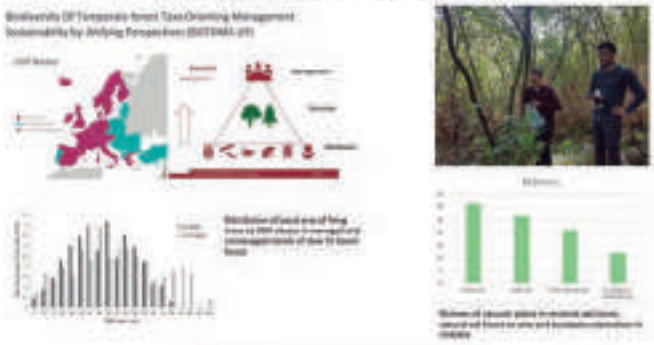
Plant Community Diversity and Ecology



Coastal Habitats Management and Conservation

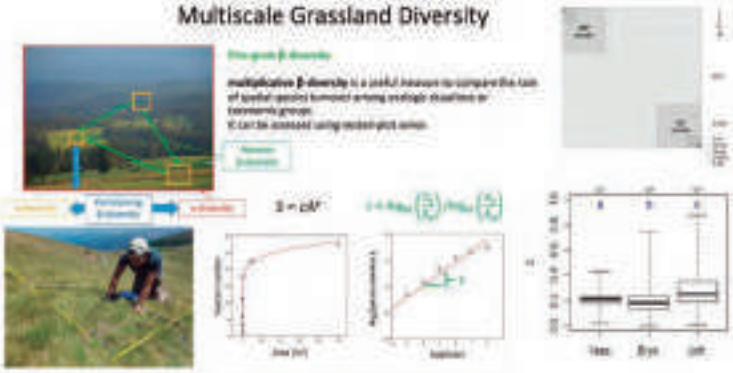


Forest Diversity and Management



Mire Restauration and Monitoring

Multiscale Grassland Diversity



Models of Climate Impacts on Plant Diversity

Adaptive Diversification and Plant Population Genomic Diversity

Vegetation-plot databases

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Development of tools based on ecosystem services for land management

Miren Onaindia, Ibone Ametzaga-Arregi, Lorena Peña, Jasone Unzueta, Beatriz Fernández de Manuel, Leire Méndez-Fernández
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KEY WORDS: Indicators, Mapping, Models, Green Infrastructure

The aim of our research group is to provide the information and tools required by the decision-makers for a sustainable land management based on Ecosystem Services (ES), which are the varied benefits that humans freely gain from the natural environment and from the properly functioning of the ecosystems. In this context, we are developing the **project "Ecosystem Services Assessment of Euskadi"**, in which we are performing the following lines of research and generating the following tools:

1. Defining concepts related to ES and identifying ES in the territory:
   - ✓ Catalog of ES of Biscay and Catalog of ES of Urdaibai.
   - ✓ Contribution of the Natura 2000 Network of Euskadi to the supply of SE
   - ✓ Other related ES approaches: Green Infrastructure and Nature-based Solutions.
2. Mapping of the ES with the aims of knowing the spatial distribution of the ES; proposing a Green Infrastructure; analyzing the synergies and trade-offs to increase the supply of ES; analyzing the conflicts between the supply and demand of ES to prioritize actions; and analyzing future scenarios to identify response options:
   - ✓ Methodological guide for the mapping of SE in Euskadi
   - ✓ Cartography of 11 ES that can be downloaded from the FTP of Geoeuskadi
3. Integration of the SE approach in territory management:
   - ✓ Inclusion in the Review of the Territorial Planning Guidelines (DOT)
   - ✓ Model for the implementation of compensatory measures for loss of SE (COPSE)
   - ✓ Practical guide for the integration of SE in the formulation of territorial and urban plans and programs.
4. Analyzing the perception and demands about ES:
   - ✓ Interviews to users of urban and periurban green infrastructures in different locations: Green Belt of Bilbao, Green Ring of Vitoria-Gasteiz, Ullia Mountain in Donostia Urdaibai Biosphere Reserve, Zalla…
   - ✓ Interviews, workshops and SWOT matrix with administration technicians about the integration of ES in the planning of the territory.
5. Studying ES in different environments: urban ecosystems, aquatics ecosystems, agroecosystems…
   - ✓ Urban ecosystems: Relationship of the presence of green spaces with different factors: temperature in cities, people's health ...; evaluation of the provision and demand of SE in Bilbao.
   - ✓ Aquatics ecosystems: Evaluation of regulating ES in rivers of Urdaibai Biosphere Reserve.
6. Disseminating and training in ES:
   - ✓ Organization of workshops, conferences and courses; attendance to national and international meetings; press and radio, releases; participation in international networks; scientific publications;

Moreover, through RENATUR-Interreg project we are working with other European partners in order to improve the landscape management of the periurban open spaces through the improvement of the "*FEDER*".

Acknowledgments

We are very greatful to the financial support from the Department of Environment of the County Council of Biscay (*Millennium Ecosystem Assessment of Biscay Project*) and from the Department of Environment and Landscape Policy of the Basque Government (*Millennium Ecosystem Assessment of Basque Country Project*).

Desarrollo de herramientas basadas en los servicios de los ecosistemas para la ordenación del territorio

Miren Onaindia, Ibone Ametzaga, Lorena Peña, Jasone Unzueta, Beatriz Fernández de Manuel, Leire Méndez

Grupo de Investigación: Evaluación del Capital Natural: Funciones y Servicios de los Ecosistemas. Aplicación a la Planificación Territorial.

Departamento de Biología Vegetal y Ecología (UPV/EHU)

** Agradecimientos por el apoyo financiero al Departamento de Sostenibilidad y Medio Natural de la Diputación Foral de Bizkaia y al Departamento de Medio Ambiente y Planificación Territorial y Vivienda del Gobierno Vasco.*

El **objetivo de nuestro grupo de investigación** es proporcionar la información y las herramientas necesarias para una gestión sostenible del territorio basada en los servicios de los ecosistemas (SE), que son los beneficios que los ecosistemas proporcionan a la sociedad.
En este contexto, estamos desarrollando el proyecto **"Evaluación de los Servicios de los ecosistemas de Euskadi"**, en el cual llevamos a cabo las siguientes líneas de investigación, y a partir de las cuales hemos generado las siguientes herramientas:

1. **Definir conceptos relacionados con los SE e identificar SE en el territorio:**
   * Conceptos relacionados: Impulsores de cambio, Infraestructura Verde (IV), Soluciones basadas en la Naturaleza (SBN)
   * Catálogo de SE de Bizkaia (http://www.ehu.eus/cdsea/web/wp-content/uploads/2017/03/CatalogoServicios.pdf) y Catálogo de SE de Urdaibai.
   * Contribución de la Red Natura 2000 de Euskadi al aporte de SE

2. **Cartografiado de los SE con el objetivo de conocer la distribución espacial de los SE, proponer una Infraestructura Verde, analizar las sinergias y trade-offs para aumentar la oferta de SE, analizar los conflictos entre la oferta y la demanda de SE para priorizar acciones y analizar escenarios de futuro para identificar opciones de respuesta.**
   * Guía metodológica para el cartografiado de los SE en Euskadi (http://www.ehu.eus/cdsea/web/wp-content/uploads/2017/03/Gu%C3%ADa-Metodologica_2018_Final.pdf)
   * Cartografía de 11 SE que se pueden descargar del FTP de Geoeuskadi (ftp://ftp.geo.euskadi.net/cartografia/Medio_Ambiente/Servicios_Ecosistemas)

3. **Integración del enfoque de SE en la gestión del territorio:**
   * Inclusión en la Revisión de la Directrices de Ordenación Territorial (DOT) (https://www.euskadi.eus/directrices-de-ordenacion-territorial-dot/web01-a2lurral/es/)
   * Modelo para la implementación de medidas compensatorias por pérdida de SE (COPSE)
   * Guía práctica para la integración de los SE en la formulación de planes y programas territoriales y urbanísticos.

4. **Análisis de la percepción y la demanda sobre los SE:**
   * Entrevistas a los usuarios de IV urbanas o periurbanas: *Cinturón Verde del Bilbao Metropolitano, Anillo Verde de Vitoria-Gasteiz, Monte Ullia en Donostia, Reserva de la Biosfera de Urdaibai, Zalla ...*
   * Entrevistas, talleres y matriz DAFO con técnicos de la administración sobre la integración de los SE en la ordenación del territorio.

5. **Estudio de los SE a distintas escalas: ecosistemas urbanos, ecosistemas acuáticos, agroecosistemas…**
   * **Ecosistemas urbanos:** Relación de la presencia de espacios verdes con diferentes factores: temperatura en las ciudades, salud de las personas…; evaluación de la provisión y demanda de SE en Bilbao.
   * **Ecosistemas acuáticos:** Evaluación de los servicios de regulación en los ríos de Urdaibai

6. **Difusión y formación en SE**:
   * Organización de talleres, conferencias y cursos, asistencia a congresos nacionales e internacionales, publicación de noticias en prensa y entrevista de radio, participación en redes internacionales, publicaciones científicas, redes sociales …

Además, a través del proyecto RENATUR-Interreg estamos trabajando con otros socios europeos para mejorar la gestión del paisaje de los espacios abiertos periurbanos mediante la mejora de los FEDER.

Artículos del grupo relacionados

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- *Palacios-Agundez, I., Onaindia, M., Uria, A., & Rodríguez-Loinaz, G. (2018). Naturaren onurak gizarteratzeko hezkuntza: ekosistemen zerbitzuen ikasketa-irakasketarako inplementazio didaktikoa. IKASTORRATZA. e-Revista de Didáctica, 21, 87-106.*
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- *Castillo-Eguskitza, N., Schmitz, M.F., Onaindia, M., Rescia, A.J., 2019. Linking Biophysical and Economic Assessments of Ecosystem Services for a Social–Ecological Approach to Conservation Planning: Application in a Biosphere Reserve (Biscay, Spain). Sustainability 11 (11), 3092.*
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A human chaperone network solubilizes protein aggregates related to neurodegeneration

Aitor Franco, Lorea velasco, Leire Dublang, José-Ángel Fernández-Higuero, Fernando Moro, Adelina Prado and Arturo Muga

Instituto Biofisika (CSIC-UPV/EHU) and Department of Biochemistry and Molecular Biology, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48080 Bilbao, Spain

KEY WORDS: chaperones, protein aggregation, α-synuclein, neurodegeneration, protein disaggregation.

Protein aggregation is one of the hallmarks of several neurodegenerative diseases, such as Parkinson, Alzheimer, etc. Protein solubility can be compromised due to an increase in concentration, mutations, stress conditions and interactions with other cellular components. Under these conditions, proteins aggregate following a complex and multistep process in which different oligomerization states with distinct structural properties are generated. A controversial relationship between these states and cellular toxicity has been reported, with pathogenicity assigned to both oligomers and fibrillar species. The accepted current view is that oligomers and small fibrils are the dominant cytotoxic species, in contrast to the inert and relatively cytoprotective large amyloid aggregates. In this context, α-synuclein (α-syn) aggregation is related to a group of diseases termed synucleinopathies, which includes Parkinson's Disease (PD), Lewy Body Dementia (LBD), and Multiple Systems Atrophy (MSA). To cope with the deleterious effects of protein aggregates, cells have evolved sophisticated system, including complex chaperone networks. Among these networks, a human disaggregase machinery, built by members of the Hsp70, Hsp40 and Hsp110 families, can interact with amorphous or ordered –fibrils- protein aggregates, extract unfolded protein monomers and refold them into their non-toxic, active conformation.
Despite the importance that clearance of α-syn aggregates might have in the abovementioned pathologies, it remains unknown whether the human disaggregase can solubilize the different toxic intermediates known to populate the aggregation process of this protein. In this study, we show that a specific combination of human chaperones: Hsc70 (Hsp70), DnaJB1 (a class B Hsp40) and Apg2 (Hsp110) can solubilize the toxic species of α-syn into monomeric, non-toxic conformations with high efficiency. Moreover, it can also remodel some –E46K, A53T, and specific N- and C-terminal deletion mutants- but not all the pathological variants of this sequence. These results highlight the possibility to consider this chaperone network as a target to find small chemical molecules that upregulate its disaggregase activity or activated variants of this protein combination to ameliorate neurodegeneration.

ACKNOWLEDGEMENTS: Research supported by grants BFU2016-75983-P from Ministerio de Economía y Competitividad and by the Basque Government under grant IT1201-19. AH, LV and LD are recipients of fellowships from the Basque Government, University of the Basque Country and Ministerio de Economía y Competitividad, respectively.

A human chaperone network solubilizes protein aggregates related to neurodegeneration

Aitor Franco, Lorea Velasco, Leire Duhlang, Yovana Cabrera, José-Ángel Fernández-Higuero, Natalia Orozco, Fernando Moro, Adelina Prado and Arturo Muga

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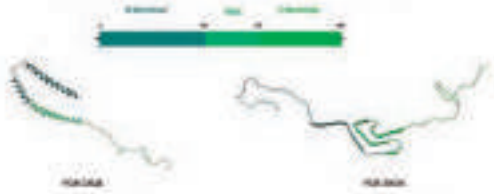
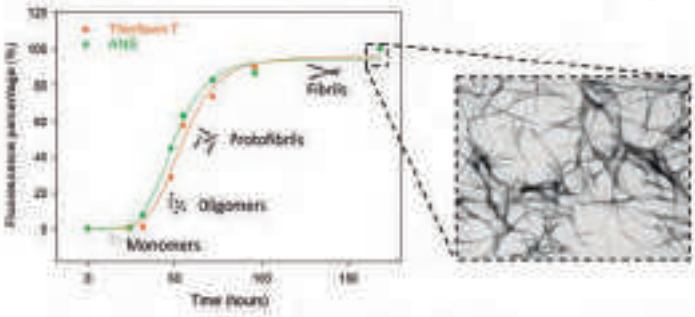
KEY WORDS: chaperones, protein aggregation, α-synuclein, neurodegeneration, protein disaggregation

α-synuclein structure



α-synuclein is an intrinsically disordered protein that can adopt different conformations in the cell and "in vitro". Some of these are aggregation prone conformations. They can generate nucleation cores that evolve towards oligomeric structures and later, after various intermediary stages, will originate different fibril structures.

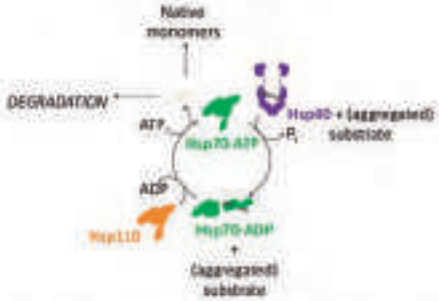
α-synuclein aggregation and toxicity



Amyloids show a fibrillar appearance by Electron Microscopy and bind fluorescent probes such as Thioflavin T and ANS. The distinct oligomerization states generated during the aggregation process (oligomers, protofibrils and mature fibrils) differ in size, structure and cytotoxicity.

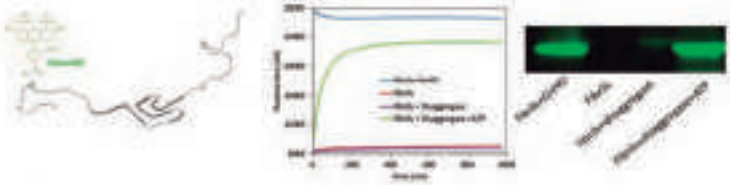
Our data indicate that oligomers and small fibrils (obtained by sonication) are more cytotoxic (lower cell viability) than amyloid mature fibrils and monomers.

Human disaggregase

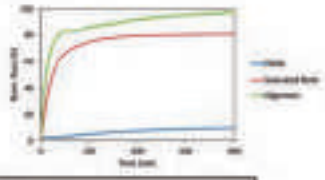


In harsh conditions protein aggregation cannot be avoided. The cell can either recycle these aggregated species or solubilize and refold their components. The later alternative can be achieved by the joint action of representatives of the Hsp40, Hsp70 and Hsp110 families that build the human disaggregase. The functional cycle is driven by the ATPase activity of its central component, Hsc70, which provides the energy required to remodel the aggregated substrate.

Disaggregation of α-synuclein



To follow disaggregation of different α-synuclein polymorphs, we label α-syn monomers with a fluorescence probe and recorded the de-quenching of the fluorescence signal due to disaggregation. We see that human disaggregase releases monomers from α-synuclein aggregates, working efficiently on oligomers and sonicated fibrils, the toxic protein aggregates.



Research Lines

1-. **Identification of Hsc70/Hsp110 inhibitors with antitumoral activity.** Cancer cells show a higher demand for chaperone activity to survive due to their higher metabolic needs and inappropriately activated signaling pathways. Thus, inhibitors of these chaperones could be used as anti-cancer drugs.

2-. **Coupling of the human disaggregase system with other cellular machineries** to resolve toxic aggregates of proteins related to neurodegeneration. The disaggregase activity of the human system might be facilitated by other cellular machineries like the proteasome.

3-. **Characterization of the functional regulation of the disaggregase system by phosphorylation.** Recent studies indicate that chaperone phosphorylation regulates important cellular processes (cell cycle, apoptosis, protein degradation, resistance to anticancer therapeutics,..). However, how this process occurs is not known.

Conclusion

The human disaggregase targets the most cytotoxic oligomerization states of α-syn, rendering non-toxic protein monomers.

Acknowledgements

Research supported by grants BFU2016-77980-P from Ministerio de Economía y Competitividad and by the Basque Government under grant IT1031-19. AF and JA are recipients of fellowships from the Basque Government and University of the Basque Country, respectively. LD and YC were recipients of fellowships from the Ministerio de Economía y Competitividad and University of the Basque Country, respectively. NO technical assistance was received by Fundación Biofísika Bizkaia.

Implication of ceramide 1-phosphate in preadipocyte proliferation. Possible role in obesity

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KEY WORDS: preadipocytes, cell proliferation, ceramide 1-phosphate (C1P), obesity, sphingolipids.

Ceramide 1-phosphate (C1P) is a bioactive sphingolipid that in mammals is synthesized through phosphorylation of ceramide by ceramide kinase. C1P was first demonstrated to stimulate cell growth in fibroblasts and macrophages, and was later shown to be implicated in inflammatory responses. In the present study, we show for the first time that C1P promotes proliferation of mouse preadipocytes, an action that is associated with adipocyte expansion and increased risk of obesity. Investigation into the mechanisms by which C1P stimulates preadipocyte proliferation revealed that C1P was able to induce phosphorylation of janus kinase (JAK) and the subsequent phosphorylation and activation of signal transducer and activator of transcription 3 (STAT3), suggesting that the JAK/STAT pathway might be involved in the mitogenic effect of C1P. This hypothesis was confirmed using selective inhibitors of JAK and STAT3. Specifically, we found that AZD1480, a specific inhibitor of JAK2 or Stattic, which inhibits STAT3 potently, substantially decreased C1P stimulated preadipocyte proliferation, suggesting that JAK2/STAT3 is a key pathway for stimulation of preadipocyte growth by C1P. These findings may be relevant when considering novel strategies to develop therapeutic compounds to treat obesity or obesity associated diseases.

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Implication of ceramide 1-phosphate in preadipocyte proliferation. Possible role in obesity.

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Introduction

Hyperplasia caused by adipocyte proliferation and hypertrophy caused by adipogenesis are the main reasons for fat deposition in vivo, the majority of it being stored as triacylglycerol (TG). Excess fat deposition or dysfunction of the adipose tissue lead to metabolic diseases, most notably obesity, which causes chronic low-grade inflammation [1]. The biological causes of obesity are complex, and although there is evidence involving sphingolipids in the onset and progression of the disease [2], the molecular mechanisms that are implicated in obesity are not well understood. Initial studies from our lab showed that ceramide kinase (CerK), the enzyme that catalyzes the formation of ceramide 1-phosphate (C1P), was upregulated during adipocyte differentiation [3]. We now show that C1P stimulates preadipocyte proliferation, pointing to a possible role of this phosphosphingolipid in fat accumulation. In addition, we demonstrate that at least part of the mechanism by which C1P stimulates preadipocyte proliferation involves activation of the JAK-2/STAT-3 pathway.

Results

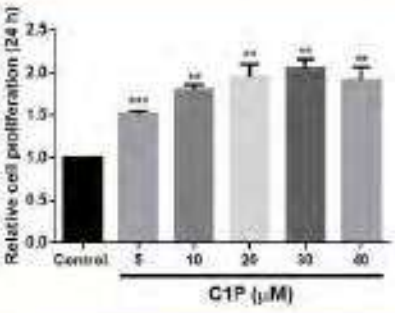

Figure 1. C1P stimulates preadipocyte proliferation. Cell proliferation was determined by staining the cells with crystal violet at 24h. Results are the mean ± SEM of 4 independent experiments performed in triplicate (**p < 0.01; ***p < 0.001).

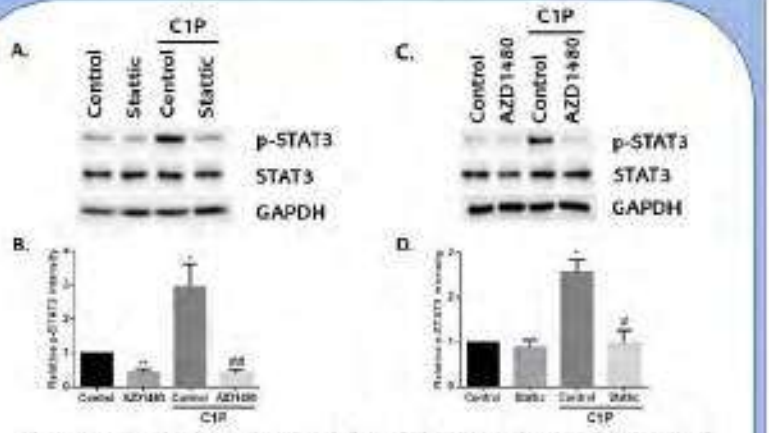

Figure 2. C1P stimulates phosphorylation of signal transducer and activator of transcription 3 (STAT-3), a transcription factor activated by membrane receptor-associated Janus kinases (JAK). This action is blocked by selective inhibitor of STAT-3 and JAK-2 (Stattic and AZD1480, respectively). Cells were stimulated with 20 μM C1P for 5 min. When used, 1 μM Stattic or 2 μM AZD1480 were added to the cells and preincubated for 1 hour prior to addition of C1P. Protein levels were detected by western blotting using specific antibodies. Equal loading of protein was monitored using a specific antibody to GAPDH (A and C). B and D: Normalized results of the scanning densitometry of the exposed films. Results are the mean ± SEM of 3-5 independent experiments (*p < 0.05; **p< 0.01; #p < 0.05; ##p < 0.01).

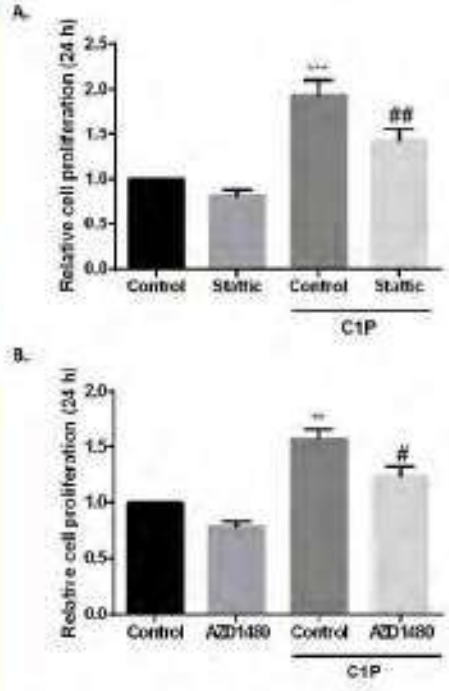

Figure 3. C1P-stimulated preadipocyte proliferation is partially blocked by STAT-3 and JAK-2 inhibitors. Cell proliferation was determined by staining the cells with crystal violet at 24h. When used, 1 μM Stattic (A), or 2 μM AZD1480 (B) were added to the cells and preincubated for 1 hour prior to addition of 20 μM C1P. Results are the mean ± SEM of 4-8 independent experiments performed in triplicate (**p < 0.01; ***p < 0.001; #p < 0.05; ##p < 0.01).

Conclusions

1. C1P stimulates preadipocyte proliferation.
2. C1P-stimulated preadipocyte proliferation involves activation of the JAK2/STAT3 pathway.

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Acknowledgements

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Molecular mechanisms of familial hypercholesterolemia: from biochemistry to theranostics

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KEY WORDS: Familial hypercholesterolemia, LDL, Cardiovascular disease, cholesterol.

Familial hypercholesterolemia (FH) is an autosomal dominant disorder characterized by high blood-cholesterol levels mostly caused by mutations in the low-density lipoprotein receptor (LDLr). With a prevalence as high as 1/200 in some populations, genetic screening for pathogenic LDLr mutations is a cost-effective approach in families classified as 'definite' or 'probable' FH and can help to early diagnosis. However, with over 2000 LDLr variants identified, distinguishing pathogenic mutations from benign mutations is a long-standing challenge in the field. In 1998, the World Health Organization (WHO) highlighted the importance of improving the diagnosis and prognosis of FH patients thus, identifying LDLr pathogenic variants is a longstanding challenge to provide an accurate genetic diagnosis and personalized treatments. In recent years, accessible methodologies have been developed to assess LDLr activity in vitro, providing experimental reproducibility between laboratories all over the world that ensures rigorous analysis of all functional studies. Our research group has been very active in developing new methodologies to functionally characterize mutations in the main genes causative of FH: LDLr, ApoB and PCSK9 in order to provide an accurate FH diagnosis.

Importantly, high cholesterol levels do not have any direct symptoms so many people usually ignore that they suffer FH. Typically, 200 mg/dL total cholesterol and 100 mg/dL LDL-C are considered threshold values over from which the risk of suffering CVD increases dramatically . Therefore, prevention and treatment of FH is critical. Nowadays, statins constitute the gold standard treatment of FH, but historically other drugs or drug-combination have been commonly used. We recently have proved that the effect of evinacumab, a novel anibody developed to diminish LDL-C in FH homozygous patients is independent of LDLr activity. In addition, we are developing a new treatment strategy based on improvement of reverse cholesterol transport using nanoparticles resembling HDL. This methodology allows labelling of the nanoparticles and monitorizing the effect on atheroma plaque regression.

Lately our group is studying the molecular mechanism by which the statin treatment induces development of type 2 diabetes mellitus and the implication of microRNAs in the process.

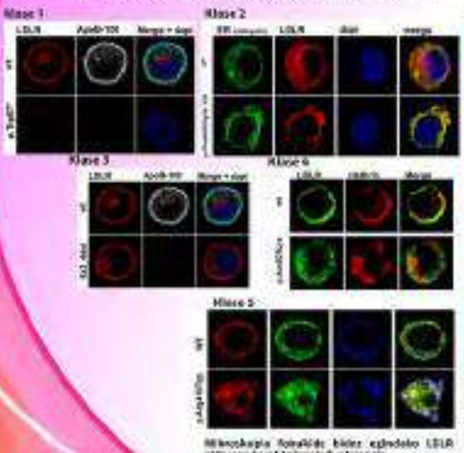
Mecanismos Moleculares de la Hipercolesterolemia Familiar

- Caracterización de mutaciones en LDLR, ApoB-100, PCSK9 y ApoE.
- Generación de rHDL y su uso en terapia antiaterogénica.
- Efecto de estatinas sobre el MIRnoma y desarrollo de diabetes tipo 2.

LDLR, APOB eta PCSK9-en mutazioen balioztapen funtzionala

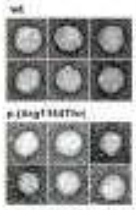
Helburua: LDLR, ApoB-100 eta PCSK9 proteinetan agertzen diren hainbat mutazioen balioztapen funtzionala egitea. Lan honek gaixotasunaren diagnostiko zuzen bat finkatzea baimentzen du, diagnosi genetikoak ekar ditzakeen positibo faltsuak ekidinez eta mutazioak dakarren akatsaren larritasuna zehaztuz.

Metodologia: Fluxuzko zitometria, mikroskopia konfokala, Western blot, espektroskopia infragorria, ELISA, mikroskopia elektronikoa,...



Mikroskopia fokalaren bidez egindako LDLR aldaeren karakterizazio funtzionala.

LDL katabolismoaren akatsen irudikapena: (A) LDLR bidezko barneraketa; (B) 2. klaseko LDLR mutanteak, [illegible]; (C) 3. klaseko mutanteak, LDL-LDLR lotura akatsa; (D) 4. klaseko mutanteak, LDL-LDLR [illegible]; (E) 5. klaseko mutanteak, [illegible]; (F) [illegible] ApoB-100-ek eragindako LDL-LDLR lotura akatsa; (G) PCSK9 funtzio areagotzaile mutanteak.

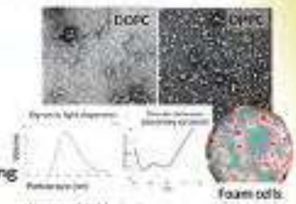


LDL partikulen morfologia eta neurriaren azterketa tindaketa negatiboko mikroskopia elektronikoa bidez.

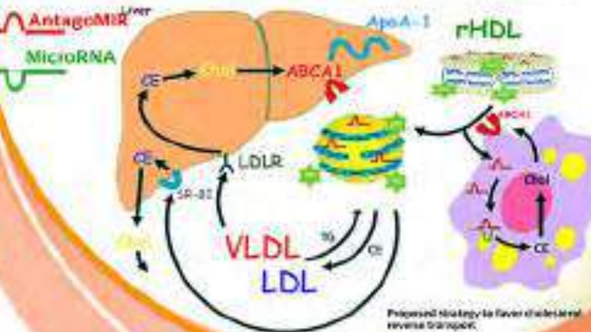
AntagoMIR-based theranostics

Aim: to favor cholesterol reverse Transport from cells residing at Atheroma plaque by targeting specific intracellular microRNAs.

Methodology: use of antagoMIRs Loaded ApoAI-nanodisc micmicking pre-HDL.



Nanoparticle biophysics characterization and foam cell formation



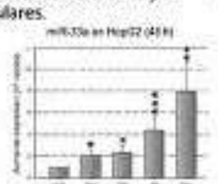
Proposed strategy to favor cholesterol reverse transport.

Efecto de estatinas sobre el MIRnoma y diabetes tipo 2

Objetivo: determinar la relación de la Asociación del tratamiento con estatinas y desarrollo de diabetes tipo 2.

Metodología: análisis del mirNOMA en pacientes con hipercolesterolemia familiar tratados con estatinas y en cultivos celulares.

Predicción de proteínas diana de Mir-33a



Sobreexpresión de Mir-33a inducida por el tratamiento con estatinas.

Taldea

GrAL edo MAL gure taldean egin nahi baduzu, gurekin harremanetan jarri.

Si te apetece hacer el TFG o TFM en nuestro grupo, contáctanos por email.

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- Shengjun Wang, **Universidad de Copenhague**, Dinamarca
- Lourdes Palacios, **Progenika, Grifols**, España
- Poulabi Banerjee, **Regeneron Pharmaceuticals**, USA.

Membrane Permeabilization by Pore-Forming RTX Toxins: What Kind of Lesions Do These Toxins Form?

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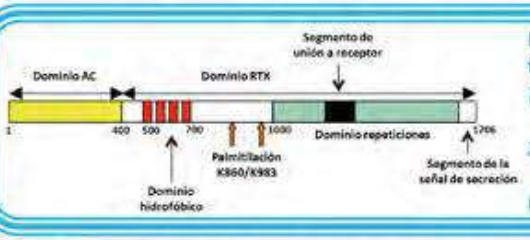
KEY WORDS: Gram-negative bacteria; RTX toxins; bacterial protein toxins; pore-forming proteins; toroidal pores.

Pore-forming toxins (PFTs) form nanoscale pores across target membranes causing cell death. The pore-forming cytolysins of the RTX (repeats in toxin) family belong to a steadily increasing family of proteins characterized by having in their primary sequences a number of glycine- and aspartate-rich nonapeptide repeats. They are secreted by a variety of Gram-negative bacteria and form ion-permeable pores in several cell types, such as immune cells, epithelial cells, or erythrocytes. Pore-formation by RTX-toxins leads to the dissipation of ionic gradients and membrane potential across the cytoplasmic membrane of target cells, which results in cell death. The pores formed in lipid bilayers by the RTX-toxins share some common properties such as cation selectivity and voltage-dependence. Hemolytic and cytolytic RTX-toxins are important virulence factors in the pathogenesis of the producing bacteria. And hence, understanding the function of these proteins at the molecular level is critical to elucidating their role in disease processes. In this review we summarize the current state of knowledge on pore-formation by RTX toxins, and include recent results from our own laboratory regarding the pore-forming activity of adenylate cyclase toxin (ACT or CyaA), a large protein toxin secreted by *Bordetella pertussis*, the bacterium causative of whooping cough.

Membrane Permeabilization by Pore-Forming RTX Toxins: What Kind of Lesions Do These Toxins Form?



La toxina adenilato ciclasa de *Bordetella pertussis* es el agente causativo primario de la tos ferina en humanos. Se trata de una toxina bifuncional con dos dominios bien definidos:

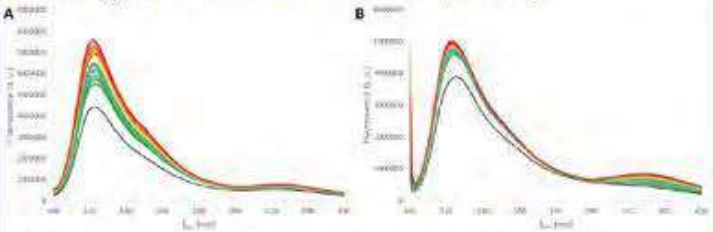
1. El dominio catalítico, el cual se transporta a través de la membrana de las células diana convirtiendo el ATP intracelular en cAMP hasta concentraciones toxicas.
2. El dominio formador de poros o RTX, el cual forma poros en las membranas permeabilizándola.

La sinergia entre ambas actividades producen la citotoxicidad característica de la patología.

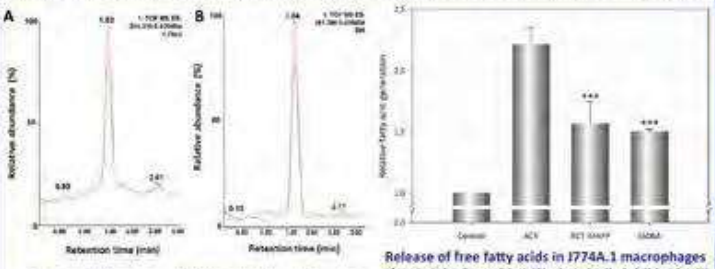
Intrinsic Phospholipase A Activity of Adenylate Cylase Toxin Mediates Translocation of its Adenylate Cyclase Domain

Aim: the catalytic domain of the toxin is translocated directly across the plasma membrane of target cells, mediated by an unknown mechanism. The aim of this study is to investigate whether a novel lipase activity of ACT is involved in the transport of the domain though the membrane.

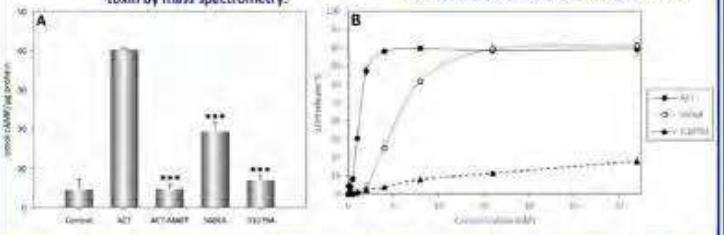
Methodology: analysis of the production of free fatty acids *in vitro* (model membranes) and *in vivo* (J774A.1 macrophages) by different biophysical methodologies and its contribution to overall cytotoxicity.



Measure of the release of fatty acids of positions *sn-1* (A) and *sn-2* (B) of fluorogenic phospholipids PED-A1 and PED6 by fluorescence spectroscopy, measuring fluorescence increase at 515 nm after the addition of ACT.



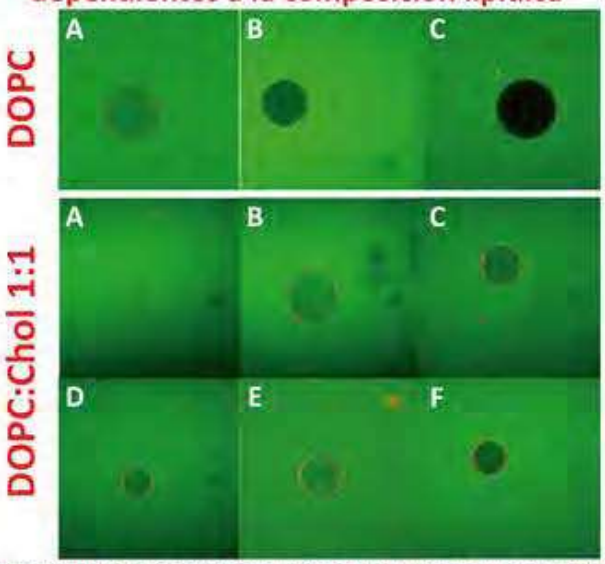
Measure of the release of fatty acids of positions *sn-1* (A) and *sn-2* (B) of POPC liposomes incubated with the toxin by mass spectrometry.



Measure of intracellular generation of cAMP (A) and cytotoxicity measured by LDH release (B) in J774A.1 cells.

Conclusion: chemical inhibition by MAFP or inhibition by mutagenesis (S606A mutant) of phospholipase activity of ACT abrogates free fatty acid release in model membranes and macrophages. This inhibition abolishes intracellular cAMP generation and, therefore, overall cytotoxicity.

Análisis de los cambios en el tamaño del poro producido por la toxina adenilato ciclasa dependientes a la composición lipídica



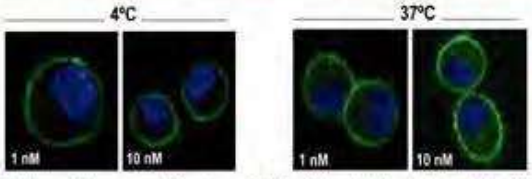
Permeabilización analizada mediante microscopia confocal de vesículas unilamelares gigantes (GUVs) de DOPC y DOPC:Chol 1:1 respecto a sondas fluorescentes de diferentes diámetros hidrodinámicos: Alexa 488 (A), 4 kDa Dextran (B), 10 kDa Dextran (C), 20 kDa Dextran (D), 40 kDa Dextran (E) y 70 kDa Dextran (F).

Conclusión: en presencia de colesterol el diámetro del poro formado por la ACT en las bicapas lipídicas aumenta significativamente

Adenilato Ziklasa toxinaren poro-eragile aktibitateak makrofagoetan duen toxikotasuna

Helburua: ACT toxinak eragiten duen mintz-iragazkortasuna aztertzea, zelulak iragazkortasun honi erantzuteko dituen mekanismoetan sakonduz.

ACTak eratzen dituen poroen iragazkortasun mekanismoen azterketa fluxuzko zitometriaz. Ioduro propidioaren (PI) presentzian J774A.1 makrofagoak poroaren domeinua soilik duen mutantearekin (ΔN482) inkubatu zieren. Poroak eratuz gero, PI-a zelulen barrura iragaziko dira, lortzen diren seinaleak, bai FSC baloreetan (zelulen tamainan) eta FSC baloreetan (ioduro propidioaren seinale fluoreszentea) aldaketak eraginez.



ΔN482 toxina mutantearen endozitoziaren azterketa. Mikroskopia konfokalaren bidez ΔN482-ren (berdez) kokapen zelularraren azterketa bi kontzentrazio (1 eta 10 nM) eta bi tenperatura desberdinetan (4°C eta 37°C). Nukleo zelularra Hoestch sondarekin markatu zen (urdina). 37°C-tan egindako saioan toxina zelulen barnealdean ikusten da, zelulak toxina endozitatu duela adieraziz.

Taldea

H. Ostolaza J. Amuategi C. Martin

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Bacterial conjugation inhibitors against the spread of antibiotic resistance among bacteria, CONJURA

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KEY WORDS: Antibiotic resistance, bacterial conjugation, plasmids

Infections caused by bacteria that have acquired resistance to several antibiotics [multiresistant (MDR) bacteria] have become one of the greatest threats to Public Health, due to the cost in lives and the resulting economic expense. But although the most dramatic consequences are observed in the clinical milieu, the problem of the dissemination of resistance to antibiotics has its origin in the environment (i.e., agricultural, livestock and urban environments). This situation poses a challenge that requires an approach that integrates the different clinical, agro-livestock and urban scenarios.

Bacterial conjugation is the main process by which bacteria acquire such resistance, where a conjugative plasmid is transferred from a donor to a host bacterium. These plasmids encode not only the antibiotic resistance genes (ARG) but also the genes of the proteins involved in this process. Thus, the recipient bacterium acquires both antibiotic resistance traits and the capacity to transfer the plasmid to new recipient bacteria, contributing to the dissemination of antibiotic resistance in the bacterial community.

Therefore, a promising strategy to fight against the ARG dissemination could be focused on the inhibition of bacterial conjugation. In this regard, the coupling protein (T4CP) is an essential protein involved in this process and it is present in all conjugative plasmids. The set of different T4CPs constitutes a protein family.

Hence, CONJURA group aims to find specific inhibitors against T4CPs that, combined with conventional antibiotics, could allow us not only to address the infection but also to restrain and control the ARG dissemination among bacteria.

Bacterial conjugation inhibitors against the spread of antibiotic resistance among bacteria CONJURA

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CONTEXT

Infections caused by bacteria that have acquired resistance to several antibiotics, **multiresistant (MDR) bacteria**, have become one of the greatest threats to Public Health, due to the cost in lives and the resulting economic expense. But although the most dramatic consequences are observed in the clinical milieu, the problem of the dissemination of resistance to antibiotics has its origin in the environment (i.e., agricultural, livestock and urban environments). This situation poses a challenge that requires an approach that integrates the different clinical, agro-livestock and urban scenarios.

Bacterial conjugation is the main process by which bacteria acquire such resistance, where a conjugative plasmid is transferred from a donor to a recipient bacterium. These plasmids encode not only the **antibiotic resistance genes (ARG)** but also the genes of the proteins needed in bacterial conjugation. Thus, the recipient bacterium acquires both antibiotic resistance traits **(ARG)** and the capacity to transfer the plasmid to new recipient bacteria, contributing to the dissemination of antibiotic resistance in the bacterial community.

BACTERIAL CONJUGATION, TYPE IV SECRETION SYSTEMS (T4SS) AND COUPLING PROTEINS (T4CPs)

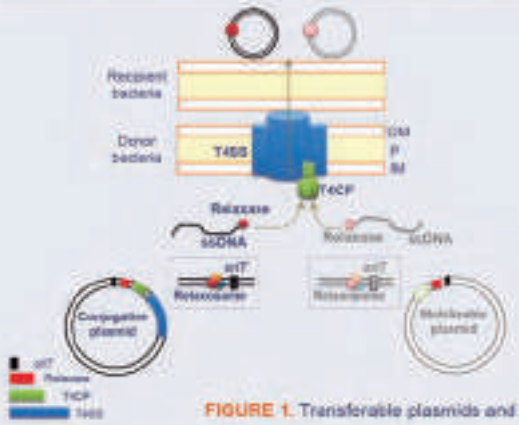

FIGURE 1. Transferable plasmids and bacterial conjugation

Bacterial conjugation-related genes are divided into two modules: **MOB (mobility) and MPF (mating pair formation)** genes (**Figure 1**). Conjugative plasmids have both modules and, therefore, harbour genes that encode all the proteins needed for conjugation.

The **MOB module** consists of three sequences necessary for substrate processing: (i) ***oriT* sequence**, which marks the starting point for DNA processing; (ii) the **relaxase** that specifically recognizes the *oriT* sequence of its plasmid; (iii) the **T4CP**, which recognizes the relaxosome in the cytosol and connects it with the secretion channel located in the membrane.

The **MPF module** encodes the proteins that build the transfer channel (T4SS).

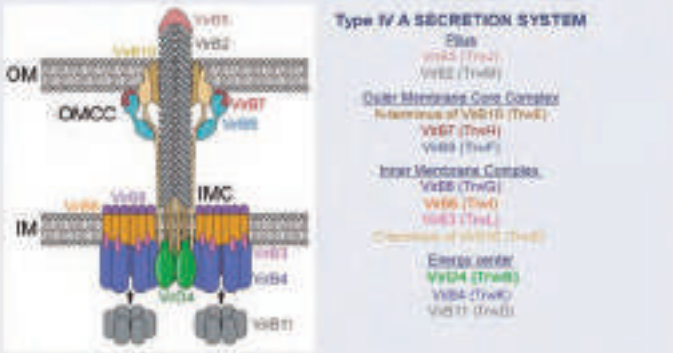

FIGURE 2. Molecular architecture of the T4ASS showing the location of the T4CP

Type IV secretion systems (T4SS) are macromolecular assemblies that can transport DNA and/or proteins formed by **three different functional units or modules** (**Figure 2**):
The first module, formed by three ATPases [**VirD4 (the T4CP)**, VirB4, VirB11] is the energy center. These proteins interact with the second module, a larger infrastructure called the inner membrane complex (IMC) that is responsible for substrate translocation through the inner membrane (IM), and it is connected to the outer membrane core complex (OMCC), the third module, responsible for substrate translocation through the periplasm and the outer membrane (OM).
Finally, the conjugative pilus, a structure essential for the direct contact between bacterial cells, is composed of VirB2 and VirB5 proteins.

T4CPs AS DRUG TARGETS

Coupling proteins (T4CPs), present in all conjugative plasmids, are essential proteins for bacterial conjugation.
CONJURA group aims to **find specific inhibitors against T4CPs** as a **new strategy to fight against the dissemination of antibiotic resistance among bacteria**, through the interdisciplinary research in microbiology, biochemistry and biophysics.
Taking into account the **essential role of T4CPs in bacterial conjugation**, it is important to study in depth these proteins since their **biochemical, biophysical and structural characteristics will help us to use T4CPs as drug targets** for the development of inhibitors against antibiotic resistance spread by bacterial conjugation.
Conjugation inhibitors can be tested in bacteria isolated from urban and agro-livestock settings, as well as from hospitals, to analyze their capability to inhibit the dissemination of antibiotic resistance in recognized hot spots under a **One Health approach.**

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Joint research laboratory on environmental antibiotic resistance

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KEY WORDS: antibiotic resistance, environment, bacterial infections

It is estimated that, by 2050, 10 million people will die annually from infections caused by multidrug-resistant bacteria (**MDB**). In the European Union, every year 33,000 people die for the same reason. The increasing concentrations of antibiotics in the environment exert pressure on bacteria to keep and disseminate antibiotic resistance genes (**ARGs**). ARGs can be spread by mobile genetic elements (**MGEs**) (e.g., plasmids, integrons, transposons, etc.). The **coexistence of ARGs and MGEs** in environmental samples (soil, food crops, river water, estuaries, etc.) is indicative of the **risk of dissemination of antibiotic resistance** from environmental bacteria to human pathogens.

The ***Joint Research Laboratory (JRL) on Environmental Antibiotic Resistance*** is an interdisciplinary collaborative consortium that aims to get a better insight into antibiotic resistance dynamics through the holistic **One Health** approach (healthy people, healthy animals, safe and healthy food, healthy environment).

Our research is based on three principles:

1. Antibiotics exert pressure on bacteria to keep and disseminate antibiotic resistance genes (**ARGs**).
2. ARGs can be spread by mobile genetic elements (**MGEs**).
3. The **coexistence of ARGs and MGEs** in environmental samples is indicative of the **risk of dissemination of antibiotic resistance** from environmental bacteria to human pathogens.

Since emergence and dissemination of **resistance to antibiotics** occurs through different exposure routes that imply humans, animals, food and the environment**, a One Health approach will be necessary** to design an **action plan** to find solutions to the ARG dissemination problem.

We aim to deepen our knowledge about **ARG dissemination dynamics through MGE** to **develop monitoring techniques and surveillance procedures for risk assessment** of antibiotic resistance spread in contaminated terrestrial and aquatic ecosystems.

The ***JRL on Environmental Antibiotic Resistance*** was created in 2018 and since then this multidisciplinary team formed by Research groups of the UPV/EHU, Neiker, and BC[3] has shared the knowledge of each research group to carry out different scientific, teaching and dissemination activities.

Joint Research Laboratory on Environmental Antibiotic Resistance

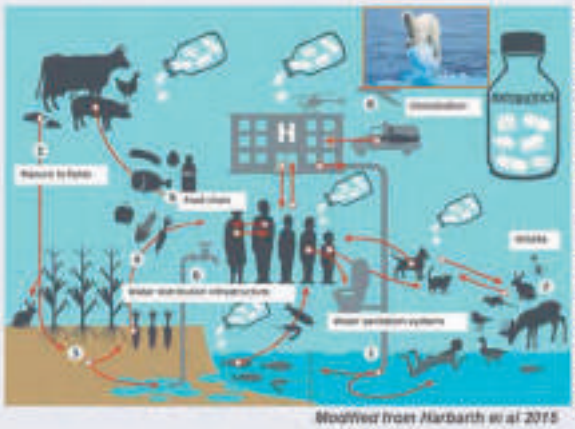
Itziar Alkorta[1], Nèstor Etxebarria[1], Lucía Gallego[1], Maite Lacuesta[1], Manu Soto[1,2], Estilita Ruiz[1], Luis Javier R. Barrón[1], Usue Pérez[1], María J. Sanz[3], Carlos Garbisu[4]

* [1]University of the Basque Country, [2]Plentzia Itsas Estazioa, [3]Basque Centre for Climate Change, [4]NEIKER

CONTEXT

It is estimated that, by 2050, 10 million people will die annually from infections caused by multidrug resistant bacteria (**MDB**). In the European Union, every year 33,000 people die for the same reason. The increasing concentrations of antibiotics in the environment exert pressure on bacteria to keep and disseminate antibiotic resistance genes (**ARGs**). ARGs can be spread by mobile genetic elements (**MGEs**) (e.g., plasmids, integrons, transposons, etc.). The **coexistence of ARGs and MGEs** in environmental samples (soil, food crops, river water, estuaries, etc.) is indicative of **risk of dissemination of antibiotic resistance** from environmental bacteria to human pathogens. The ***Joint Research Laboratory (JRL) on Environmental Antibiotic Resistance*** is a interdisciplinary collaborative consortium that aims to get a better insight into antibiotic resistance dynamics through the holistic **One Health** approach (healthy people, healthy animals, safe and healthy food, healthy environment).

METHODOLOGY/WORK PLAN



Modified from Narbarth et al 2015

Given that the **emergence and dissemination** of many of the **resistance to antibiotics** occur in the environment through different exposure routes to reach people, the One Health approach will help to design an **action plan where the ARG dissemination will be addressed at multiple levels: humans, animals, food and the environment.**

This scenario asks for **deepening our knowledge about ARG dissemination dynamics** through MGE by surveying and monitoring the **key players** of antibiotic resistance spread. The **main objective** is to **develop monitoring techniques and surveillance procedures for risk assessment** of antibiotic resistance spread in contaminated terrestrial and aquatic ecosystems.

MAIN RESULTS, COLLABORATIONS, OUTCOMES

SUMER COURSE (UPV/EHU)
"Resistencia a antibióticos en el medio ambiente: origen de un escenario apocalíptico"
July 18 and 19 at the Plentzia Marine Station (PiE)

COLLABORATIONS

Dr. Michel Mench
Dr. Sabine Houot
INRA

Dr. Elisabeth Grohmann
BEUTH HOCHSCHULE FÜR TECHNIK BERLIN
University of Applied Sciences

Dr. Fatima M'Zali
université BORDEAUX

Dr. Nevine Fam
Theodor Bilharz Research Institute - TBRI

Dr. Paul G Higgins

CONCLUSIONS

The ***JRL on Environmental Antibiotic Resistance*** was created a year ago and since then this multidisciplinary team has shared the knowledge of each research group to carry out different scientific, teaching and dissemination activities. From this experience it can be concluded that **multidisciplinary work with a common objective ensures very satisfactory results.**

MAIN CONTACT

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Group of Cell Signaling and Lipid Metabolism

Gomez Muñoz A[1], Trueba M[1], Carracedo A[1,2], Presa N[1], Camacho L[1], Domínguez Herrera A[1] and Gómez Larrauri A[1].
[1] Department of Biochemistry and Molecular Biology, Faculty of Sciences and Technology.
University of the Basque Country (EHU-UPV).
[2] CIC bioGUNE, Bizkaia.

KEY WORDS: sphingolipids, adipogenesis, obesity, inflammation, prostate cancer.

Sphingolipids are long-chain aliphatic amines containing two or three hydroxyl groups, and often a distinctive trans-double bond in position 4. Despite being essential in eukaryotic cell membrane architecture, they also play fundamental roles as signaling molecules in different processes such as proliferation, differentiation, adhesion, migration or apoptosis.

Our group has a wide experience in studying the role of sphingolipids in the regulation of cellular processes and their possible implication in the development of different diseases. Currently, our main investigation lines are: (i) adipogenesis regulation by bioactive sphingolipids and their impact on obesity development, and (ii) the control of pulmonary disease- and prostate cancer- associated inflammatory processes.

GROUP OF CELL SIGNALING AND LIPID METABOLISM

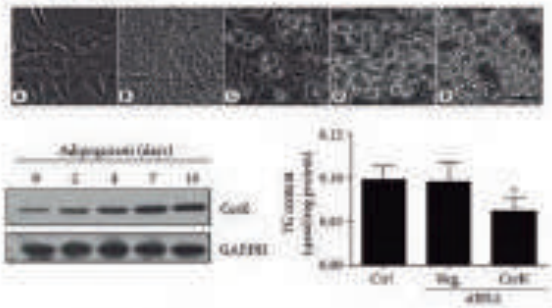
Gómez Muñoz A [1], Trueba M [1], Carracedo A [1,2], Presa N [1], Camacho L [1], Domínguez Herrera A [1] and Gómez Larrauri A [1].
[1] *Department of Biochemistry and Molecular Biology, Faculty of Sciences and Technology. University of the Basque Country (EHU-UPV).*
[2] *CIC bioGUNE, Bizkaia.*

Sphingolipids are long-chain aliphatic amines containing two or three hydroxyl groups, and often a distinctive trans-double bond in position 4.
Despite being essential in eukaryotic **cell membrane architecture**, they also play fundamental roles as signaling molecules in different cell processes such as **inflammation, proliferation, differentiation, adhesion, migration** or **apoptosis.**

1 Regulation of adipogenesis by bioactive sphingolipids and their impact on obesity development

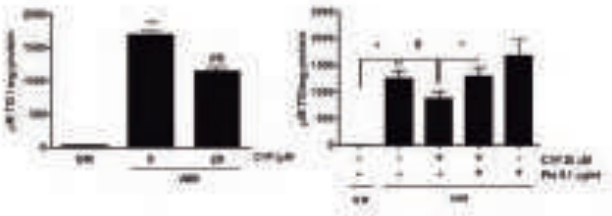
Ceramide kinase (Cerk) is a novel regulator of adipogenesis

Ceramide kinase, the enzyme that phosphorylates ceramide to the bioactive sphingolipid ceramide 1-phosphate (C1P) .Is overexpressed during the differentiation of pre-adipocytes to mature adipose cells. We can block adipogenesis by silencing Cerk expression.



Exogenous ceramide 1-phosphate (C1P) inhibits dipogenesis

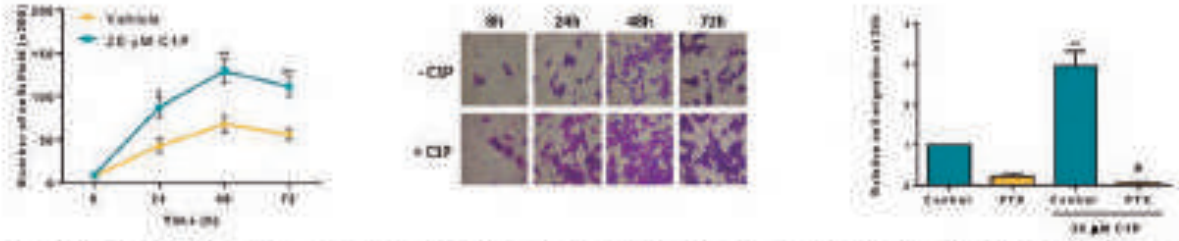
The administration of exogenous C1P inhibits the adipogenic process by reducing the accumulation of triglicerydes in the form of lipid droplets. This action is reversed by pertussis toxin, suggesting the intervention of a G, protein-coupled receptor previously identified for C1P.



2 Regulation of inflammatory processes in pulmonary diseases and prostate cancer

Ceramide 1-phosphate (C1P) inhibits cigarette smoke (CS)-induced lung inflammation and partially prevents emphysema in mice

Ceramide 1-phosphate (C1P) stimulates PC-3 prostate cancer cell migration through a G, protein-coupled receptor



Work in ASM laboratory is supported by "Departamento de Educación del Gobierno Vasco (Diputación Foral de Vizcaya, Basque Country, Spain)" grant number IT-1106-16, and "Ministerio de Ciencia, Innovación y Universidades" (Madrid, Spain)" grant number SAF2016-79695-R.

Mechanistic insights into the role of nucleophosmin/APE1 in DNA damage repair: regulation of the repair machinery?

David J. López, Ander de Blas, Jon Mentxaka*, Igor de la Arada, Mikel Hurtado**, Mikel García-Alija*, Marián Alonso-Mariño, M. Ángeles Urbaneja, Sonia Bañuelos*

Biofisika Institute (UPV/EHU-CSIC) and Department of Biochemistry and Molecular Biology, University of the Basque Country (UPV/EHU), Leioa, Spain.

*TFG (end-of-degree project) students; ** TFM (end-of-master project) student

KEY WORDS: nucleophosmin, NPM1, APE1, DNA damage repair, DDR, BER, protein-protein interaction.

Our genome is constantly challenged by factors, either exogenous (such as sun radiation, cigarette smoke, pollutants, certain medical treatments) or endogenous, that cause lesions in the DNA. This damage can result in mutations, and thus be deleterious for the organism. Cells have evolved a number of surveillance mechanisms to either repair those lesions or signal the arrest of the cell cycle or even apoptosis. Various repair pathways exist, which rely on different protein machineries. The most frequent damage, oxidation, implies chemical modification of the DNA bases, and is corrected by the Base Excision Repair (BER) pathway. We are interested on two nuclear proteins involved in DNA damage repair (DDR), namely nucleophosmin (NPM1) and APE1, and try to understand how their interplay could regulate the repair mechanism.

We have long studied NPM1, an abundant, nucleolar protein in charge of several functions related to cell growth and homeostasis, such as ribosome assembly, response to stress and DNA damage repair. The roles of NPM1 in different repair pathways remain however to be elucidated. NPM1 is a multidomain oligomer, where a pentameric core is connected to small, C-terminal globular domains through long, flexible linkers. To perform its multiple activities, NPM1 is able to continuously shuttle between cytoplasm, nucleoplasm and nucleolus. NPM1 has been reported to interact with apurynic apyrimidinic endonuclease 1 (APE1), a key enzyme in the BER pathway. APE1 incises the damaged DNA strand at the 5´side of “abasic sites”, i.e. where the damaged base has been removed by a repair glycosidase or either spontaneously lost. APE1 catalysis has been described in molecular detail, but little is known about its modulation, which could be mediated by interaction with NPM1.

To gain insight into the possible role of NPM1 in BER, we have explored the correlation between the subnuclear localization of both APE1 and NPM1, the *in vitro* interaction they establish, the effect of binding to abasic DNA on APE1 conformation, and the modulation by NPM1 of APE1 binding and catalysis on DNA. We have found that, upon oxidative damage, part of NPM1 is released from nucleoli and locates on patches throughout the chromatin, perhaps co-localizing with APE1, and that this traffic could be mediated by phosphorylation of NPM1 on T199. Therefore, NPM1 might locate, together with APE1, in repair platforms and directly participate in the BER route. NPM1 and APE1 form a complex *in vitro*, involving, apart from the core domain, at least part of the linker region of NPM1, whereas the C-terminal domain is dispensable for binding, which explains that an AML leukemia-related NPM1 mutant with an unfolded C-terminal domain can bind APE1. APE1 interaction with abasic DNA stabilizes APE1 structure, as based on infrared and circular dichroism spectroscopies. By fluorescence anisotropy binding assays we have analyzed the effect of NPM1 on APE1 association to an abasic lesion-mimicking oligonucleotide. Our data suggest that NPM1, maybe by keeping APE1 in an “open” conformation, favours specific recognition of abasic sites on DNA, competing with off-target associations. Based on our results, we propose that NPM1 might directly participate in the BER route favouring APE1 target selection as well as turnover from incised, product DNA, which could explain NPM1 stimulation of APE1 incision activity. NPM1 regulation of APE1 repair activity represents a novel therapeutic target that could be exploited for chemosensibilization / radiosensibilization.

Mechanistic insights into the role of nucleophosmin/APE1 interaction in DNA damage repair: regulation of the repair machinery?

David J. López, Ander de Blas*, Jon Mentxaka*, Igor de la Arada, Mikel Hurtado**, Mikel García-Alija*, Marián Alonso-Mariño, M. Ángeles Urbaneja, Sonia Bañuelos

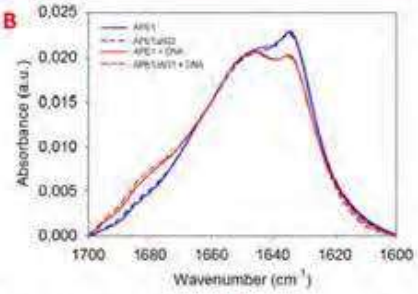
*TFG (end-of-degree project) and ** TFM (end-of-master project) students

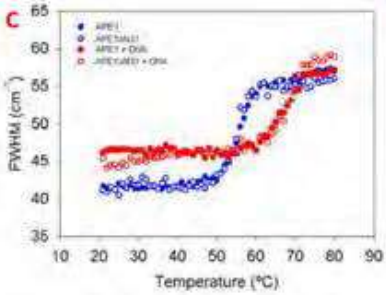
Biofisika Institute (UPV/EHU-CSIC) and

Dpt. of Biochemistry and Molecular Biology, University of the Basque Country (UPV/EHU)

Nucleophosmin (NPM1) might participate in the BER repair pathway regulating APE1.

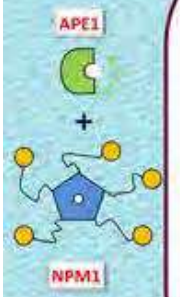
Apurynic apyrimidinic endonuclease 1 (APE1) is a key enzyme of the Base Excision Repair (BER) pathway, which corrects lesions of DNA bases. In spite of a wealth of information on APE1 structure and activity, its regulation is less understood. APE1 interacts with nucleophosmin (NPM1) (Vascotto *et al.* 2009), a multifunctional, homopentameric protein abundant in nucleoli, involved in the cell response to stress and DNA damage repair. We have focused on the interaction between NPM1 and APE1 to unravel how NPM1 could regulate APE1 function and participate in the BER route.



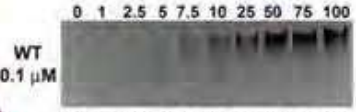


The crystal structure of APE1 hardly changes when it binds to abasic DNA (**A**, free APE1 (4QHE, Het et al., 2014) in blue, and bound to a substrate and product DNA (green, 5DFI and red, 5DFF, respectively, Freundenthal et al., 2015). FT-IR spectroscopy, however, reveals a conformational change (**B**) and significant thermal stabilization (**C**) of the protein upon binding to an abasic-mimicking "product" oligonucleotide. It must be noted that there is a ca. 45 aa long flexible N-terminal segment not visible in the crystal structure. The changes detected by FT-IR are not attributable to the N-terminal segment, since they occur also in the truncated mutant APE1ΔN33.

➔ **APE1 conformation / dynamics is sensitive to DNA binding.**



$(NPM1^{wt})_5$-$APE1^{wt}$
K_D 0.4 ± 0.1 μM



$(NPM1^{mutA})_5$-$APE1^{wt}$
K_D 0.9 ± 0.2 μM

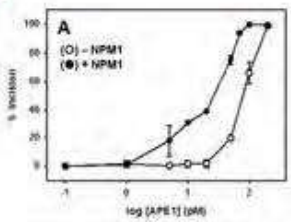
$(NPM1^{\Delta C108})_5$-$APE1^{wt}$
K_D 0.7 ± 0.2 μM

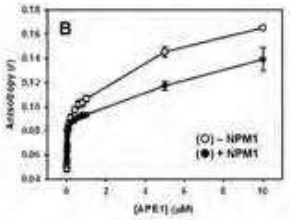
$(NPM1^{core})_5$-$APE1^{wt}$
K_D 8.8 ± 3.2 μM

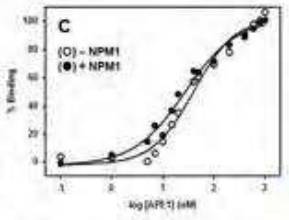
$(NPM1^{wt})_5$-$APE1^{\Delta N33}$
K_D 24 ± 15 μM

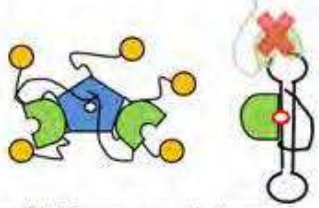
We have analyzed, by native electrophoresis, the interaction between different constructs of NPM1 and APE1. The wild-type, full-length proteins bind with a K_D of 0.4 ± 0.1 μM, forming a complex where probably several molecules of APE1 bind to pentameric NPM1. NPM1 mutant A, associated to AML leukemia, is also able to bind APE1. The comparison between different constructs reveals that the core domain plus the first half of the linker of NPM1, both of acidic character, and the positively charged N-terminal region of APE1 are primarily responsible of the recognition.

➔ **NPM1 / APE1 interaction engages NPM1 core and part of the linker, and APE1 N-terminal region.**









NPM1 stimulates APE1 incision activity on a model of abasic DNA, as followed by an electrophoretic assay (**A**). Fluorescence anisotropy analysis of APE1 binding to a labelled oligonucleotide indicates that NPM1 competes with low affinity binding of APE1 to non-abasic sites (**B**), but enhances its affinity for abasic sites (**C**).

➔ **NPM1 promotes specific binding of APE1 to abasic sites and inhibits association to alternative sites, thus favouring catalysis.**

CONCLUSION:

NPM1 might keep APE1 in an optimal conformation for catalysis, perhaps with the N-terminal "arm" open and the active site exposed. This regulatory mechanism would favour specific binding to abasic sites and thus contribute to enhance repair efficiency.

Ref.: López D.J. *et al.* (2020) DNA Repair 88:102809

Molecular biology of cancer

Ana Aguirre[1], Endika de la Iglesia[1], Larraitz Fernández[1], Asier Fullaondo[1], Alejandro García[1], Iraia García-Santisteban[1], Mohaddase Hamidi[1], Ainhoa Iglesias-Ara[1], Gartze Mentxaka[1], Jone Mitxelena[1,2], Noor Mustafa[1], Beatriz Peñalver[1], José Antonio Rodríguez[1], María Sendino[1], Jon Vallejo-Rodríguez[1], & Ana M. Zubiaga[1]

[1]Department of Genetics, Physical Anthropology and Animal Physiology, [2]Biochemistry and Molecular Biology, UPV/EHU, [2]Ikerbasque, Basque Foundation for Science

KEY WORDS: Cancer, Cell Cycle, Mitosis, Tumor suppressor, Ubiquitination, Gene knockout, Genomics, Proteomics.

The main feature that defines tumor processes is the alteration of cellular homeostasis. Deregulation of the cell cycle, abnormal gene regulation, and defects in protein posttranslational modifications are among the mechanisms that contribute to this alteration. The detailed characterization of these mechanisms, and how they contribute to the neoplastic transformation constitute the main objectives of our research group. Their elucidation could contribute to the search for new therapeutic strategies for cancer treatment.

Our research group is a multidisciplinary team whose components are specialized in the areas of genetics, molecular and cellular biology, proteomics, and bioinformatics. The group has been working for more than a decade in the field of molecular biology of cancer, considered to be a strategic research field by the Euskampus initiative of the UPV/EHU, because of its biomedical and social relevance. The research team has been recognized and funded by the Department of Education of the Basque Government as a "Consolidated Group" continuously since 2001.

We are applying genomic and proteomic approaches, together with classical methods of genetic and biochemical analysis, to identify and characterize the proteins and pathways that play a key role in the control of cellular proliferation and cell fate, including the dysregulation that contributes to oncogenesis. Current areas of research in the laboratory focus on the following topics:

RESEARCH LINE 1: Cell cycle regulation and tumor development

- 1.1 Transcriptional networks regulated by E2F transcription factors
- 1.2 Tumor suppressor function of E2F transcription factors
- 1.3 Mitotic regulation

RESEARCH LINE 2: Ubiquitylation and nuclear export of proteins in tumor development

Molecular Biology of Cancer

Universidad del País Vasco / Euskal Herriko Unibertsitatea

Visit our research group: **http://www.ehu.es/es/web/molbiolcancer/home**

Ana Aguirre[1], Endika de la Iglesia[1], Ainhoa Eriz[1], Larraitz Fernández[1], Asier Fullaondo[1], Alejandro García[1], Iraia García-Santisteban[1], Mohaddase Hamidi[1], Ainhoa Iglesias-Ara[1], Gartze Menteaka[1], Jone Mitxelena[1,2], Noor Mustafa[1], Beatriz Peñalver[1], José Antonio Rodríguez[1], María Sendino[1], Jon Vallejo-Rodríguez[1], & Ana M. Zubiaga[1]

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- 1.2 Tumor suppressor function of E2F factors
- 1.3 Mitotic regulation

RESEARCH LINE 2: Ubiquitylation and nuclear export of proteins in tumor development

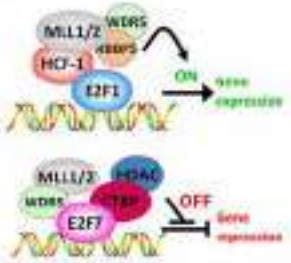
RESEARCH LINE 1: Cell cycle regulation and tumor development

Mammalian E2F transcription factors are essential for the correct DNA replication and cell cycle progression. In fact, the transcriptional activity of these factors is deregulated in virtually all cancers. The focus of our research is to define the mechanisms by which E2Fs regulate cellular homeostasis, and to understand how this process is deregulated in tumor cells.

RESEARCH LINE 1.1: GENOMIC ANALYSES: RNA-Seq, ChIP-Seq, proteomics

- Transcriptional regulatory networks controlled by E2Fs

- Interactome of E2Fs

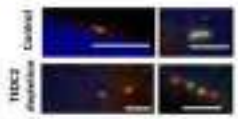


RESEARCH LINE 1.3: Mitotic regulation. *TEDC2*, a novel E2F target gene

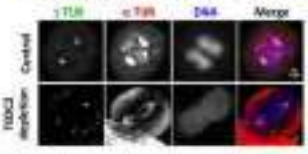
- TEDC2 localizes to the centrioles

- TEDC2 localizes to the midbody during cytokinesis

- TEDC2 regulates centriolar splitting

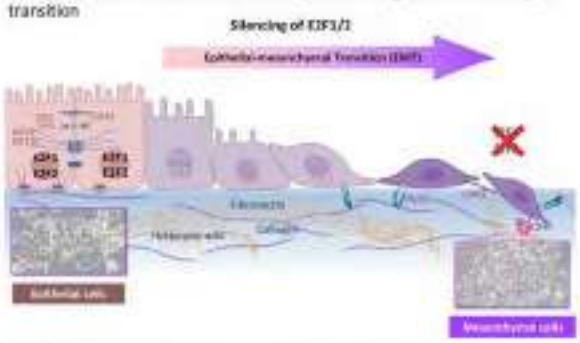


- TEDC2 depletion results in aberrant mitosis



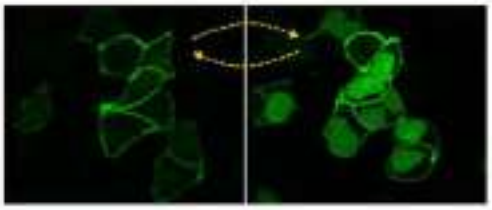
RESEARCH LINE 1.2: GENETIC ANALYSES: Gene knockout, RNA interference, CRISPR/Cas9, transgenics

- Tumor suppresser function of E2Fs. Role of E2F1 and E2F2 in the maintenance of epithelial cell differentiation and in repression of epithelial-mesenchymal transition



- Role of E2Fs in the control of DNA replication, cellular senescence and apoptosis

RESEARCH LINE 2: Ubiquitination and nucleocytoplasmic transport of proteins in tumor development



FUNDING AND COLLABORATIONS

Karolinska Institutet · CNIO · cost · UC San Diego

Genomics and human and animal health

Begoña M. Jugo[1], Elena Díaz-Ereño[2], Ana María Valle[3], Jaime Zubero[4], Naiara Abendaño[1], Itxazne García-Ceciaga[2], Endika Varela-Martínez[1], Martín Bilbao-Arribas[1], Oier Cabrera-Ramos[1]
[1]Genetics, P. Anthropology and Animal Physiology Dpt. and [3]Mathematics, Statistics and Operational Research Dpt., Fac. of Science and Technology; [2]Physiology Dpt. and [4]Nursery Dpt., Fac. of Medicine and Dentistry

KEY WORDS: genomics, obesity, dietary patterns, gene-environment interactions, infectious diseases, adjuvants, autoimmunity, RNA-seq, miRNAs, non-coding RNAs

Human health: dietary patterns and genetics in obesity

Obesity and its associated comorbidities represent one of the biggest public health challenges today. Our main interest in human health is the disentangling of environment-genes interaction in relation to obesity in work environments.

- In the genetic analysis, of the 17 selected genes that previously showed significant association with obesity in GWAS studies, four of them showed statistically significant associations, especially with abdominal obesity. Specifically, SNPs located in genes PPARG, FAIM2, CETP and BDNF have shown association with body mass index or hip waist index, depending on the SNP. The results suggest that the PPARG gene could contribute to the development of general obesity whereas, the FAIM2 and CETP genes contributed to abdominal obesity.
- Based on the results of the exploratory analysis of dietary patterns, the predominant pattern of this working population has been the Western one. The second emerging pattern has been called Prudent. Lastly, a third different pattern, associated with very specific foods, has been detected in the sample disaggregated by sex. This difference reflects a differentiated food choice by gender that opens up new perspectives to explore dietary patterns.

Animal Health and biotechnological applications: relationship between the action of aluminium as adjuvant in vaccines and non-coding RNAs.

We are mainly interested in the characterization and quantification of different non-coding RNAs in relation to aluminium adjuvants in vaccines, as the mechanism of how they exert beneficial effects is still not fully understood. For that, total RNA sequencing and miRNA sequencing have been performed. We have analysed lncRNs and circRNAs in two different tissues.

- The lncRNAs are long transcripts, with a length of at least 200 nu., that do not encode proteins. The information that can be derived from one species to another about its structure and function is very scarce. About 5000 reliable transcripts of this type were detected in parietal lobe cortex and in PBMCs. Some of them have maintained their genomic position in nearby species, although the degree of conservation of the sequences has been high in few of them. In addition, differential expression was detected in several lncRNAs in animals that have received vaccination with aluminum adjuvant. More analyses are needed to determine the functional relationship of these lncRNAs with mRNAs and miRNAs.
- Circular RNAs (circRNAs) are covalently closed circular non-coding RNAs. Due to their structure, circRNAs are more stable and have longer half-lives than linear RNAs making them good candidates for disease biomarkers. Despite the scientific relevance of these molecules, the study of circRNAs in non-model organisms is still in its infancy.
  We analysed total RNA-seq data to identify circRNAs in sheep from peripheral blood mononuclear cells (PBMCs) and parietal lobe cortex. Out of 2510 and 3403 circRNAs detected in, a total of 1379 novel circRNAs were discovered in the two different tissues. Remarkably, around 63% of all detected circRNAs were found to be completely homologous to a circRNA annotated in human.

This study can help to identify molecular signatures activated by vaccines and their adjuvants, providing insight into the mechanism that underlie the immune response by combining the molecular information provided by sequencing of different RNA types.

GENOMICS AND HEALTH research group

Begoña M. Jugo[1], Elena Díaz-Ereño[2], Ana María Valle[3], Jaime Zubero[4], Naiara Abendaño[1], Endika Varela-Martínez[1], Itxazne Garcia-Ceciaga[2], Martín Bilbao-Arribas[1], Oier Cabrera-Ramos[1]

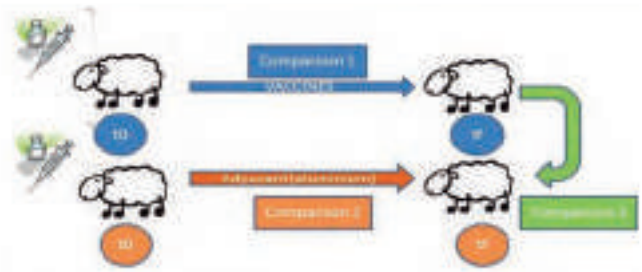
[1]Genetics, P. Anthropology and Animal Physiology Dpt. and [3]Mathematics, Statistics and Operational Research Dpt., Fac. of Science and Technology; [2]Physiology Dpt. and [4]Nursery Dpt., Fac. of Medicine and Dentistry

1 ANIMAL HEALTH: MECHANISM OF ACTION OF ALUMINIUM

The main aims of this research line are:

- To identify possible adverse reactions to the adjuvant due to the repetitive inoculation that is performed in sheep during the year.
- To identify gene signatures that are activated by vaccines and their adjuvants in the form of aluminium salts *in vivo*, by means of RNA and miRNA sequencing.
- To characterize new non-coding RNAs and decipher their possible regulatory role.

EXPERIMENTAL DESIGN



LONG NON-CODING RNAs

Annotation of novel long non-coding RNAs

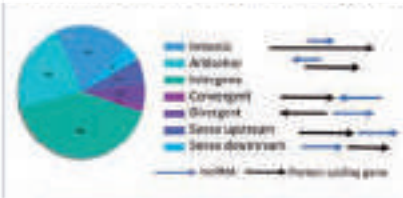


Figure 1. Classification of novel lncRNAs in relation with their closest coding gene

LncRNAs are long transcripts, that do not code proteins but are involved in several biological processes. They are generally not conserved between species and are lowly expressed. About 5000 reliable lncRNAs were detected in brain and in PBMCs. In addition, several lncRNAs were differentially expressed in the presence of aluminium, which could be related to the regulation of the immune response.

Circular RNAs

Circular RNAs (circRNAs) are a new class of covalently closed circular non-coding RNAs, formed when a splice donor and upstream acceptor from a linear RNA are linked together. Using rRNA depleted RNA-seq libraries, 2,510 and 3,403 circRNAs detected in encephalon and PBMCs, redpectively. 36.32% of the PBMC circRNAs were also detected in encephalon. circRNAs are highly conserved between sheep and human, with nearly 63% of the detected circRNAs in both tissues having an homologous human circRNA.

Figure 2: Conservation of circRNAs in sheep. In the y-axis the number of circRNAs in each category and in the x-axis the different categories. a) Encephalon; b) PBMCs. Homologous, sheep circRNAs completely concordant to human circRNAs in CIRCpedia database; 3'/5' site utilized, only one coordinate of the junction is concordant with a human circRNAs; Both sites utilized, both junction coordinates are concordant with different human circRNAs; Not aligned, sheep circRNAs that could not be translated to human coordinates.

Conclusions

Taken together, these experiments demonstrated that aluminium containing adjuvants are not simple delivery vehicles for antigens, but also induce endogenous danger signals that can stimulate and modulate immune system.

Future Work

Identification of the molecular signatures that are activated by vaccines and adjuvants in granulomas and other tissues.

2 HUMAN HEALTH: LIFE STYLE AND GENETICS IN OBESITY

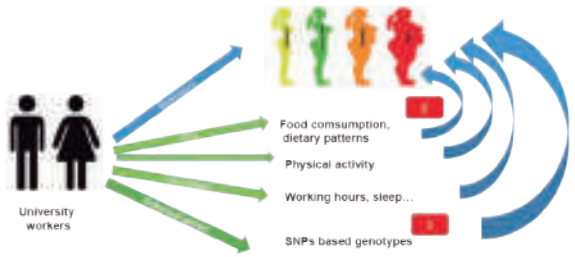
The main aims of this research line are:

- To estimate the prevalence of weight overload and its relationships with environmental, behavioural and genetic factors.

Genetics of obesity: - To explore associations between some previously obesity-related SNP and some adiposity anthropometric index

Nutrition: - To identify principal dietary patterns

EXPERIMENTAL DESIGN



Results

1. GENETICS OF OBESITY

In the genetic analysis, of the 17 selected genes that previously showed significant association with obesity in GWAS studies, four of them showed statistically significant associations, especially with abdominal obesity. Specifically, SNPs located in genes PPARG, FAIM2, CETP and BDNF have shown association with body mass index or hip waist index, depending on the SNP. The results suggest that the PPARG gene could contribute to the development of general obesity whereas the FAIM2 and CETP genes contributed to abdominal obesity.

2. DIETARY PATTERNS

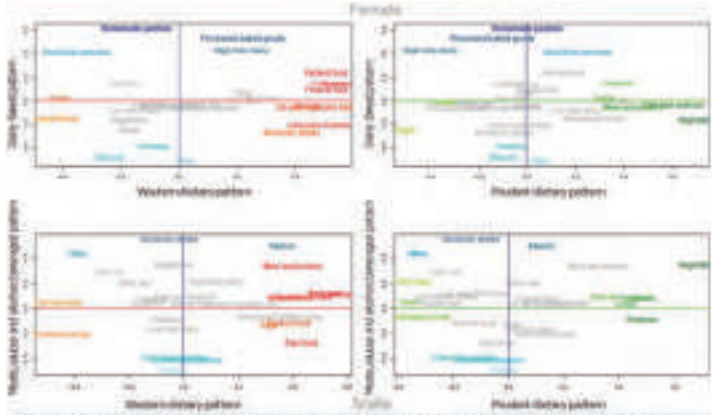


Figure 3: Contribution of the food groups to each dietary pattern. In green, food contributing to Prudent pattern, in red , to Western pattern and in blue food adhering to the third dietary pattern. The colour gradient shows the degree of contribution (higher intensity higher contribution)

The predominant dietary pattern of this working population has been the Western one (fast food, red meat,...). The second emerging pattern has been called Prudent (vegetables, fish...). Lastly, a third different pattern, associated with very specific foods, has been detected in the sample disaggregated by sex.

Conclusions

The difference in dietary patterns reflects a differentiated food choice by gender that opens up new perspectives to explore dietary patterns.

Future Work

Association of all this information with genetic polymorphisms of selected candidate genes.

Human evolutionary biology

Concepción de la Rúa[1], Neskuts Izagirre[1], Montserrat Hervella[1], Imanol M. Laza[1], Nerea G. Ventades[1], Asier San Juan[1] Santos Alonso[1], Isabel Smith[2], Arrate Sevilla[1], Sonia Olaechea-Lázaro[1].

[1]Dept. of Genetics, Physical Anthropology and Animal Physiology. Faculty of Science and Technology. University of the Basque Country (UPV/EHU). Leioa, Spain; [2]Dept. of Zoology and Animal Cell Biology. Faculty of Science and Technology. University of the Basque Country (UPV/EHU). Leioa, Spain.

KEY WORDS: Neanderthal, archaic and modern humans, Next Generation Sequencing, paleogenomics, paleopathology, bioinformatics, skin pigmentation, melanoma, genetic expression, human diversity, resequencing, aptamer.

PALEOGENOMICS: RECONSTRUCTION OF THE HUMAN EVOLUTIONARY HISTORY

The aim of our research is to understand the evolutionary path of our species using paleogenomics analysis. The development of the Next Generation Sequencing (NGS) techniques allows the comparison of the genomic data of our species with other closely related extinct species as Neanderthals. Up to the present we have recovered the complete genome of both the first Homo sapiens in Europe (35 kya) and the most ancient human (at least 165 kya) in the Basque Country (Lezetxiki, Gipuzkoa). The human of Lexetxiki is related to the ancestor species of Neanderthals. Another field of research is the study of skeletal remains from a molecular and anthropological perspective to understand the influence of both genetic and environmental factors in the genesis of rheumatic diseases (e.g. Ankylosing Spondylitis, Rheumatoid Arthritis, Osteoarthritis). We are analysing rickets and rheumatic diseases in the population recovered from the Cathedral of Santa María (Vitoria-Gasteiz, Álava, 11th-19th centuries), considering demographic, historic, environmental and archaeological data recovered from the city of Vitoria-Gasteiz during medieval and modern period. The study of both present-day patients and past populations allowed us to understand the influence of environmental factors (such as “Little Ice Age” period) in the genetic susceptibility to suffer rheumatic pathologies. Methodological innovation in ancient DNA analysis has been carried out through the design of genotyping chip, which includes a hundred SNPs associated to several rheumatologic diseases. The aim of this study is to design a risk haplotype in order to establish an early diagnosis of a heterogeneous group of rheumatic pathologies.

SKIN PIGMENTATION, MELANOMA AND POPULATION GENOMICS

There are genetic and environmental factors that determine the risk to melanoma susceptibility. In particular, light-skinned individuals are less protected against photocarcinogenesis and/or photoaging after solar irradiation. Therefore, we are trying to identify genetic variation associated with skin pigmentation in humans in order to infer its adaptive value and assess its biomedical implications. For that reason, we are focusing on the detection of differentially expressed genes in melanocytic cell lines from individuals with different skin pigmentation, using expression chips. We are also analysing the effect of vitamin D on pigmentation using different techniques: RNA-seq., ChIP-seq and methylation analysis by MeDIP-Seq. Subsequently, a subset of loci is selected to analyse their sequence diversity by resequencing and their variation in the copy number of their exons. In collaboration with other groups, we analyse the variability in melanoma patients and healthy individuals. We are evaluating the adaptive value and the potential biomedical implications (predisposition to/protection against cutaneous melanoma) of these polymorphisms by means of bioinformatics. On the other hand, we design aptamers, single-stranded oligonucleotides that bind with high affinity to metabolites of interest, like the alfa-MSH hormone, a ligand of MC1R. These aptamers will allow the detection and the quantification of biomarkers in individuals of light and dark skin pigmentation, and they may also serve as tumour markers for clinical diagnosis of melanoma. Besides, we are analysing the mutational load of driver mutations in melanoma biopsies and in serum of melanoma patients (cell-free DNA) by Digital PCR so as to determine if the mutational load can be used as a diagnosis or prognosis biomarker.

Another branch of our research group focuses in the study of population genomics and environmental adaptations in African populations. Precisely, we are investigating Cameroon due to its extraordinary genetic, ethnic and linguistic diversity, its rich climate and vegetation diversity and the wide variety of subsistence strategies of its inhabitants. To explore this and taking advantage of next-generation sequencing techniques, we are analysing the genetic diversity and population structure in this country, as well as looking for selection signals associated to the different environmental conditions that affect its subgroups.

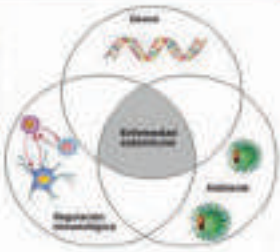
BIOLOGÍA EVOLUTIVA HUMANA

Concepción de la Rúa, Neskuts Izagirre, Montse Hervella, Imanol Martín, Nerea G. Ventades, Santos Alonso, Isabel Smith, Arrate Sevilla, Sonia Olaechea-Lázaro

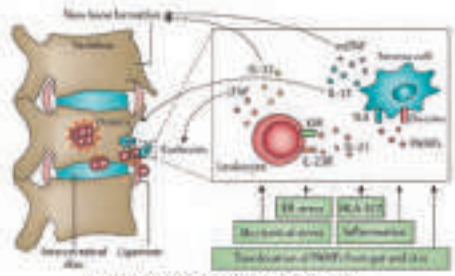
UPV/EHU. FCyT. Dpto. de Genética, Antropología Física y Fisiología Animal.

Reconstrucción de nuestra historia evolutiva: enfermedades y genes.

Las **Artropatías Inflamatorias** (AIs) son un grupo de enfermedades reumáticas autoinmunes y autoinflamatorias, desencadenadas por una combinación de factores genéticos y ambientales.



Análisis antropogenético de AIs en los restos óseos del País Vasco de la Edad Media y Moderna: la Catedral de Santa María (Vitoria-Gasteiz, s. XI-XIX) y la necrópolis de San Miguel de Ereñozar (Ereño, Bizkaia, s. XIII-XVI), considerando datos demográficos, históricos, ambientales y arqueológicos.



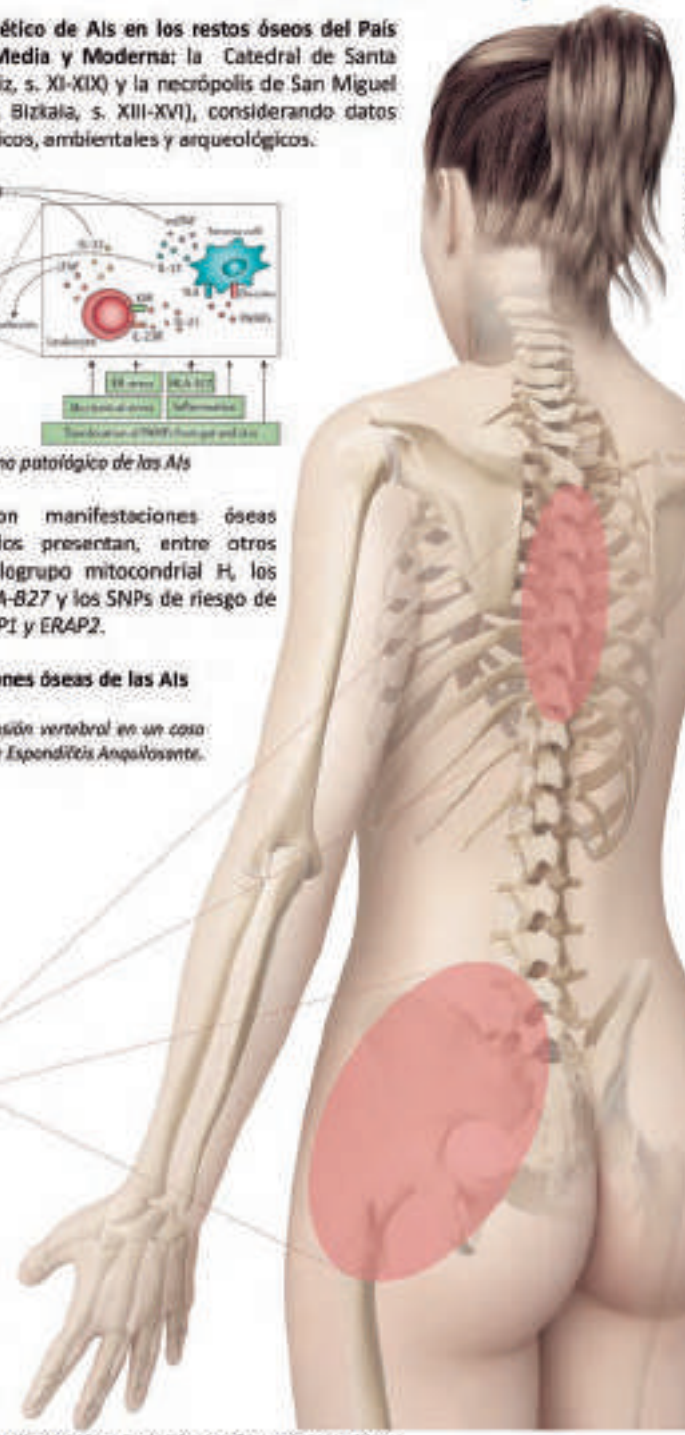
Mecanismo patológico de las AIs

Los individuos con manifestaciones óseas reumáticas analizados presentan, entre otros marcadores, el haplogrupo mitocondrial H, los alelos *HLA-B40* y *HLA-B27* y los SNPs de riesgo de los genes *IL23R, ERAP1* y *ERAP2*.

Manifestaciones óseas de las AIs

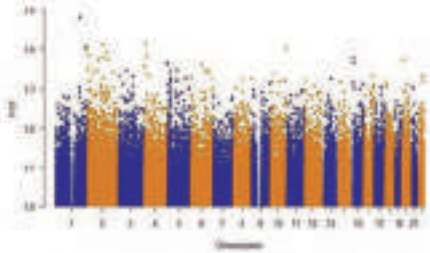
Fusión vertebral en un caso de Espondilitis Anquilosante.

Anquilosis de la articulación coxofemoral y sacroiliaca en otro caso de Espondilitis Anquilosante.

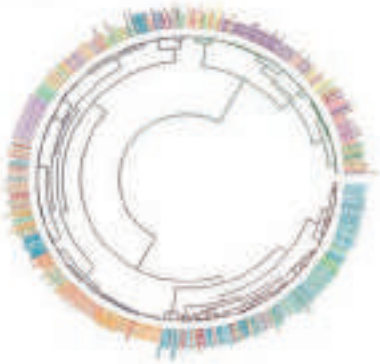


Análisis de rasgos complejos de interés adaptativo y biomédico.

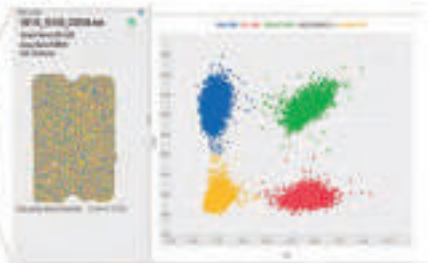
El análisis bioinformático de datos procedentes de secuenciación masiva o **Next-Generation Sequencing (NGS)** permite, entre otros, la detección de adaptaciones evolutivas asociadas a presiones ambientales.



Análisis de estructuración poblacional en base a la diversidad haplotípica en Camerún. Los individuos se agrupan genéticamente en base a su origen étnico, modo de vida y ecosistema.



La **PCR digital (dPCR)** permite la detección y cuantificación de variantes asociadas al **riesgo de melanoma** presentes en una biopsia.



Existe una compleja relación entre la vitamina D y la pigmentación de la piel: **la vitamina D podría estimular la melanogénesis.**

Agradecimientos: Esta investigación ha sido posible gracias a la financiación recibida del Gobierno Vasco (IT1138-16), del MICIN (CGL2017-88031-P) y de la concesión de becas predoctorales del Gobierno Vasco a N. G. Ventades (PRE_2018_1_0130) y a S. Olaechea-Lázaro (PRE_2018_1_0068).

Fungal and bacterial biomics research group
Fungal pathogens: the emerging infectious diseases

A. Ramirez-Garcia, A. Antoran, X. Guruceaga, L. Martin-Souto, L. Aparicio, U. Perez-Cuesta, M. Areitio, A. Abad-Díaz-de-Cerio, F.L. Hernando and A. Rementeria
Fungal and Bacterial Biomics Research Group. Department of Immunology, Microbiology and Parasitology. Faculty of Science and Technology. University of the Basque Country (UPV/EHU)

KEY WORDS: Fungal infections, *Aspergillus*, *Candida*, *Lomentospora*, *Scedospoprium*, Genomics, Transcriptomics, Proteomics, Biomics, CRISPR/Cas9.

The incidence of fungal infections is increasing globally in the last years. In fact, infections caused by microscopic fungi affect millions of individuals, mainly immunocompromised, every year with unacceptable mortality rates, which usually exceed 50%. The main factors that cause these fatal results are the delay in diagnosis due to the lack of rapid, specific, and sensitive detection methods and the resistances of many of these fungi to the antifungal drugs. Therefore, the Fungal and Bacterial Biomics Research Group from the University of the Basque Country (UPV/EHU) focuses its efforts on shedding light on the pathobiology of the most important fungal pathogens, mainly *Candida*, *Aspergillus*, and *Scedosporium*/*Lomentospora*, with the aim of understanding their virulence mechanisms. Currently, the group is mainly researching into the following three lines:

1. On the one hand, we study the most prevalent airborne pathogenic filamentous fungus, *Aspergillus fumigatus*. Our purpose is to delve into the knowledge of the infection by *A. fumigatus* and contribute to the general knowledge of this fungus. For that, by transcriptomic studies using AWAFUGE v.1, a whole genome custom microarray, we deepen in the genomic expression dataset. Then, we use CRISPR/Cas9 to obtain knockout mutants of selected genes allowing us to know more about its virulence mechanisms and new therapeutic targets. In addition, other techniques such as infections into different animal (mouse and *Galleria mellonella*) and cell line models, immunological and histological techniques, expression analysis using RT-qPCR, sequencing and bioinformatics are frequently used.

2. On the other hand, we search for the identification of new diagnostic and therapeutic targets of the group *Scedosporium*/*Lomentospora*. Of particular concern is their high resistance to almost all antifungal treatments available nowadays, which make them very dangerous for immunosupressed patients where they cause very high mortality rates. Moreover, they are the second filamentous fungi in cystic fibrosis patients. To accomplish this research line, we combine several omics technologies, such as multidimensional electrophoresis and mass spectrometry, to study samples obtained from infections in animal models and different hospital collaborators. Currently, we are designing a serologic method to detect *Scedosporium*/*Lomentospora* in cystic fibrosis patients and monitorize them.

3. Finally, we also study the role of *Candida albicans* on cancer and metastasis. In this sense, we have demonstrated that the inflammatory response produced in response to *C. albicans* presence in the liver favors the adhesion of tumor cells to the hepatic endothelium, leading to liver metastasis *in vitro* and *in vivo*. Furthermore, we identified several molecules as putative candidates to be enhancers of the response and receptors involved in the process. We have also produced monoclonal antibodies to inhibit the effect of the identified molecules and, currently, we are studying the direct effect of *C. albicans* on on tumor cell malignant phenotype: proliferation, adhesion, cytokine production ...

Summarizing, the Fungal and Bacterial Research group places special emphasis on the characterization of the cellular, molecular and genetic bases involved in the genesis and development of different fungal diseases from a multidisciplinary approach.

Grant: Basque Government IT1362-19

Fungal and Bacterial Biomics Research Group
Fungal pathogens: the emerging infectious diseases

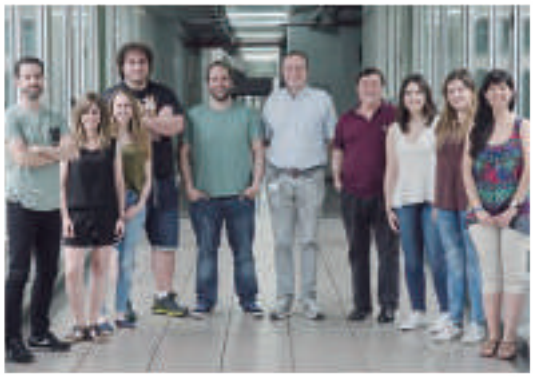
A. Ramirez-Garcia, A. Antoran, X. Guruceaga, L. Martin-Souto, L. Aparicio, U. Perez-Cuesta, M. Areitio, A. Abad-Díaz-de-Cerio, A. Rementeria and F.L. Hernando

University of the Basque Country UPV/EHU, Fungal and Bacterial Biomics Research Group. Dept. of Immunology, Microbiology & Parasitology, Leioa, Spain

INTRODUCTION

The incidence of fungal infections is increasing globally in the last years. In fact, infections caused by microscopic fungi affect millions of individuals, mainly immunocompromised, every year with unacceptable mortality rates, which usually exceed 50%. The main factors that cause these fatal results are the delay in diagnosis due to the lack of rapid, specific, and sensitive detection methods and the resistances of many of these fungi to the antifungal drugs.

Therefore, the Fungal and Bacterial Biomics Research Group from the University of the Basque Country (UPV/EHU) focuses its efforts on shedding light on the pathobiology of the most important fungal pathogens, mainly *Candida*, *Aspergillus*, and *Scedosporium/Lomentospora*, with the aim of understanding their virulence mechanisms.



RESEARCH OBJECTIVES

BIOLOGY OF THE PATHOGENIC FUNGUS *Aspergillus fumigatus*

We study the most prevalent airborne pathogenic filamentous fungus, ***Aspergillus fumigatus***. Our purpose is to delve into the knowledge of the infection by *A. fumigatus* and contribute to the general undestanding of this fungus. For that, by transcriptomic studies using AWAFUGE v.1, a whole genome custom microarray, we deepen in the genomic expression dataset. Then, we use CRISPR/Cas9 to obtain knockout mutants of selected genes allowing us to know more about its virulence mechanisms and new therapeutic targets. In addition, other techniques such as infections into different animal (mouse and *Galleria mellonella*) and cell line models, immunological and histological techniques, expression analysis using RT-qPCR, sequencing and bioinformatics are frequently used.

IDENTIFICATION OF NEW DIAGNOSTIC AND THERAPEUTIC TARGETS OF THE GROUP *Scedosporium/Lomentospora*

We search for the identification of new diagnostic and therapeutic targets of the group ***Scedosporium/Lomentospora***. Of particular concern is their high resistance to almost all antifungal treatments available nowadays, which make them very dangerous for immunosupressed patients where they cause very high mortality rates. Moreover, they are the second filamentous fungi in cystic fibrosis patients. . To accomplish this research line, we combine several omics technologies, such as multidimensional electrophoresis and mass spectrometry, to study samples obtained from infections in animal models and different hospital collaborators. Currently, we are designing a serologic method to detect *Scedosporium/Lomentospora* in cystic fibrosis patients and monitorize them.

STUDY THE ROLE OF *Candida albicans* ON CANCER AND METASTASIS

We have demonstrated that the inflammatory response produced in response to ***Candida albicans*** presence in the liver favors the adhesion of tumor cells to the hepatic endothelium, leading to liver metastasis *in vitro* and *in vivo*. Furthermore, we identified several molecules as putative candidates to be enhancers of the response and receptors involved in the process. We have also produced monoclonal antibodies to inhibit the effect of the identified molecules and, currently, we are studying the direct effect of *C. albicans* on tumor cell malignant phenotype: proliferation, adhesion, cytokine production ...

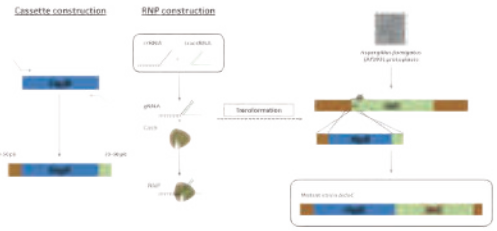
TECHNIQUES

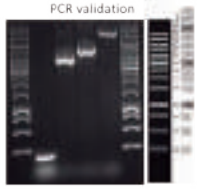
TRANSCRIPTOMIC ANALYSIS

AWAFUGE v.1 Microarray

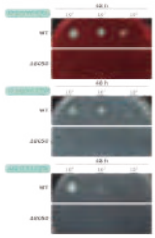
PCR, qPCR, RT-PCR

GENE DELETION TECHNOLOGY
Production of knockout strains by CRISPR/Cas9

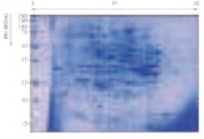




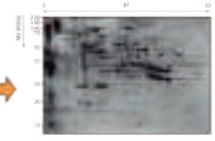
Phenotypic characterization



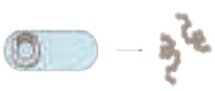
PROTEOMIC ANALYSIS
(2-DIMENSIONAL GEL ELECTROPHORESIS)



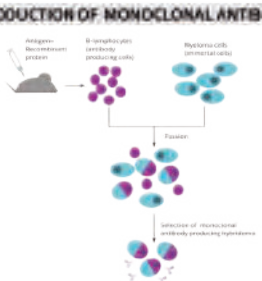
IMMUNOPROTEOMICS-BASED ANALYSIS
WESTERN BLOT



- ✓ Identification of diagnostic targets using LC-MS/MS technology
- ✓ Production of recombinant proteins



PRODUCTION OF MONOCLONAL ANTIBODIES

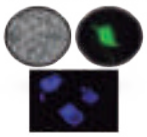


DEVELOPMENT OF DETECTION METHOD

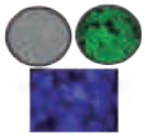
Serologic diagnosis + monitoring

INFECTION MODELS

Cell Line: RAW 264.7
Cell type: Macrophages



Cell Line: A549
Cell type: Alveolar epithelium



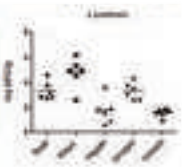
Galleria mellonella

Mouse infection model
Intravenous – Intranasal via

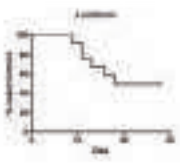
Analysis of fungal pathobiology

Histopathological analysis of infected organs

Number of microorganism infecting the organs (CFU/g)



Survival study



SUMMARY

The Fungal and Bacterial Research group places special emphasis on the **characterization of the cellular, molecular and genetic bases** involved in the genesis and development of different **fungal diseases** from a multidisciplinary approach.

Social networks

https://www.facebook.com/microbiomics2EHU/
https://twitter.com/microbiomicsehu
https://www.instagram.com/microbiomicsu/

Acknowledgements

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✓ LM-S, MA, LA and XG were supported by predoctoral fellowships from the Basque Government or UPV/EHU.

Publications

✓ Ramirez-Garcia et al. (2018) Med. Mycol. 56: S102-S125
✓ Pellon et al. (2018) Int. J. Antimicrob. Agents 51: 10-15
✓ Ramirez-Garcia et al. (2018) Mycopathologia 183:273-289
✓ Pellon et al. (2018) Cel. Microbiol. 20: e12847
✓ Guruceaga et al. (2018) Virulence 9: 1548-1561
✓ Buldain et al. (2019) Vaccines 7: 212
✓ Perez-Cuesta et al. (2020) Int. Microbiol. 23: 55-63
✓ Guruceaga et al. (2020) Toxins 12: 7

Bacterial resistance to stress. *Vibrio* spp. in the aquatic systems in the time of global warming

Maite Orruño[1,2], Iciar Martínez[2-3], Harkaitz Eguiraun[2,4], Vladimir Kaberdin[1-3] and Inés Arana[1,2]
Elixabet Ogayar[1], Laura Fernández-Camarero[1], Josu Galarza[1]
[1]Department of Immunology, Microbiology and Parasitology (UPV/EHU), [2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV/EHU; Plentzia Marine Station), [3]IKERBASQUE, Basque Foundation for Science, [4]Department of Graphic Expression and Engineering Projects

KEY WORDS: *Vibrio*, adverse environments, ocean warming

Human activity profoundly changes the global environment by affecting not only the major biogeochemical cycles but also the evolution of marine ecosystems. Changes in sea surface temperature and associated alterations trigger numerous changes in the physiology and distribution of marine organisms including a large variety of microorganisms. In the last decade, the presence of facultative pathogenic *Vibrio* strains and the incidence of *Vibrio*-borne diseases related to water use have increased. Some adaptation mechanisms (e.g. induction of the viable but nonculturable state (VBNC), increases in bacterial adhesion to biotic and abiotic surfaces or morphological changes) have been proposed to promote the persistence of *Vibrio* spp. in marine ecosystems. At the same time, bacteria-controlling microorganisms are also affected by global warming, which control their own survival and predatory/lytic activity on bacteria.

The distribution and survival of *Vibrio* spp. present in Basque Country coasts have not been extensively studied. However, considering our geographical location and the coastal water uses, the possible changes in their distribution as a consequence of global warming could have an important health, tourism and environmental impact. In this context, our group is carrying out the study of the temporal/spatial distribution of *Vibrio* spp. in the coast, estuaries and open water of the Basque coastal area.

We have recently found that survival of *Vibrio* spp. under starvation conditions is a temperature-dependent process, which is accompanied by a reduction of cell size, changes in the composition of cell proteome and occasionally leads to the acquisition of the VBNC phenotype. Similarly, solar radiation and other essential abiotic factors, such as salinity, also affect survival of *Vibrio* spp. Nevertheless, we have observed differences in the survival patterns of laboratory (CECT) and environmental strains (isolated from seawater) that could be attributed to the complexity and diversity of *Vibrio* genus.

In the environment, predation by protozoa is one of the main factors eliminating *Vibrio* spp. and temperature modulates the complex interrelationships established between the bacterivorous protozoa and their preys. To escape protozoan grazing and to colonize new areas, vibrios can adhere to the surface of marine organisms (crustacean, zooplankton and others). Besides being a defense strategy, cell adhesion also represents an initial step that facilitates host-pathogen interactions. Therefore, analysis of *Vibrio* spp. adhesion ability to marine organisms and comparison of the survival responses developed by planktonic and adhered populations under stress conditions constitute one of our current objectives.

The techniques and methodologies used include epifluorescence microscopy, fluorescence *in situ* hybridization, analysis of bacterial proteome, etc.

Bacterial resistance to stress

Vibrio spp. in the aquatic systems in the time of global warming

Maite Orruño[1,2], Iciar Martínez[2,3], Harkaitz Eguiraun[2,4], Vladimir Kaberdin[1,2] and Inés Arana[1,2]
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Indicator of climatic change

Changes in sea surface temperature and associated alterations

↓

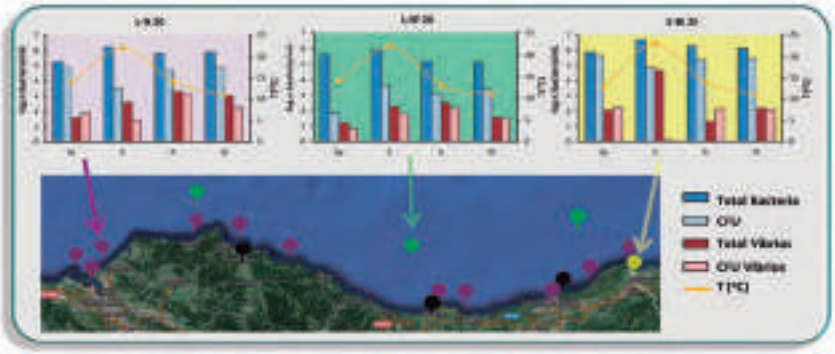
Changes in the physiology and distribution of marine organisms (microorganisms)

↓

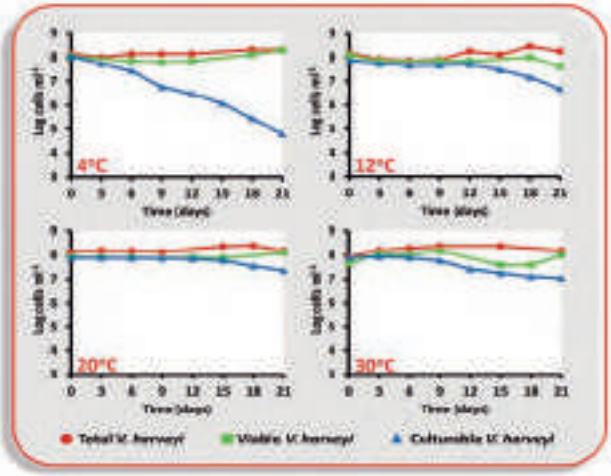
Increases of presence of facultative pathogenic *Vitrio* strains and the incidence of *Vibrio*-borne diseases related to water use

OUR MAIN OBJECTIVES

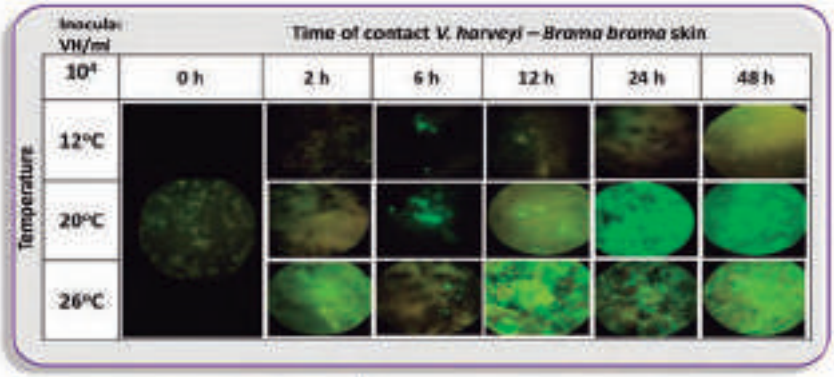
How does the climate change affect the distribution of vibrios in the Basque coastal area?



Which are the survival strategies of *Vibrio* spp.to face climate change?



How do vibrios colonize new areas?



Other researches

Response of vibrios to other environmental factors:

- **Abiotic factors:** Nutrients, salinity, pH
- **Biotic factors:** Predation

Environmental strains *vs* laboratory strains

Tools

Bacterial counts

- Total direct counts
- *Vibrio* CARD-FISH
- CFU on different culture media
- Active *Vibrio*

Proteomic studies

Image analysis

Adhesion ability

FUTURE STUDIES

Study of *Vibrio* spp. adhesion ability to marine organisms and comparative analysis of the survival responses developed by planktonic and adhered populations under stress conditions.

Analysis of *Vibrio harveyi* adaptation to climate change

Vladimir Kaberdin[1-3], Itxaso Montánchez[1], Maite Orruño[1,2], Inés Arana[1,2], Ander Hernández Plágaro[1], Kaan Gundogdu[1], Amaia Leunda[1], Andoni Casen Gil[1], Judith Llanes[1]

[1]Department of Immunology, Microbiology and Parasitology (UPV/EHU), [2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV/EHU), [3]Basque Foundation for Science (IKERBASQUE), Bilbao; e-mail: vladimir.kaberdin@ehu.eus

KEY WORDS: Global warming, gene expression analysis, *Vibrio harveyi*, small regulatory RNAs

The pervasiveness of microorganisms is largely conferred by their unique abilities to adapt and survive under hostile and continuously changing conditions. In our work, we use the Gram-negative bacterium *Vibrio harveyi* (*V. harveyi*) ubiquitously present in natural aquatic systems to study microbial responses to climate change (e.g. elevated temperature, acid pH and low salinity) at the transcriptional and post-transcriptional levels. Our major research lines are briefly outlined below.

1. Addressing the impact of cell size reduction on adaptation of *Vibrio harveyi* in aquatic systems
Our recent work has revealed that adaptation of *V. harveyi* to some abiotic stress conditions could occasionally trigger cell size reduction and acquisition of coccoid-like morphology. As the mechanisms and conditions that lead to the acquisition of coccoid-like morphology by marine vibrios are poorly characterized, we are currently assessing the individual and joint contribution of environmental factors (different salinities, solar radiation, iron scarcity and pH) to cell size reduction. Moreover, due to potential contribution of the coccoid-like morphology to cell resistance to stress and *V. harveyi* fitness in marine ecosystems, we are planning to use advance fluorescent microscopy and quantitative proteomic / transcriptomic tools to address the impact of this phenotype on the capacity of *V. harveyi* to resist various stress factors.

2. High-throughput screening and analysis of antisense RNAs with new roles in *V. harveyi* stress responses
Recent studies revealed a new class of small antisense RNAs (sRNAs) that are involved in regulatory mechanisms controlling bacterial responses to environmental changes. We have recently employed RNA sequencing to discover a number of new sRNAs in *V. harveyi*. While anticipating important roles for the newly discovered sRNAs in bacterial adaptation and virulence, we employ a combination of genetic, molecular biology and biochemical tools to address the biological functions of these regulatory RNAs and their possible contribution to cell adaptation and survival.

3. Development of DNA sequencing protocols for the identification and quantification of *Vibrio* spp. in environmental samples
This research line is centered on using next-generation sequencing (NGS) for analysis of metagenomic DNAs isolated from environmental samples. The developed tools will be used to determine the interannual dynamics of the *Vibrio* populations in seawater sampled in the Biscay Bay. The results of this analysis will further be used to assess the risk of the climate-dependent appearance and spread of *Vibrio*-associated diseases.

Some of the most recent results include:

- Characterization of the long-term physiological and phenotypical responses of *V. harveyi* to starvation at low, moderate and elevated temperatures;
- Identification of numerous protein-coding (e.g. genes encoding transporters, transcription factors and essential metabolic enzymes) and sRNA (e.g. genes encoding GcvB and Qrr1) genes important for adaptation of *V. harveyi* in natural aquatic systems;
- Defining the primary transcriptome of *V. harveyi;*
- Discovery and validation of new regulatory small RNAs in *V. harveyi*.

Analysis of *Vibrio harveyi* adaptation to climate change

Vladimir Kaberdin[1-3], Itxaso Montánchez[1], Maite Orruño[1,2], Inés Arana[1,2], Ander Hernández Plágaro[1], Kaan Gundogdu[1], Amaia Leunda[1], Andoni Casen Gil[1], Judith Llanes[1]

*[1]Department of Immunology, Microbiology and Parasitology, Faculty of Science and Technology & [2]Research Centre for Experimental Marine Biology and Biotechnology (PiE-UPV), Plenzia Marine Station, [3]Basque Foundation for Science (IKERBASQUE), Bilbao; **e-mail: vladimir.kaberdin@ehu.eus***

Background

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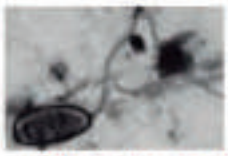
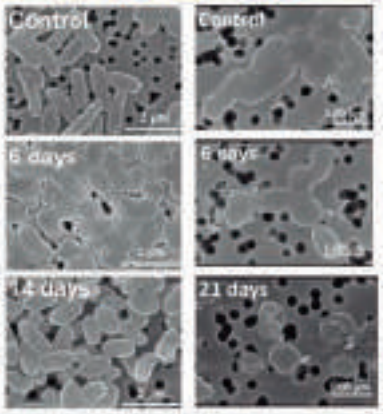


Vibrio harveyi

Analysis of phenotypical changes at 20°C & 30°C



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2. High-throughput screening of antisense RNAs with new roles in *V. harveyi* stress responses

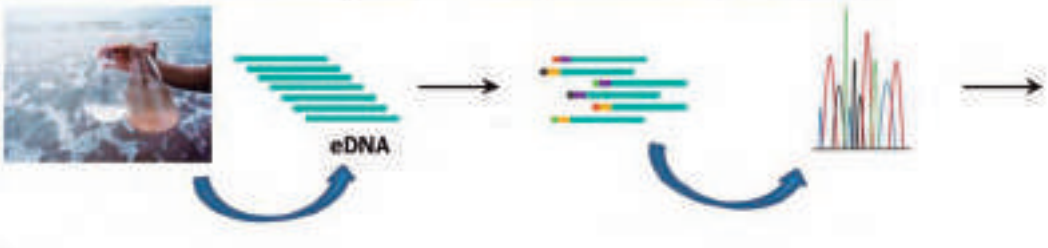
Recent studies revealed a new class of small antisense RNAs (sRNAs) that are involved in regulatory mechanisms controlling bacterial responses to environmental changes. We have recently employed RNA sequencing to discover a number of new sRNAs in *V. harveyi*. While anticipating important roles for the newly discovered sRNAs in bacterial adaptation and virulence, we employ a combination of genetic, molecular biology and biochemical tools to address the biological functions of these regulatory RNAs and their possible contribution to cell adaptation and survival.

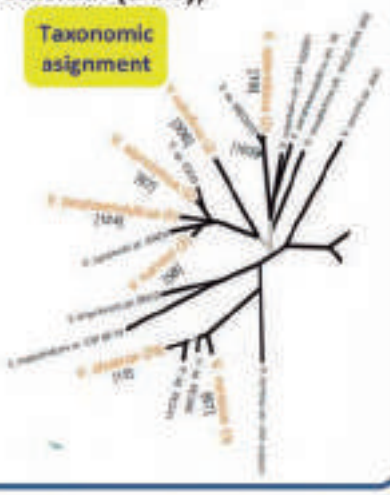
Northern blot validation (on the right) of putative *V. harveyi* small RNA identified by differential RNA-seq (on the left).

3. Development of DNA sequencing protocols for the identification and quantification of *Vibrio* spp. in environmental samples (in collaboration with Prof. Peter Pearman (BC3))

This research line is centered on using next-generation sequencing (NGS) for analysis of metagenomic DNAs isolated from environmental samples. The developed tools will be used to determine the interannual dynamics of the *Vibrio* populations in seawater sampled in the Biscay Bay. The results of this analysis will further be used to assess the risk of the climate-dependent appearance and spread of *Vibrio*-associated diseases.

Isolation of environmental DNA (eDNA) → **Locus-specific barcoding & sequencing** → **Taxonomic asignment**





Role of marine microbes in a changing world

Z. Baña[1], N. Abad[1], I. Artolozaga[1], I. Azúa[1], C. Calcedo[1], O. Sainz[1], M. Unanue[1], A. Uranga[1], B. Ayo[1, 2]
[1]Dept. of Immunology, Microbiology and Parasitology. Faculty of Science and Technology. University of the Basque Country UPV/EHU. Leioa, Spain; [2]Research Center for Experimental Marine Biology and Biotechnology PiE-UPV/EHU, Plentzia-Bizkaia, Spain.

KEY WORDS: climate change, marine microbes, metabolic potential, temperature, enzymatic activities, microplastics, seawater.

The high abundance and functional diversity of the marine microbes represent an important ecological and metabolic potential, which partly explains the functioning of the ocean and can be used for solving many of the problems of the XXI century related to climate change, pollution, health, and energy, among others. However, the complexity of their interactions and their temporal and spatial variability limits our knowledge of their abilities. Our work focuses on several aspects of the activity of the marine microbes that can help to improve life and society.

Marine microbes process about half of the global flow of key elements for life, such as carbon, nitrogen, phosphorus, sulfur and iron, and therefore play a fundamental role in the trophic networks and biogeochemical cycles of the oceans. The temperature of the upper ocean is expected to warm up to 1-3°C during the XXI century, leading to several changes in the functioning of the global ocean. The information about the temperature-sensitivity of most of the microbial processes is scarce, which causes uncertainty about how the microbial communities may respond to rising temperatures. In this sense, we have focused on the study of the temperature sensitivity of bacterial respiration, production and extracellular enzyme activities, in order to gain predictive power about the changes in the **remineralization of the organic matter under future scenarios of global warming**.

The identification of innovative and nature-based solutions to the problems that is facing our planet is also challenging. The great metabolic versatility exhibited by marine microbial communities makes them a good starting point for **microbial bioprospecting** and searching new chemical compounds (microbial growth inhibitors, enzymes of biotechnological interest) and metabolic capacities (degradation of pollutants). On one hand, marine microbial **enzymes** are especially stable and active at different conditions, which makes them of great **biotechnological interest** as new drugs or food additives, and useful compounds for different industrial processes. On the other hand, marine microbes are a feasible source of new natural compounds with **antimicrobial activity** to confront the emergence of new diseases and pathogens resistant to antibiotics. Another aspect of the applications of the metabolic potential of marine microbes is the **bioremediation of environmental pollutans** like the plastic waste. The consumption and production of synthetic polymers has increased dramatically in the last decade and, since their degradation is a slow and complex process, their accumulation in terrestrial and especially marine environments has become a serious environmental and health problem on a global scale. Some microbes are able to biodegrade microplastics without producing an adverse impact on the environment, which makes them potential tools to reduce pollution. However, little is known about this topic and further research is needed to characterize the capabilities of different microbes to degrade microplastics and to determine how those capabilities are constrained by environmental conditions.

In summary, our research group aims to gain knowledge about each of these aspects, in order to obtain predictive tools about the role of marine microbes in future scenarios of global warming, and to detect microbial compounds useful in industrial, biomedical or environmental applications.

Role of marine microbes in a changing world

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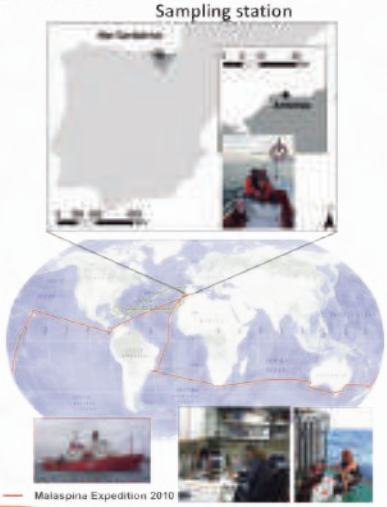
The high abundance and functional diversity of the **marine microbes represent an important ecological and metabolic potential**, which partly explains the functioning of the ocean and can be used for solving many of the problems of the XXI century related to climate change, pollution and health, among others. However, the complexity of their interactions and their temporal and spatial variability limit our knowledge of their abilities.

Our work focuses on several aspects of the activity of the marine microbes, in order to obtain PREDICTIVE TOOLS about the role of marine microbes in future scenarios of global warming, and to detect microbial compounds useful in INDUSTRIAL, BIOMEDICAL OR ENVIRONMENTAL APPLICATIONS.

Sampling station



Malaspina Expedition 2010

CHARACTERIZATION

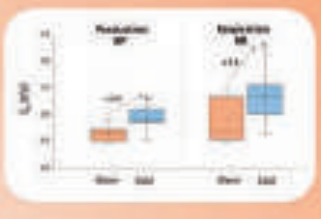
To explore the biodiversity and the functional role of the microbes in the transformations of marine organic matter in coastal waters of the Bay of Biscay.

The annually recurrent seasonal pattern identified is driven by blooms of eukaryotic and prokaryotic phytoplankton in April (T1) and September (T2), respectively.
There is a succession of species and an alternation of communities dominated by ALNY (ASV free-living) and BTPD (ASV attached to particles), which are related to different levels of carbon flow, low and high respectively. This replacement of abundant taxa is related to environmental changes, suggesting the relevance of specialist bacteria in the metabolic response.

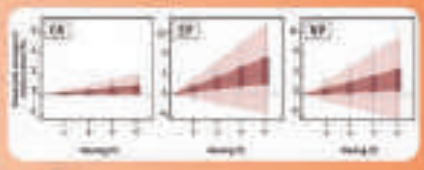
Different bacterial communities can grow with similar and high efficiencies provided they are adapted to the resources and biological components of their environment. But under transitional situations (T), the predominant members are replaced, bacterial carbon consumption (BCD) is reduced, and bacterial growth efficiency (BGE) is decreased. Thus, BGE should be considered a good indicator of the level of adaptation of the community to the environment.

CLIMATE CHANGE

To assess the impact of global change in the microbial communities of coastal waters and open ocean.



Both BP and BR are sensitive to temperature (activation energy, E_a), and consequently, the microbial loop will be more active under a global warming scenario. But BR will increase to a greater extent, leading to an imbalance in the carbon cycle, so a greater proportion of CO_2 will return to the atmosphere, feeding back the global warming. The imbalance will be greater under low surface seawater temperatures (< 16 °C) in the Eastern Cantabrian Sea, which will affect the sustainability of this ecosystem.



The different temperature sensitivity of several extracellular ectoenzymatic activities that hydrolyse specific dissolved organic matter compounds will lead to:

- Substantial stoichiometric shifts toward more nutrient-poor organic matter (increase in C:N, C:P and N:P).
- The expansion of low-nutrient regions in the ocean.

Marine microbial communities

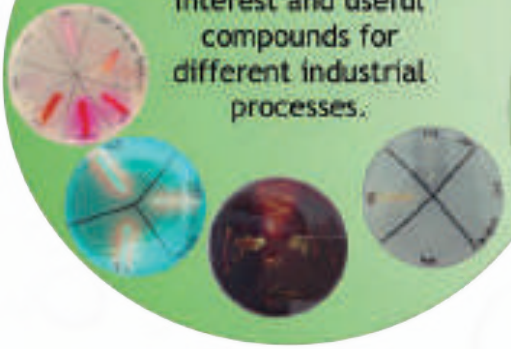
Community

Isolates

Interactions

INDUSTRY

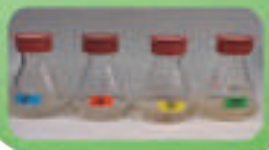
To detect enzymes with biotechnological interest and useful compounds for different industrial processes.



BIOPROSPECTION

POLLUTION

To isolate microbes capable to biodegrade environmental pollutants like petroleum or microplastics.



HEALTH

To identify microbes capable to produce new natural compounds with antimicrobial activity.

Understanding disorders of the visual system and promoting repair and regeneration

Arantxa Acera[1], Javier Araiz[2], Nerea Ayucar[1], Jimena Baleriola[1,3], Maite Blanco[1,3], Miguel de la Fuente[1], Juan Durán[2], Alex Fonollos[2,4], Marta Galdós[4], Julen Goicoechea[1], Silvia López-Plandlolit[2,5], Itziar Martinez-Soroa[2,6], Xandra Pereiro[1], Sergio Pinar-Sueiro[5], Lara Rodríguez[1], Noelia Ruzafa,[1] Haritz Urcol[2,7] and Elena Vecino[1]

[1]*Department of Cell Biology and Histology, University of Basque Country UPV/EHU, Leioa.*

[2]Department of Ophthalmology, University of the Basque Country, UPV/EHU, Leioa.

[3]Achucarro Basque Center for Neuroscience; and Ikerbasque Foundation, Leioa.

[4]BioCruces Health Research Institute, Cruces University Hospital, UPV/EHU, Baracaldo.

[5]Donostia Universtiy Hospital, Ophthalmology, UPV/EHU San Sebastián.

[6]Basurto University Hospital, Ophthalmology, UPV/EHU, Bilbao.

[7]Araba University Hospital, Vitoria

KEY WORDS: visual system, eye, repair, regeneration, GOBE.

The GOBE (Grupo de Oftalmo Biología Experimental, **www-ehu.es/GOBE**) is a multidisciplinary research group interested in eye research. Ophthalmologists, biologists and biochemists integrate the group. Currently, GOBE have 18 members: 13 doctors and 2 PhD, 1 Master Student and 2 undergraduate. The director of the group is Prof. Elena Vecino from the Faculty of Science and Technology; the laboratory is placed in the Faculty of Medicine, in the Department of Cell Biology and Histology. The group is a consolidated group that has been collaborating for more than 25 years in which has been formed 20 Doctors half of them Ophthalmologist that work in Hospitals of the Basque Country. The members of the group are also attached to Biocruces, BioDonosti and BioAraba. Moreover, we collaborate with national and international groups in Universities of Munich, New York, Cambridge and Bordeaux among others. Moreover, we have close collaborations with the industry like IMG-Pharma and Tecnalia as well as Technological Institutions like CIDETEC and POLYMAT.

The methods and techniques that we use include animal models of glaucoma, primary cell culture, immunohistochemistry, ELISAs, proteomic, lipidomic, electron microscopy as well as the use of biomaterials etc. And our objective is to understand the cellular and molecular basis of a disease with the idea of future clinical applications. We have at present projects in collaboration with companies PUE, Elkartek and Hazitec.
The group have five principal lines of research:

1- Neuroprotection and Glaucoma (Prof. Elena Vecino and Dra. Xandra Pereiro). Glaucoma is a neurodegenerative disease that is the leading cause of irreversible blindness that it is caused by the death of the ganglion cells (RGCs) that communicate the eye with the brain. Retinal glia cells are supportive cells and their relationship with ganglion cells is important for normal function. We are studying the molecular interactions between neurons and glia trying to prevent the neuronal damage.

2- Neurodegeneration (Prof. Elena Vecino and Dra. Noelia Ruzafa). Other neurodegenerative diseases, such as Parkinson disease, affect RGCs as other neurons in the brain. We are analyzing the mechanism of infection of these neurons that could mimic Parkinson and other neurodegenerative diseases. In addition, we are trying to characterize molecular markers of neurodegenerative diseases from tear samples from patients in order to do an early diagnostic.

3- Ocular Surface and Nanomaterials (Prof. Juan Durán and Dra. Arantxa Acera). The main objective is identifying biomarkers in tears, as a source of information for the ocular surface in different diseases with the idea to design artificial tears that could promote the repair of the injured ocular surface.

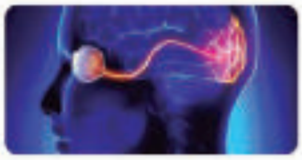
4- Analysis of aqueous humor in glaucoma (Dr. Haritz Urcola). Aqueous humour is a transparent, gelatinous fluid located in the anterior part of the eye. The lack of circulation of aqueous humour is one factor that induce glaucoma. We analyze the biophysical properties of aqueous humour in patients with glaucoma to detect changes compared with healthy eyes. Alterations in its composition may help us understand how glaucoma progresses.

5- Retina (Dr. Javier Araiz and Dr. Alex Fonollosa). Inflammatory diseases in the retina can produce swelling and destruction of eye tissues. We are analyzing the epiretinal membrains obtained from patients with retina detachment as well as we are studying the equilibrium of the cell adhesions and could be affected in inflammatory diseases like diabetic retinopaty and uveitis.

www.ehu.eus/GOBE

NEURO-OPHTALMO BIOLOGY GROUP

Understanding disorders of the visual system and promoting repair and regeneration



Who are we?

We are a multidisciplinary research group of ophthalmologists, biologists and biochemists all interested in eye research.

The group is a consolidated group that has been collaborating for more than **25 years** in which has been formed 20 Doctors half of them ophthalmologist that work in Hospitals of the Basque Country.

The Principal Investigator of the group is Prof. Elena Vecino Prof. at the Faculty of Science and Technology; the laboratory is placed in the Faculty of Medicine, in the Department of Cell Biology and Histology.

We collaborate with national and international groups and we have projects with the industry as well as Technological Institutions.

Dra. Elena Vecino

Full Prof. Cell Biology UPV/EHU. Group Leader of the GOBE. Life Member Clare hall Cambridge, UK. ISEs Prof. Bordeaux. She has published 120 JCR articles, given more than 80 conferences and directed 15 PhD Thesis

Dr. Juan Durán

Full Prof. Ophthalmology UPV/EHU. Fellow Massachussets Eye and Ear Infirmary, Harvard Eye Institute. Medical Director ICQO Bilbao. Eye surface specialist

Dr. Javier Araiz

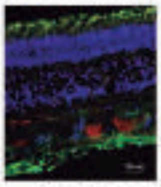
Prof. Ophthalmology UPV/EHU. Fellow Massachussets Eye and Ear Infirmary, Harvard Eye Institute. San Eloy Hospital and ICQO Bilbao. Retina specialist

Dra. Arantxa Acera

Researcher UPV/EHU, PhD in Ophthamology is Responsible of Clinical Trials in Ophthalmology in Donostia Hospital. 10 years experience in Biotechnology Company. Tears researcher specialist

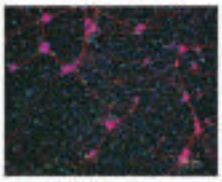
Techniques that we use

Immunohistochemisty



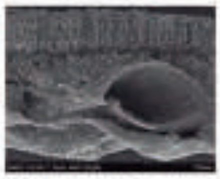
Retina Section

Cell Culture



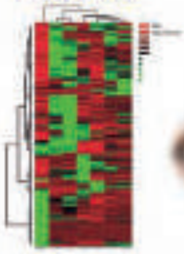
Neuronal culture

Electron Microscopy

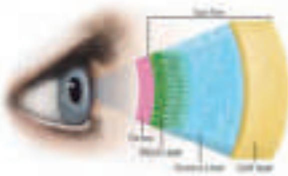


Scanning election microscopy

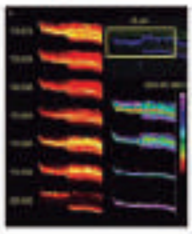
Proteomics



Heatmap of proteomic analysis of retinal cells



Lipidomics



Lipidomic analysis of the retina

Our lines of research

1- Neuroprotection and Glaucoma (Prof. Elena Vecino and Dra. Xandra Pereiro). Glaucoma is a neurodegenerative disease that is the leading cause of irreversible blindness that it is caused by the death of the ganglion cells (RGCs) that communicate the eye with the brain. Retinal glia cells are supportive cells and their relationship with ganglion cells is important for normal function. We are studying the molecular interactions between neurons and glia trying to prevent the neuronal damage.

2- Neurodegenerative diseases (Prof. Elena Vecino and Dra. Noelia Ruzafa). Other neurodegenerative diseases, such as Parkinson disease, affect RGCs as other neurons in the brain. We are analyzing the mechanism of infection of these neurons that could mimic Parkinson and other neurodegenerative diseases. In addition, we are trying to characterize molecular markers of neurodegenerative diseases from tear samples from patients in order to do an early diagnostic.

3- Retina (Dr. Javier Araiz and Dr. Alex Fonollosa). Inflammatory diseases in the retina can produce swelling and destruction of eye tissues. We are analyzing the epiretinal membranes obtained from patients with retina detachment as well as we are studying the equilibrium of the cell adhesions and could be affected in inflammatory diseases like diabetic retinopathy and uveitis.

4- Ocular Surface and Nanomaterials (Prof. Juan Durán and Dra. Arantxa Acera). The main objective is identifying biomarkers in tears, as a source of information for the ocular surface in different diseases with the idea to design artificial tears that could promote the repair of the injured ocular surface.

Status of our research Projects

Collaborations

- HARVARD UNIVERSITY (USA)
- CAMBRIDGE UNIVERSITY (UK)
- MUNICH UNIVERSITY
- CALIFORNIA DAVIS UNIVERSITY (USA)
- NY MEDICAL COLLEGE (USA)
- PEN UNVERSITY VETERINARY (USA)
- SALAMANCA UNIVERSITY
- BORDEAUX CENTRE FOR NEUROSCIENCE
- CAMBRIDGE BRAIN REPAIR CENTRE
- ACHUCARRO CENTER FOR NEUROSCIENCE (SP)
- POLYMAT FUNDATION (SP)
- CIDETEC
- TECNALIA
- IMG PHARMA (SP)
- SYLENTIS Grupo Celtia (SP)
- VTV Therapeutics (USA)

If you are interested in joining the group, contact us!

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Microorganisms, plants and invertebrates as biological indicators for soil health after sewage sludge disposal

E. Urionabarrenetxea[1]; N. García-Velasco[1]; M. Anza[3]; C. Garbisu[3]; U. Artetxe[2]; R. Lacalle[2]; J.M. Becerril[2]; M. Soto[1]

[1]CBET Research Group, Dept. Zoology and Animal Cell Biology;
Research Centre for Experimental Marine Biology and Biotechnology PiE-UPV/EHU,
[2] ECOFISCO Research Group. Dept. Plant Biology and Ecology
University of the Basque Country UPV/EHU, Basque Country
[3]NEIKER-Basque Institute of Agricultural Research and Development, Basque Country
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A higher population density, along with increasing industrial activity and the scarcity of useful land, have contributed to the proliferation of dumps, landfills and waste disposal points at different urban, peri-urban and natural areas in the Basque Country. According to the Basque Country Landfill Inventory (2005), the total number of landfills in this region is 1.277, thus being one of the most important ground pollution sources (affecting water sources and air quality as well). Among these inventoried landfills, "Landfill 17" is located at 43°19'28.9"N 2°40'30.9"W. This landfill was employed as sewage sludge disposal point for, at least, two decades. Among the species more likely to be affected by such disposal, plants, microorganisms and soil invertebrates like earthworms must be remarked due to their close contact to the soil matrix and, hence, soil pollutants. The aim of the present work was to assess the ecotoxicity exerted by pollutants present in the sewage sludge repeatedly spilled into Landfill 17 as a preliminary step to remediation (considering phytoremediation, bioremediation and vermiremediation technologies). For ecotoxicological evaluation, and in order to assess impacts at different levels of biological complexity, different standardized tests (OECD-222 and OECD-207) and the Calcein-AM assay (cell viability) were carried out using earthworms. Earthworms were maintained for 7, 14 and 28 days in soil amended with the sewage sludge containing heavy metals (Pb, Ni, Cd and Cr), PAHs (benzo(a)pyrene) and pesticides (dieldrin). At day 7 and 14, measurements of weight loss, mortality and coelomocyte viability (Calcein-AM assays) were obtained. Effects on earthworm reproduction were assessed after 56 days of exposure. In addition, germination and root elongation plant bioassays were carried out in order to quantify soil phytotoxicity and therefore, pollutant phytobioavailability. To this purpose, bioassays with *Lactuca sativa* and *Allium cepa* were performed. Microbial soils properties and other edaphic parameters were also assessed. Different sewage-induced effects were observed, compared to control soil (OECD standard soil), at different levels of biological complexity, demonstrating the accuracy of the combination of earthworm, plant and microorganism tools for soil ecotoxicity assessment. Acknowledgements: Basque Gov (IT810-13; ITO18-16), CTM2017-87766-R, AGL 2015-64481-C2-1-R and AGL2016-76592-R from MINECO, PhytoSUDOE-SOE1/P5/E0189.

Microorganisms, plants and invertebrates as biological indicators for soil health after sewage sludge disposal

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[1] CBET Research Group, Dept. Zoology and Animal Cell Biology, Research Centre for Experimental Marine Biology and Biotechnology PIE-UPV/EHU,
[2] ECOPHYS Research Group, Dept. Plant Biology and Ecology, University of the Basque Country UPV/EHU, Basque Country
[3] NEIKER-Basque Institute of Agricultural Research and Development, Basque Country

Introduction and objectives

Industrial activity, together with a high human population density and scarcity of useful land, have contributed to the proliferation of dumps, landfills and waste disposal points at different urban, peri-urban and natural areas in the Basque Country. According to the Basque Country Landfill Inventory (2005), the total number of landfills in this region is 1.277, thus being one of the most important ground pollution sources (affecting water sources and air quality as well). Among these inventoried landfills, "Landfill 17" can be found. This landfill was employed as sewage sludge disposal point for, at least, two decades. Among the species more likely to be affected by such disposal, plants, microorganisms and soil invertebrates like earthworms must be emphasized due to their close contact to the soil matrix and, hence, soil pollutants.

The aim of the present work was to assess the ecotoxicity exerted by pollutants present in the sewage sludge repeatedly spilled into Landfill 17 as a preliminary step to remediation option appraisal, considering phytoremediation, bioremediation and vermiremediation technologies.

Material & Methods

EXPERIMENTAL SOILS

- OECD standard soil (Control)
- Natural soil + Sewage sludges (MN-3)

Over local legislation: Cd, Ni, Pb, Cr, BaP, dieldrin

BIOASSAYS

ENDPOINTS

Organism	Test		Endpoints
Earthworms	Standard toxicity tests	Acute toxicity test AT OECD 207	Mortality, weight loss
		Reproduction test RT OECD 222	Cocoon production, juvenile production
	Biomarkers	Different biological complexity levels	Cell viability
Cucumis sativus, Allium cepa & Lactuca sativa	Standard toxicity tests	Root elongation test	Root elongation rates
Microbes	Biomarkers	EcoPlate™	Presence of Microbial communities

Results and discussion

Soil testing with earthworms

AT 14d

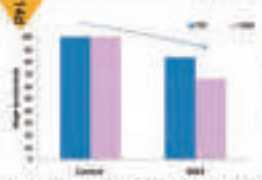

Fig. 1 Weight loss (% to the control) of earthworms exposed to a OECD soil (control) and a study soil containing sewage sludges with several inorganic and organic pollutants.

- No mortality
- Higher weight losses at polluted soils (not sig.)
- Higher weight losses after 14d (vs 7d) (not sig.)
- No differences on cell viability (7d vs 14d)

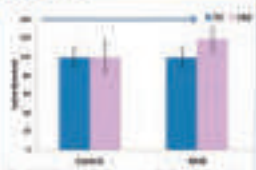

Fig. 2 Cell viability (% to the control) of coelomocytes extruded from earthworms exposed to a OECD soil (control) and a study soil containing sewage sludges with several inorganic and organic pollutants 7 and 14 days. Means, standard deviations and significant differences (*) are shown.

RT 28d/56d

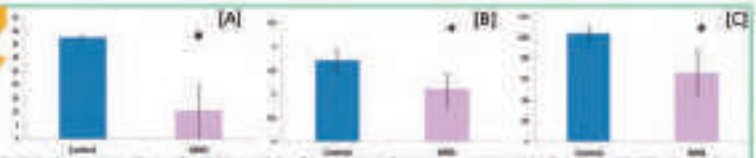

Fig. 3. Number of cocoons (A), juveniles (B), biomass of the offspring (C) counted/measured in experimentation soils (control and MN3) at day 56 after exposing earthworms to a OECD soil (control) and a study soil containing sewage sludges with several inorganic and organic pollutants. Means, standard deviations and significant differences (*) are shown (*, p<0.05).

- No earthworm mortality was observed after 28 days
- Not significant weight loss differences between groups after 28 days
- Significantly lower cocoon, juvenile or biomass production was observed at polluted treatments

Soil testing with bacteria

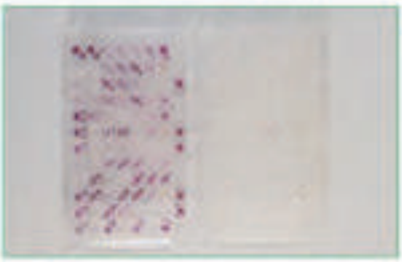

Fig. 5 Biolog made with the control soil and the study soil containing sewage sludges with several inorganic and organic pollutants.

- Microbial comunities were grown in the control soil
- No microbial comunity growed on the polluted group
- Growth inhibition in the polluted soil it is still being studied

Soil testing with plants

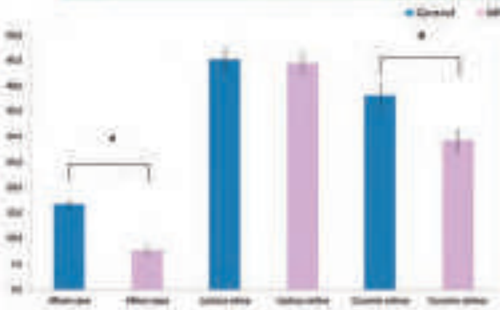

Fig. 4 Root elongation of onion, lettuce and cucumber plants exposed to a control and a study soil containing sewage sludges with several inorganic and organic pollutants for 72 hours (lettuce) and 48h (onion and cucumber). Means, standard deviations and significant differences (*) are shown.

- Significative lower elongation rates were observed between control group and polluted soil for onions and cucumbers
- No differences were observed between groups for lettuce
- Cucumber (*Cucumis sativus*) and onion (*Allium cepa*) showed to be more sensitive to pollution in this case

Conclusions

- No acute effects or short term effects were observed in earthworms after 7 and 14 days of exposure to polluted soils
- But chronic effects or long term effects were observed as reproductive impairment for earthworms exposed for 28 days to polluted soils
- No phytotoxicity was obstserved for lettuce after 72h of exposure
- But significant phytotoxicity was observed for onion and cucumber after 48h of exposure
- Microbial comunities were grown in the control group but some factor showed to inhibit growth on the soil polluted with sewage sludges

References

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Acknowledgements

Funded by the Basque Government (IHOBE) within the Ecoinnovation call (BIOREM project) and the University of the Basque Country

The concept of One Health developed in Plentzia Marine Station (PiE-UPV/EHU): 2012-2020

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48620 Plentzia – Bizkaia, Basque Country

KEY WORDS: Ocean Health, Research, Formation, Networking, Transference.

PiE-UPV/EHU is a unique research institute that develops top class scientific and technological research and strive for international leadership in its area of research. The founding idea was to promote research, education and dissemination aimed at protecting both ocean health and human wealth and at promoting environmental science, technology and awareness. In the PiE-UPV/EHU, research is focused, first, upon conducting high quality experimentation under controlled lab and field conditions. Second, upon studying phenomena in the areas of cell biology, molecular biology and genetics, experimental physiology, toxicology and pathology, analytical chemistry, stress biology, systems biology, marine ecology and biopharmacy. And finally, upon applying advanced methodologies of manipulation and experimentation with marine organisms, in vitro assays, genomics, proteomics, metabolomics, antibody technology, cryotechnology, spectroscopy, microscopy, duirect effect analysis, HR image analysis and data treatment, including satellite and climate data, modelling and downscaling.

OCEAN HEALTH.

In the last decade, the ecosystem health paradigm has been intensively studied, developed and applied in several countries, with special emphasis on the utilization of physicochemical, biological and ecological parameters with potential as bioindicators of the effects of environmental disturbances (e.g., pollution) on ecosystem health. Thanks to great advances achieved in the fields of environmental toxicology, bioanalytical chemistry and marine genomics during the last 20 years, nowadays scientists have a better understanding of the effects of chemical pollutants and other environmental stressors at molecular, cellular, and organism level. Besides, notwithstanding achievements have been done in the study of the relation between biological responses at molecular and cell levels and plausible effects at population level. The research groups workin g togetherat PiE-UPV/EHU have contributed to significative advances in the fields of environmental ecotoxicology, bioanalytical chemistry and marine genomics and ecosystem health within the past several years, as reflected by scientific contributions in congresses, international publications, etc. and active participation in relevant scientific societies and research projects at the national and European level.

Oceanic Bioprospection aims to discover and unravel the mechanisms and strategies that underlie in certain marine organisms of interest, seeking its practical application. Unravel the evolutionary legacy present in marine organisms is a great challenge with vast applications in pharmacology, chemistry, cosmetics industries or in food technology. Functional bioprospection is conducted to identify animal models and processes by means of experiment and basic research based on the biology of species showing unique features that can contribute to the discovery of molecules and processes of interest in biomedicine and applications industrial biotechnology. The vulnerable marine ecosystems in which organisms have developed highly specialized defense mechanisms, such as coral reefs, or extreme environmental conditions, such as hydrothermal vents, deep benthos, polar seas or environments subject to natural or chronic pollution, are emerging as potential areas of interest. In this context, the PiE-UPV/EHU is developing a strategy to implement the functional bioprospecting in Atlantic areas. A first step has been the creation, implementation and development of the Biscay Bay Environmental Biospecimen Bank, which is part of European and global networks of biobanks. A second step has been the development of a multidisciplinary group with the expertise of zoologists, ecologists, microbiologists, chemists, cell and molecular biologists, pharmacologists to gain knowledge on model species for targeted search for substances of pharmacological interest. Bioprospection and Biobanking are the two priority areas. However, the most important action in this area is the integration of PiE-UPV/EHU, with ECIMAT consortium (Marine Station of the University of Vigo), as the Spanish node of the European infrastructure (ERIC) called EMBRC (European Marine Biological Resources Centre; visit website www.embrc.eu for detailed info), in which the most prestigious European marine stations are integrated. Same integration is being pursued for Euroregional University Marine stations in the Basque Country-Navarre-New Aquitaine Euroregion (Turquoise University Hub), as Arcachon and la Rochelle. ….It will continue!!!

** Director; ** Deputy director*

The concept of One Health developed in Plentzia Marine Station (PiE-UPV/EHU): 2012-2020

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Plentziako Itsas Estazioa, PiE-UPV/EHU. www.ehu.eus/PIE
Areatza Pasealekua, z/g. 48620 Plentzia – Bizkaia, Basque Country

PiE-UPV/EHU is a unique research institute that develops top class scientific and technological research and strive for international leadership in its area of research. The founding idea was to promote research, education and dissemination aimed at protecting both ocean health and human wealth and at promoting environmental science, technology and awareness. In the PiE-UPV/EHU, research is focused, first, upon conducting high quality experimentation under controlled lab and field conditions. Second, upon studying phenomena in the areas of cell biology, molecular biology and genetics, experimental physiology, toxicology and pathology, analytical chemistry, stress biology, systems biology, marine ecology and biopharmacy. And finally, upon applying advanced methodologies of manipulation and experimentation with marine organisms, in vitro assays, genomics, proteomics, metabolomics, antibody technology, cryotechnology, spectroscopy, microscopy, direct effect analysis, HR image analysis and data treatment, including satellite and climate data, modelling and downscaling.

The motto of Plentzia Marine Station (PiE-UPV/EHU) "Ocean and health" is related to the holistic concept of "One health", which has become globally extended over the past five to six years. What does that mean? It implies that connections between human beings, animals, plants, and their shared environment are essential to obtain good results in terms of health and well-being. In other words, human health is related to animal health and -ultimately- to the environment. Health must be understand comprehensively in order to protect the environment. To achieve this, it is essential to understand the sea. To achieve this, both **basic** and **applied research** must be combined.

"Ocean and health"

It's also essential to diagnose, assess, foresee, and evaluate the scope of the damages or the impact on our ocean, and we must search for alternatives for the use and harnessing of our natural resources without repeating past errors (for example, guaranteeing biodiversity, discovering new drugs) and use them in a sustainable way.

We must bear in mind many different variables when assessing and evaluating the health of the ocean. Some are well known: overexploitation (fishing, fossil fuels), transformation of habitats, globalisation, climate change, and pollution. If someone asked us on the state of the sea in our environment, in our experience, we would say it's not as bad as some would think, but not as healthy as we would like. Considering these threats, new challenges arise. At the Plentzia Marine Station we want to find opportunities to protect the health of the Ocean.

Environmental impact and risk assessment of nanomaterials and other emerging chemicals

Amaia Orbea[1], Eider Bilbao[1], Alberto Katsumiti[1], Ignacio Martínez-Álvarez[1,2], Ada Esteban[1], Nagore González-Soto[1], Ruth Prieto[2], Virginia Martínez[2], Radmila Tomovska[3], Hélène Budzinski[4], Miren P. Cajaraville[1]

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[2] "Molecular Spectroscopy" consolidated res group, Dept. Chemical Physics. Faculty of Science and Technology. UPV/EHU.

[3] POLYMAT and Dept. Applied Chemistry, Faculty of Chemistry, UPV/EHU.

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KEY WORDS: nanomaterials, environmental toxicology, "Trojan Horse effect", photodynamic therapy of cancer.

The development of nanomaterials of diverse chemical composition and physical properties (e.g., metallic and carbon-based nanomaterials, including nanoplastics) and their implementation in industrial processes, medical applications and in many consumer products during the last decades have raised serious concerns regarding their accumulation in the environment and their potential effects on the biota. Nanomaterials are considered as emerging pollutants because they lack published health standards. Due to their small size, nanomaterials show increased bioavailability and reactivity compared to their bulk counterparts. In addition, due to their hydrophobic nature and large specific surface, carbon-based nanomaterials and nano- and microplastics can potentially interact with other contaminants, especially with persistent organic pollutants, already present in the environment, thus modulating their bioavailability and hazard.

The "Cell Biology in Environmental Toxicology-CBET" Consolidated Research Group has been investigating the toxicological effects derived from the presence of nanomaterials in the environment since 2008. This research line in Nanotoxicology has become one of the three main research lines of the group and aims to:

1- Understand the behaviour of nanomaterials in different exposure media
2- Determine uptake, bioaccumulation, bioavailability, fate, and cellular and tissue distribution of nanomaterials in organisms
3- Identify the mechanisms of action and adverse effects of nanomaterials in organisms
4- Elucidate toxicity profiles of nanomaterials
5- Provide tools for Risk assessment of nanomaterials in aquatic and terrestrial ecosystems

Currently we are carrying out the project NanoCarrierERA-NACE ("Nanomaterials (NMs) as carriers of persistent organic pollutants in the aquatic environment: development of tools for risk assessment based on alternative methods and model organisms", Spanish MINECO, 2016-2020). NACE aims to assess the potential risks for the aquatic ecosystems posed by NMs (graphene family NMs and nano and microplastics), in combination with other persistent organic pollutants already present in the environment. A multispecies approach is employed with an especial emphasis on the use of alternative test methods such as embryo toxicity tests with two invertebrate species, mussels (*Mytilus galloprovincialis*) and brine shrimps (*Artemia* sp.), and one vertebrate, the zebrafish (*Danio rerio*) and *in vitro* toxicity tests with isolated mussel cells and with microalgae (*Isochrysis galbana*).

More recently, in collaboration with the Molecular Spectroscopy research group of UPV/EHU, we have started a research line on the use of nanomaterials as carriers of fluorescent probes for bioimaging and as carriers of photosensitizers for photodynamic therapy of cancer. Indeed, a Collaborative Project (UPV/EHU 2020-2021) has been recently granted to consolidate this collaboration. The main aim of the project is to develop novel nanodrugs for the delivery of photosensitizers, able to produce the cytotoxic species singlet oxygen, and to investigate their ability for internalization and killing of cancer cells using different human cell lines.

Other projects developed in the Nanotoxicology field are: NanoReTox (EU 7th FP, 2008-2012), NanoCancer (Spanish MEC, 2010-2012), NanoSilverOmics (Spanish MINECO, 2013-2015), Enter (EU Cost Action, 2013-2017), NanoToxT (Basque Gov Saiotek, 2013-2014), NanoGune (Basque Gov Etortek, 2014-2015), National Network of Excellence in Nanotechnology and Food (Spanish MINECO, 2017-2019) and EU project PLASTOX (JPI Oceans 2016-2019).

Environmental impact and risk assessment of nanomaterials and other emerging chemicals

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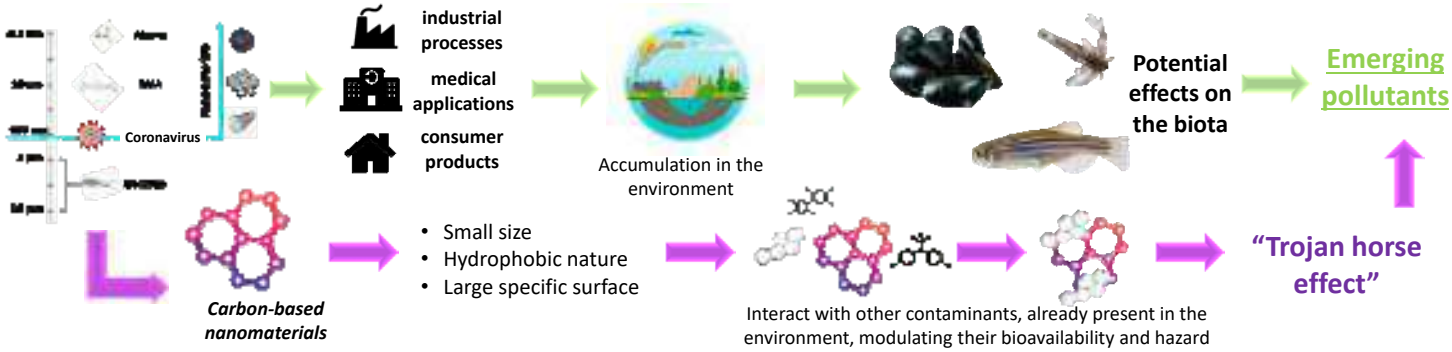
Risk of nanomaterials



Micro- and nanoplastics: a global threat for aquatic ecosystems

Plastic debris is accumulating in both terrestrial and aquatic systems globally

In 2018, global plastic production reached 359 million tons

Microplastics: plastic particles <5 mm in their largest dimension

Nanoplastics: plastic particles <100 nm

Primary microplastics: enter to the marine environment directly in micro size

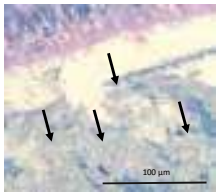
Personal care products

Plastic pellets

Secondary microplastics: largely derived from the *in situ* mechanical, chemical and biological breakdown of larger plastics

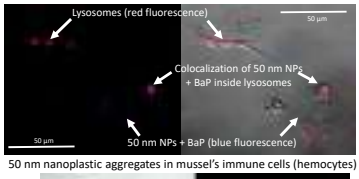
Smaller microplastics show higher sorption capacity for organic contaminants

Micro- and nanoplastics can be internalized by aquatic organisms with different feeding strategies and affects physiological and cellular functions



4.5 µm microplastics in mussel's stomach

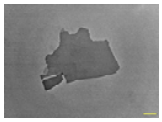
4.5 µm microplastics in mussel's immune cells (hemocytes)



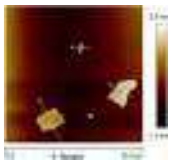
50 nm nanoplastic aggregates in mussel's immune cells (hemocytes)

50 nm fluorescent nanoplastic aggregates in 96 h zebrafish embryos

Graphene oxide nanomaterials as carriers of pollutants



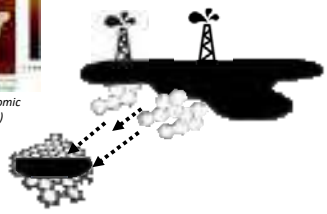
Graphene platelet under the Transmission Electron Microscope Lateral dimensions: <10 µm Thickness: 0.410 to 0.687 nm



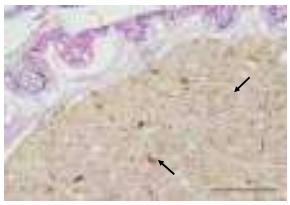
Graphene under the Atomic Force Microscopy (AFM)

High sorption capacity for dissolved pollutants from the water column, mainly hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) due to high hydrophobicity and surface/mass ratio.

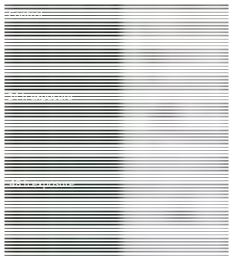
Potential application in water pollution remediation technology



Contaminated graphene oxide is released into the aquatic ecosystems and, therefore, can be uptaken by organisms



Graphene oxide in the lumen of zebrafish intestine



Fluorescent reduced graphene oxide in the digestive system of brine shrimp

Reduced graphene oxide nanoplatelets were found in the cytosol (white arrows) and in endolysosomal vesicles (black arrows) of mussel immune cells (hemocytes)

Nanoparticles as carriers of drugs

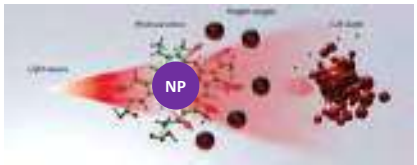
Photodynamic therapy (PDT) in cancer treatment

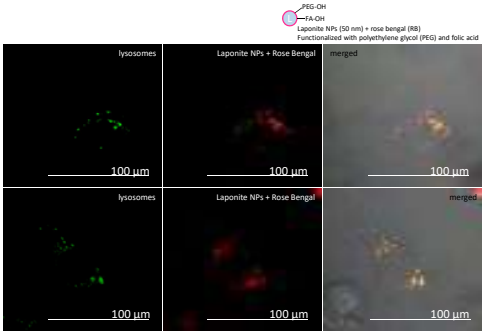
What is it?

- **Photodynamic therapy (PDT):** type of phototherapy involving: **light + photosensitising chemical substance (PS)**
- **Nanoparticles (NPs)** serve as carriers of PS and can be targeted to cancer cells

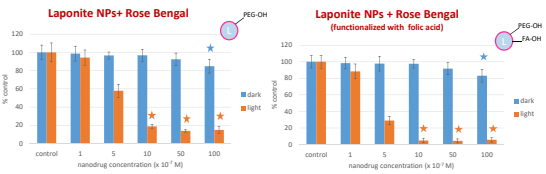
Principle to kill cancer cells

- Light ➔ **activation of PS** and **generation of ROS (mainly $^1O_2$)** - **phototoxicity**





Colocalization (yellow) of lysosomes (green) and laponite nanoparticles + rose bengal (red) confirming the internalization of nanodrugs into lysosomes of HeLa cells



Laponite + Rose Bengal

- Slight dark toxicity
- High phototoxicity
- Folic acid seems to promote higher internalization of nanodrugs, thus higher cytotoxicity
- **Good option for PDT of cancer**

Conclusions

- **Nano and microplastics and graphene family nanomaterials represent a potential threat for the aquatic species.**
- **They act as "Trojan horse" carriers of organic contaminants to aquatic organisms.**
- **Nanomaterials such as laponite nanoclays can be used as carriers of photosensitizers for PDT of cancer.**
- **The potential environmental impact and risk of nanodrugs applied in medicine need to be assessed in a life cycle perspective.**

Acknowledgements

Funded by the Spanish MINECO (NACE project, CTM2016-81130-R and SYNCOPHOBI project MAT2017-83856-C3-3-P), EU H2020 (GRACE project, grant number 679266), Basque Government (consolidated research groups IT-1302-19 and IT912-16) and the University of the Basque Country UPV/EHU (NANOPHOTOTOX collaborative project, COLAB19-01) . Work carried out within EU project PLASTOX (JPI Oceans 005/2015).

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Microestructural, magnetic and spectroscopic characterization on materials with high technological applications

Axpe E [1,4], García JA[2], Garaio E[3] and Garitaonandia JS[2], Perez J[1], Plazaola F[1], Rodrigo I[1] and Unzueta I[1]
[1]Elektrizitatea eta Elektronika Saila; [2]Fisika Aplikatua II Saila, [3]UPNA, [4]NASA.

KEY WORDS: Magnetic Nanoparticles, Hyperthermia, FSMA.

The research team is a Basque Government consolidated research-group with reference IT-1005-16. All the members of the research team come originally from two departments of the Faculty of Science and Technology (1 and 2 above). The main research lines of the team are related to biomedicine and to material science and technology. In relation to biomedicine the research team deals with building instrumentation for new therapies against cancer, and in relation to material science and technology the team is expert particularly in Positron Annihilation, Mössbauer and Photoluminescence Spectroscopies. However, they also use many other characterization techniques and theoretical codes. In short, a description of these two main research lines follows:

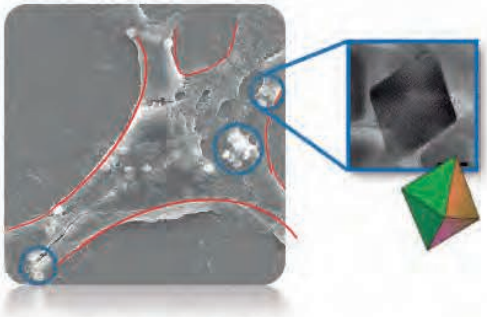
1. **BIOMEDICINE: Magnetic nanoparticles and their application to magnetic hyperthermia.** This is an ongoing activity that the research group carries out together with a multidisciplinary team formed by researchers from the BIO Foundation (Galdakao-Usansolo Hospital) and several research teams belonging to the Faculties of Science and Technology and Medicine. The main objective is the development of a new therapeutic tool to produce the selective thermal ablation of solid tumor tissues by means of magnetic nanoparticles diffused into them and exposed to an external magnetic field inductor in the range of radiofrequencies. The solid cancer tissue the team works actually is colorectal cancer, So far, several objectives have been achieved. Among them the design and manufacture of several prototypes of magnetic applicators for magnetic hyperthermia, both in-vitro and in-vivo, obtaining hyperthermia temperatures in ex-vivo experiments in WAG type rat livers infused with magnetite nanoparticles. The research team is working actually in a prototype of high applied magnetic field (about 60 kA/m) in the frequency range 70-1000 kHz, to optimize the potential proper magnetic nanoparticles for magnetic hyperthermia, and in the proper determination of the temperature of tumors in magnetic hyperthermia experiments with animal. This last point it is one of the very important subjects for the development of the cited therapy. Moreover, we are engaged in the [applied magnetic field, frequency] area determination that does not produce secondary effects in animal experiments.

2. **MATERIAL SCIENCE and TECHNOLOGY: Magnetic materials for technological applications**. Ni based Ni-Y-Z Heusler alloys attract great interest due to the multifunctional properties they exhibit, such as giant magnetorresistance, magnetocaloric effect, large magnetic-field-induced strain, and shape-memory effects, that could be implemented in practical devices. These properties are linked to the occurrence of a thermoelastic martensitic transformation (MT) between magnetically ordered phases. In the so-called metamagnetic shape-memory alloys, like Ni_2Mn-Z (Z = In, Sn, and Sb), the thermoelastic martensitic transformation is followed with a large variation of the magnetization at the MT temperature and as a result, additional multifunctional properties arise, enabling the development of practical applications in sensing, magnetic refrigeration and energy harvesting. The multifunctional properties of these alloys are directly related with the occurrence of the MT. The optimization of the multifunctional properties requires a deep understanding of the characteristics of the transformation for the technological application of these materials and it is the main aim of this research line.

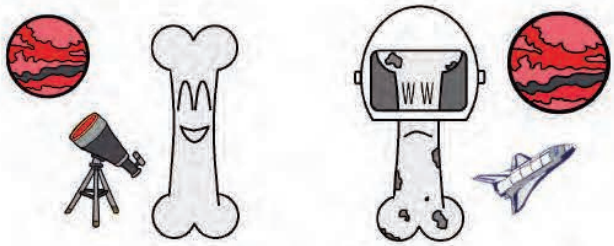
MIMASPEC

E. Axpe, E. Garaio, J. A. García, J. S. Garitaonandia, , D. Mérida, **J. Pérez-Muñoz**, F. Plazaola, I. Rodrigo, I. Unzueta

MICROSTRUCTURAL...



➢ Célula **cancerosa** con **nanopartículas** dentro.



➢ Estudio de la aparición de **osteoporosis en astronautas** al vivir en gravedad cero.

MAGNETIC...

Desarrollo de **terapia no invasiva contra el cáncer mediante ablación con campos magnéticos y nanopartículas.**

1. El paciente desarrolla un tumor.

2. Se le inyectan nanopartículas de magnetita.

3. Se someten a campos magnéticos.

4. Se calientan las nanopartículas y queman el tumor.

5. El tumor se debilita, inutiliza o elimina.

SPECTROSCOPIC...

Espectroscopía Mössbauer

Estas dos muestras **parecen iguales**...

Pero quizás no, ¡usemos **MÖSSBAUER**!

¡Es **magnetita**! ¡**Maghemita**!

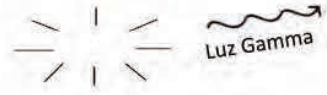
¡Eran diferentes!

Aniquilación de Positrones

1.

2.

3.



... in materials for **HIGH TECH APPLICATONS!**

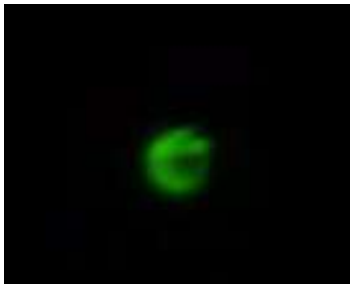
Automatic Control Group GAUDEE

V. Etxebarria, J. Jugo, J. Feuchtwanger, E. Asua, I. Arredondo, I. Badillo, A. García-Arribas, I. Sagastabeitia, I. Lizarraga, S. Alonso, A. Elejaga, B. Alberdi;
Departamento de Electricidad y Electrónica, Facultad de Ciencia y Tecnología, UPV/EHU;

KEY WORDS: RF control, particle accelerators, LINAC, smart materials

The automatic control group of the University of the Basque Country (UPV/EHU), GAUDEE, carries out research and development of advanced control systems and techniques, combining theoretical work with practical interest applications. The current activities are focused on two main areas. The first one refers to research in the field of particle accelerators science and technology. This is carried out in the IZPILab - Beam Laboratory, which was founded by GAUDEE, in collaboration with the RF and Microwave group of the Department of Electricity and Electronics. The activities in this field include the development of innovative complete key components of particle accelerators, including ion sources, beam diagnostics, RF devices and controls, and the corresponding electronics. In this area, the research group is active in several projects in collaboration with reference institutions such as IFMIF or HZB.
Another research field is centered in the research around new advanced sensors and actuators, based on new materials and principles.

PARTICLE ACCELERATOR SCIENCE AND TECHNOLOGY
The group is involved in several projects for particle accelerators. Among these it is wor



- *Compact LINAC*: A new compact proton source for low current and low energy applications has been designed and built. All the mechanical, electromagnetic, vacuum, RF and control designs have been in-house completed. To date, a low current proton beam is extracted from the source, while the next stage of the accelerator is being built.
  The ion source is the first key component of a new generation Linac aiming to achieve a 7 MeV beam, currently under design. This is being developed in the framework of the LINAC7 project under ELKARTEK program, in which different actors such as research centers take part along with the aforementioned research groups.
- *RF Systems*: The RF system is an essential part of any particle accelerator, as its main task is giving energy and stability to the particle beam. Therefore, RF control plays a key role in this kind of machines.
  Different research lines are carried out in RF control. One of them is centered in the study of advanced control techniques in collaboration with HZB synchrotron for mechanical disturbance rejection in superconducting resonant
  A second one refers to active power combiner control in cavities in order to control the phase shift between different incident RF signals to maximize the sum of incident power.

SMART MATERIAL BASED ACTUATORS
Ferromagnetic shape-memory alloys (FSMAs) are special smart materials that can experiment huge deformations, have a very fast response and can work at high frequencies when activated with a magnetic field (with the advantage of a contactless activation). A new actuator has been designed and built. This is composed of two pairs of coils: the first one generates a field that causes a deformation in an FSMA monocristal, and the second one actuates in the transversal direction. This way, the actuator can be used in a ”set and forget” mode, which allows to save energy while operating in the micrometric or nanometric range.

RF RESONANT CAVITY BASED SENSORS
Resonant cavities are closed conductive surfaces where the electromagnetic waves are constantly reflecting. Changes in their geometry result in variations in their electromagnetic properties, and more specifically in their resonance frequency. A new displacement sensor, composed of two copper resonant cavities whose dimensions change in opposite directions by means of the displacement of intermediate wall has been developed. Tiny changes in position result in huge resonance frequency shifts that are easily measurable.
This way, the results show that the device can be used as a sub-nanometric precision displacement sensor.

Automatic Control Group GAUDEE

V. Etxebarria, J. Jugo, A. García-Arribas, I.Sagastabeitia, E. Asua, I. Lizarraga, S. Alonso, J. Feuchtwanger, I. Arredondo, I.Badillo, A. Elejaga, Beñat Alberdi

Abstract

The automatic control group of the University of the Basque Country (UPV/EHU), GAUDEE, carries out research and development of advanced control systems and techniques, combining theoretical work with practical interest applications. The current activities are focused on two main areas. The first one refers to research in the field of particle accelerators science and technology. This is carried out in the IZPILab - Beam Laboratory, which was founded by GAUDEE, in collaboration with the RF and Microwave group of the Department of Electricity and Electronics. The activities in this field include the development of innovative complete key components of particle accelerators, including ion sources, beam diagnostics, RF devices and controls, and the corresponding electronics. In this area, the research group is active in several projects in collaboration with reference institutions such as IFMIF or HZB.

Another research field is centered in the research around new advanced sensors and actuators, based on new materials and principles.

Particle Accelerator Science and Technology

Compact LINAC:

A new compact proton source for low current and low energy applications has been designed and built. All the mechanical, electromagnetic, vacuum, RF and control designs have been in-house completed. To date, a low current proton beam is extracted from the source, while the next stage of the accelerator is being built.

The ion source is the first key component of a new generation Linac aiming to achieve a 7 MeV beam, currently under design. This is being developed in the framework of the LINAC7 project under ELKARTEK program, in which different actors such as research centers take part along with the aforementioned research groups.

Figure 1: The low-current compact ion source designed and built by GAUDEE.

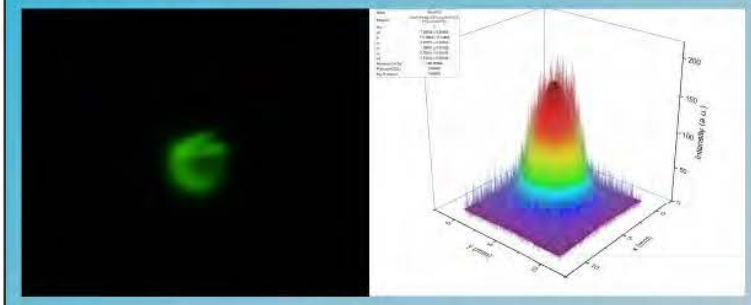


Figure 2: Impact on a phosphor screen of the proton beam stracted from the source (left) and the intensity analysis of the dot in order to get the proton density and position (right).

RF Systems:

The RF system is an essential part of any particle accelerator, as its main task is giving energy and stability to the particle beam. Therefore, RF control plays a key role in this kind of machines.

Different research lines are carried out in RF control. One of them is centered in the study of advanced control techniques in collaboration with HZB synchrotron for mechanical disturbance rejection in superconducting resonant cavities. A second one refers to active power combiner control in cavities in order to control the phase shift between different incident RF signals to maximize the sum of incident power.

Smart material based actuators

Smart materials are materials capable of responding in a revesi ble and controlled way against different physical stimulus modifyig some of their characteristics, such as their length. Due to their sensitibity, these materials can be employed in the development of sensors and actuators.

Ferromagnetic shape-memoryalloys (FSMAs) are special smart materials that can suffer huge deformations, have a very fast response and can work at high frequencies when activated with a magnetic field(with the advantage of a contactless activation).

Figure 3: The developed smart material based actuator

The actuator is composed of two pairs of coils: the first one generates a field that causes a deformation in a monocristal, and the second one, in the transversal direction. This way, the actuator can be used in a "set and forget" mode, thus saving energy consumption.

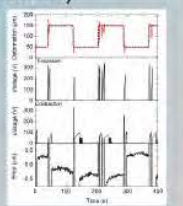


Figure 4: Control signal is sent in long time intervals, resulting in a veryenergy-efficient system

RF resonant cavity based sensors

Resonant cavities are closed conductive surfaces where the electromagnetic waves are constantly reflecting. Changes in the geometry result in electromagnetic variations, more specifically in the resonance frequency.

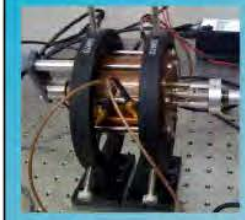


Figure 5: Displacement sensor based in a resonant cavity

The displacement sensor is composed of two copper resonant cavities which dimensions change in opposite directions by means of the displacement of a piston. Slight changes in position result in resonance frequency shifts that are easily measurable.

This way, the results show that the device can be used as a nanometric precision displacement sensor.

Regarding the results obtained,the relation between displacment and frequency changes is highly lienar and sensitive.

In order to obtain a cost effective sensor, an electronic board has been developed to avoid the use of a network analyzer.

Figure 6: Electronic setup to detect frequency changes

Digital electronics, machine learning and data mining: a cross-disciplinary approach to face the challenges of autonomous driving

Inés del Campo[1], Javier Echanobe[1], Mª Victoria Martínez[1], Estibalitz Asua[1], Óscar Mata Carballeira[1], Koldo Basterretxea[2], Guillermo Bosque[2], Unai Martínez[2], Aitor del Río[2] and Naiara Vidal
[1]Department of Electricity and Electronics; [2]*Department of Electronic Technology*.

KEY WORDS: digital electronics, system modelling, embedded systems, field-programmable gate arrays (FPGAs), machine learning, data mining, advanced driving assistance systems (ADAS)

The Digital Electronics Design Group (GDED) focuses on two main lines of research aimed at the development of innovative multidisciplinary applications. These lines are:

1. **Modelling of complex dynamic systems using data mining and machine learning:** optimization, regression and multiclass classification using computational intelligence techniques (neural networks, deep learning, fuzzy systems, neuro-fuzzy systems, genetic algorithms and genetic programming).
2. **Design of efficient embedded electronic systems for real-time applications:** systems on a chip (SoCs) based on FPGA devices, hardware/software co-design, high computational efficiency hardware accelerators, device consumption and size reduction techniques, "hardware-in-the-loop" co-simulation, and sensor technologies.

Application areas: advanced driver assistance systems (ADAS), intelligent sensors, environmental and physiological sensors, internet of things (IoT), optimum and predictive controllers, and modelling and optimization of industrial processes.

RECENT APPLICATIONS DEVELOPED BY THE GROUP AND WORK IN PROGRESS

Currently, the development of advanced Driving Assistance Systems (ADAS) is the main research area of the group. The introduction of autonomous (or semi-autonomous) vehicles and the subsequent shift in the driver's role is leading to new challenges affecting the comfort and well-being of the driver and the passengers. In this scenario, we put forward a cross-disciplinary approach based on electronics, sensor technologies, data mining, and machine learning algorithms to face the challenges of the transition to autonomous driving.

The GDED group developed an intelligent sensor for driving style recognition for ADAS enhancement. This sensor uses different driving data sources: CAN bus, inertial measurement unit, and radar. It has been successfully implemented using a field-programmable gate array (FPGA) device of the Xilinx Zynq programmable system-on-chip (PSoC). The intelligent sensor can mimic the typical timing parameters of a group of drivers as well as tune these parameters to model individual driving styles. In addition, we are applying the same strategies to the development of intelligent systems able to classify driving behaviour depending on fuel efficiency features and ecological friendliness.

The incorporation of multispectral cameras in ADAS is another relevant aim of the group. The technology of multispectral sensors and cameras of small size and reduced weight is already a reality. The rich multispectral information that these cameras are able to provide is very significant for environmental monitoring. In particular, the sophisticated sequence of complex algorithms currently used in image processing for the detection, classification and tracking of objects in ADAS can be drastically simplified by directly applying machine learning techniques to the classification of multispectral signatures of different objects in the roads. In addition, the use of application-specific processors, optimized for neural processing, and its integration into FPGA-based PSoCs will allow real-time processing of multispectral images.

In all the above application areas the group works on approaches that process very large and complex data sets by taking advantage of data mining techniques, computational intelligence solutions, machine learning algorithms, and advanced optimization strategies.

ZTF-FCT
Zientzia eta Teknologia Fakultatea
Facultad de Ciencia y Tecnología

Electrónica Digital, Machine Learning y Data Mining: un Enfoque Multidisciplinar para abordar los Retos del Futuro

Universidad del País Vasco Euskal Herriko Unibertsitatea

Grupo de Diseño en Electrónica Digital
Grupo de Investigación del Sistema Universitario Vasco

Inés del Campo, Javier Echanobe, Mª Victoria Martínez, Estibaliz Asua, Koldo Basterretxea, Naiara Vidal, Óscar Mata-Carballeira, Unai Martínez y Aitor del Río.

OBJETIVOS

1. Investigación básica. **Modelización** de sistemas dinámicos complejos mediante **Técnicas de Machine Learning**: Sistemas Fuzzy, Redes Neuronales y Algoritmos Genéticos
2. Investigación aplicada y **desarrollos eficientes de sistemas electrónicos embebidos**: diseño de hardware específico, software optimizado y sistemas mixtos Hardware/Software.
3. Estudio y desarrollo de soluciones innovadoras en el ámbito de los **Sistemas** Inteligentes para campos de aplicación de interés actual: Inteligencia Ambiental, Sistemas de Asistencia a la conducción, Eficiencia Energética,...

MACHINE LEARNING Y DATA MINING

- **Redes Neuronales Artificiales** (Neural Networks). Capacidad de aprendizaje y generalización.
- **Sistemas de Lógica Difusa** (Fuzzy Systems). Razonamientos aproximado, manejan información imprecisa, incompleta, ambigua, ...
- **Algoritmos Genéticos**. Inpirados en el proceso de selección natural de los seres vivos. Hallan soluciones a problemas utilizando una función de adaptación (Fitness).

TECNOLOGÍA
Sistemas Electrónicos Embebidos

- **FPGAs** de alta integración. Sistemas programables en un chip (SoPC)
- **Sistemas heterogéneos hardware/software** (HW/SW). Tècnicas de co-diseño
- **Descripción de sistemas**: C, C++, SystemC, VHDL, ..
- **GPUs** (Graphics Processing Units)
- **Sensores inalámbricos**

APLICACIONES
Sistemas Inteligentes

- **Inteligencia Ambiental.** Entornos Inteligentes
- **Internet of Things**
- **Reconocimiento de Imágenes Hiperespectrales**
- **Sistemas de Asistencia a la conducción**. Vehículos Inteligentes
- **Optimización de procesos industriales**

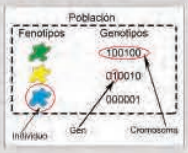
Machine Learning y Data Mining

Metodologías de computación que generan conocimiento a partir de datos. Hoy en día son indispensables en contextos de alta complejidad con gran cantidad y variabilidad de datos.

Redes Neuronales Artificiales
Se inspiran en el cerebro de los vertebrados. Las técnicas más avanzadas de Deep Learning se acercan más a la potencia perceptiva humana a través de múltiples niveles de composición. Muy interesantes para modelización y clasificación.

Sistemas Fuzzy
Se fundamentan en la imprecisión del razonamiento humano. Utilizan reglas lingüísticas formuladas sobre términos incompletos o vagos y procedimientos de inferencia. Tienen gran capacidad de predicción.

Algoritmos Genéticos
Se basan en mecanismos que simulan la evolución de las especies. Mediante estrategias de cruce, mutación y selección se acercan a las mejores soluciones. Son muy útiles para optimización.



Modelado de Sistemas Complejos

Una línea de investigación reciente del grupo es la modelización de sistemas industriales complejos en el ámbito de la **cogeneración de energía**. En la cogeneración se genera simultáneamente energía eléctrica y energía térmica, obteniéndose como ventaja una mayor eficiencia energética.

En esta línea el grupo diseña métodos de **optimización** del proceso utilizando redes neuronales y algoritmos genéticos.

Autonomía Multivehicular y Conducción Autónoma

La **automatización de la movilidad** va a jugar un papel fundamental en todos los sistemas de transporte.

Las aportaciones tecnológicas de los fabricantes de vehículos hacia la conducción autónoma son cada vez más importantes, desde las primeras fases de innovación de sistemas avanzados de asistencia al conductor (**Advanced Driver Assistance System, ADAS**), hasta los actuales vehículos autónomos que ya se prueban en las carreteras.

El proyecto AUTOLIB en el que participa este grupo pretende **generar una plataforma que permita la automatización de vehículos heterogéneos y multisectoriales** a través de la investigación y desarrollo de **módulos funcionales** basados en la fusión de algoritmos complejos de análisis y entendimiento del entorno.

El grupo trabaja en particular en el estudio y desarrollo de sistemas electrónicos embebidos relacionados con la planificación y control de los vehículos, identificación del entorno y el confort.

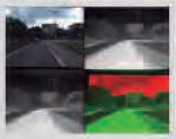
Dichos sistemas aprovechan en gran medida las ventajas que ofrecen las **plataformas hardware reconfigurables** en términos de flexibilidad, eficiencia energética, potencia de cálculo y reducción de costes.

En los desarrollos se utilizan diversos **métodos probabilísticos** así como **técnicas de optimización y de inteligencia computacional**.

Estos módulos y estas soluciones permitirán **automatizar los vehículos** y tendrán un impacto no sólo en el transporte sino también en la industria y fabricación de las piezas, ya que éstas tienen que responder a las necesidades generadas desde la automatización.

Imágenes Hiperespectrales

A través del análisis de imágenes adquiridas con cámaras hiperespectrales, es posible identificar objetos gracias a la **"firma" espectral** que posee cada tipo de superficie o material. El grupo de investigación desarrolla sistemas de *machine learning* para el procesamiento de imágenes hiperespectrales con el fin de detectar objetos de interés en el entorno de un vehículo que circula por la vía pública: señales, peatones, otros vehículos, obstáculos, etc. Estos sistemas se integrarán en el automóvil con el fin de asistir al conductor y así aumentar la seguridad, el confort y la eficiencia de la conducción.



Un Mundo Conectado

Estrechamente ligado a los entornos inteligentes, el concepto de **"Internet de las cosas"** (Internet of Things, IoT) representa la red mediante la cual se comunican entre sí todo tipo de objetos de la vida cotidiana.

En este contexto, el grupo desarrolla sistemas basados en redes de sensores inalámbricos, en los cuales el **tamaño, consumo y precio** son factores de diseño determinantes.

RF and microwave group

Nerea Otegi[1], Aitziber Anakabe[1], Juan-Mari Collantes[1], Joaquín Portilla[1], José Manuel González[2], Javier Alonso[3]
[1]Departamento de Electricidad y Electrónica, UPV/EHU
[2]Departamento de Tecnología Electrónica, UPV/EHU
[3]Tecnalia

KEY WORDS: high-frequency electronics, solid-state amplifiers, noise characterization, radio-communication systems, instrumentation for LINACs, MRI

The main research topics of the group are the analysis, characterization and design of RF and microwave circuits and systems for radio-communication, radio-navigation and scientific equipment, such as RF linear particle acceleration (LINAC) and magnetic resonance imaging (MRI), among other applications.

We have developed an extensive work on analysis and characterization of solid-state amplifiers, including circuit linearization, circuit modeling and noise characterization. As an example, we can mention the advancements on spurious oscillation detection in power amplifiers for satellite communications achieved in the framework of a several projects funded by the French Space Agency (CNES, Toulouse, France). Our group has also a relevant activity in noise characterization of RF circuits and systems, where it is worth mentioning the development of novel techniques for the amplitude noise and phase-noise measurement in the presence of large-signal excitations. We are also involved on RF instrumentation for LINACs, material characterization and RF technology for MRI experiments.

Universidad del País Vasco · Euskal Herriko Unibertsitatea

FACULTY OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF THE BASQUE COUNTRY

RF & Microwave Group

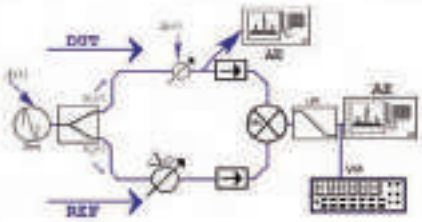
Nerea Otegi[1], Aitziber Anakabe[1], Juan-Mari Collantes[1], Joaquín Portilla[1], José Manuel González[2], Javier Alonso[3]

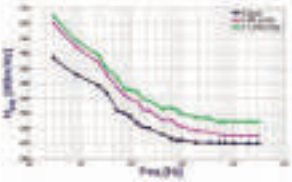
[1]Departamento de Electricidad y Electrónica, UPV/EHU
[2]Departamento de Tecnología Electrónica, UPV/EHU
[3]Tecnalia

The *RF & Microwave Group* works in the field of high frequency circuits and systems for different applications: wireless communications, radio navigation and scientific equipment. Their basic research axes are focused on the analysis and design of microwave circuits, high frequency instrumentation and the field of magnetic resonance imaging

Analysis and Noise Characterization of Microwave Power Amplifiers

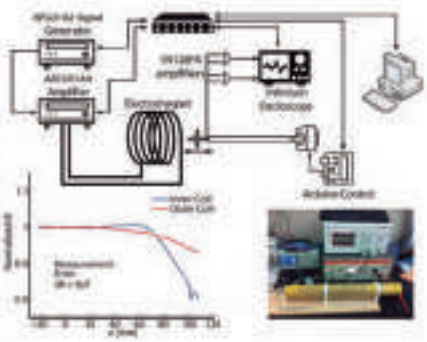
Amplifiers add noise to the desired signal producing degradation of sensitivity, resolution and signal quality in electronic systems. Amplitude Modulation (AM) and Phase- Modulation (PM) noise spectra measurement provide a complete picture of the amplifier noise behavior, including flicker and white noise contributions.





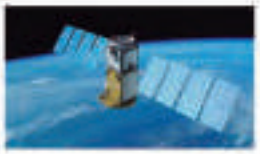
MRI

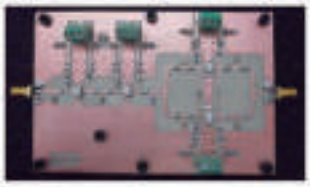
Our aim is to develop an electromagnet for MRI applications based on the Magic Angle Field Spinning technique. Our prototype is a low field, 30 mm bore magnet with a field spinning at 129 KHz

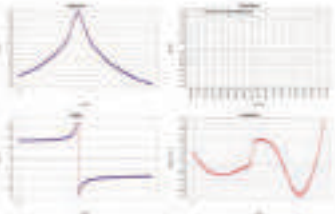


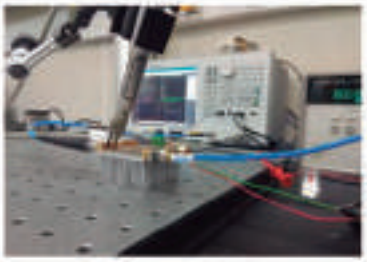
Stability Analysis of Power Amplifiers for Satellite Applications

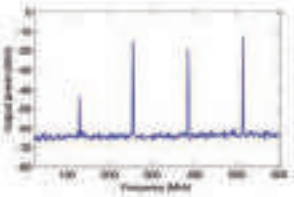
Some techniques have been proposed and developed to check stability and to improve circuit design cycles, mainly focusing on high power amplifiers for satellite communications.







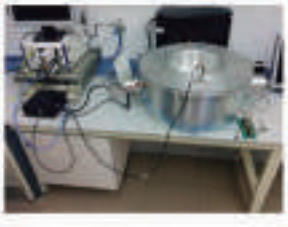


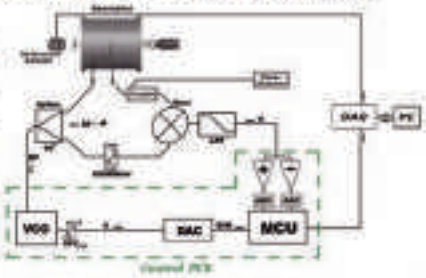


Instrumentation at high frequencies

Instrumentation for linear RF particle accelerator:
- **Beam position monitoring**
- **Control of RF signals**

Nanoposition displacement sensing through RF techniques





Magnetism and magnetic materials group

[1,6]Mª Luisa Fdez-Gubieda, [1]Jose Manuel Barandiarán,[1,6]Jon Gutierrez, [1,6]Alfredo García Arribas, [1,6]Galina Kurlyandskaya, [2,6]Ana García Prieto, [3,6]Alicia Muela, [4]David de Cos, [5]Andoni Lasheras, [1,6]Patricia Lazpita, [1,6]Volodymyr Chernenko, [6]Eduardo Fernandez , [1]Lourdes Marcano, [1]Maite Goiriena [1]David Gandía, [1,3]Lucia Gandarias, [1]Nerea Lete, [1,6]Virginia Vadillo, [1]Beatriz Sisniega, Ana Mª Schönhobel

[1]Departamento de Electricidad y Electrónica, [2]Departamento de Física Aplicada I, [3]Departamento de Inmunología, Microbiología y Parasitología, [4]Departamento de Física Aplicada II, [5]Departamento de Matemática Aplicada, [6]BCMaterials, Basque Center for Materials, Applications and Nanostructures

Nanomagnetism, Magnetotactic bacteria, Ferromagnetism shape memory alloys, Thin films, Magnetic sensors

The Magnetism and Magnetic Materials Group (GMMM) started working at the Faculty 30 years ago. As a result of the consistent and productive research performed, the group is acknowledged as an "A" class consolidated research group in the Basque Country and has international reputation. At present, it is an interdisciplinary group composed of Physicists, Electronic Engineers and Biologists working together
The main objective of the group is to prepare and characterize new magnetic materials with special properties for outstanding applications. Nowadays there are three main research lines: *Magnetotactic bacteria as theranostic agent*, *Ferromagnetic shape memory alloys* and *Magnetic Sensors*.

Magnetotactic bacteria as theranostic agent
Magnetotactic bacteria are aquatic microorganisms that swim along the geomagnetic field, using a chain of magnetic nanoparticles as a compass needle. The different species of magnetotactic bacteria synthesize perfectly stoichiometric magnetite nanocrystals, with genetically controlled sizes and shapes, surrounded by a biocompatible membrane, making them ideal for biomedical use. This research line is oriented in two complementary directions: first, the thorough study of the magnetic properties of these biosynthesized nanoparticles, and second, the exploitation of magnetotactic bacteria as a therapy agent such as a microrobot for localized drug delivery and magnetic hyperthermia.

Ferromagnetic Shape Memory Alloys (FSMA)
FSMA are active materials that develop high recoverable shape changes under the effect of mechanical stress or magnetic field in very short times (a few milliseconds). Due to their remarkable properties in actuation, vibration damping and sensing have permeated into many industries, such as the biomedical, energy or aerospace. The main objective of this research line is the combination of applied and fundamental research to improve the material performances and the comprehension of the involved physical processes

Magnetic Sensors
We design magnetic sensors based mainly on two different phenomena Giant Magneto Impedance (GMI) and Magnetoelastic (ME) effects. GMI produces huge changes in the electric impedance of a soft magnetic material and provides excellent sensitivities to small magnetic fields. ME effect consists in the magnetic state of some materials being altered by mechanical action and *vice versa*. When driven to resonance it is an extremely sensitive effect. Beside, Magnetoelectric composites are also multifunctional materials with outstanding sensitivity for sensors and excellent performance as energy harvesters.

GROUP OF MAGNETISM AND MAGNETIC MATERIALS

Departamento Electricidad y Electrónica; Departamento Fisica Aplicada I; Departamento Fisica Aplicada II; Departamento de Inmunología Microbiología y Parasitología

The Magnetism and Magnetic Materials Group (GMMM) started working at the Faculty 30 years ago. As a result of the consistent and productive research performed, the group is acknowledged as an "A" class consolidated research group in the Basque Country and has international reputation. At present, it is an interdisciplinary group composed of Physicists, Electronic Engineers and Biologists working together.

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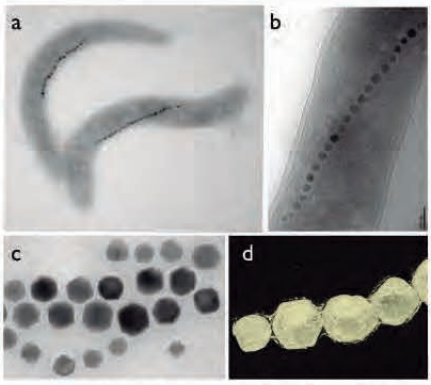
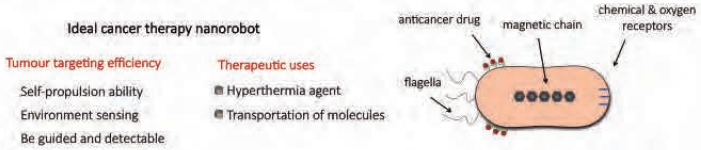
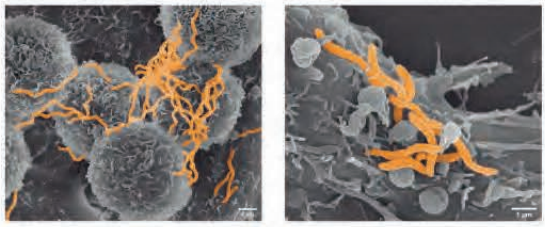
Objectives: first, the thorough study of the magnetic properties of these biosynthesized nanoparticles, and second, the exploitation of magnetotactic bacteria as a microrobot for localized drug delivery and magnetic hyperthermia



Magnetospirillum gryphiswaldense and isolated magnetosomes



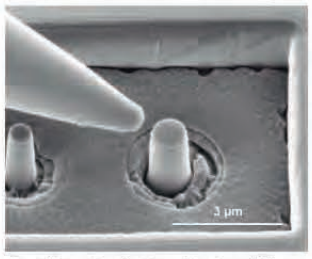


M. gryphiswaldense interacting with lung carcinoma cells

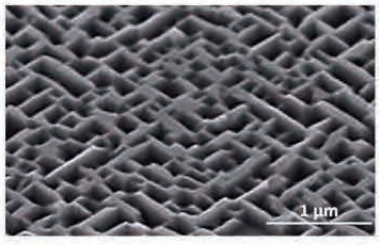
Ferromagnetic shape memory alloys

Ferromagnetic Shape Memory Alloys are active materials that develop high recoverable shape changes under the effect of mechanical stress or magnetic field in very short times (a few milliseconds). Due to their remarkable properties in actuation, vibration damping and sensing have permeated into many industries, such as the biomedical, energy or aerospace

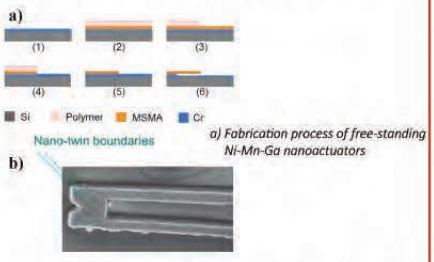
Objectives: the combination of applied and fundamental research to improve the material performances and the comprehension of the involved physical processes



Nanopillars sculpted by Focused Ion Beam (FIB) on the surface of a single crystal of NiMnGa. The big point on the left is the micromanipulator of the FIB (Collaboration with Nanogune)



SEM image of the self patterned surface of an epitaxial NiMnGa film grown onto MgO.

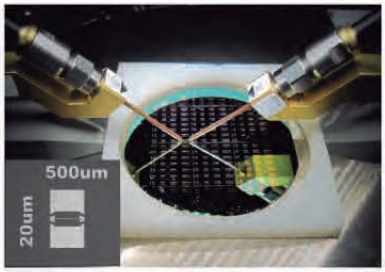


a) Fabrication process of free-standing Ni-Mn-Ga nanoactuators

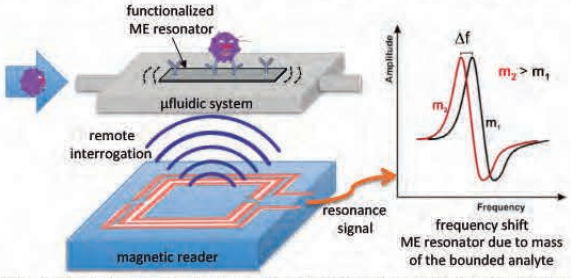
(b) Free-standing epitaxial Ni-Mn-Ga nanobeams showing nano-twin boundaries (Collaboration with Karlsruhe Institute of Technology, Germany)

Magnetic Sensors

Objectives: design magnetic sensors based on the coupling of physical properties with magnetism, such as Magneto-Impedance (MI) and Magneto-Elastic (ME) effects. MI takes advantage of the huge changes in the electric impedance of soft magnetic materials and provides excellent sensitivities to small magnetic fields. ME effect benefits from the magnetic changes produced by mechanical actions and *vice versa*. When driven to resonance it is an extremely sensitive effect. Beside, Magnetoelectric composites are also multifunctional materials with outstanding sensitivity for sensors and excellent performance as energy harvesters.



Electrical test of MI microsensors fabricated onto a Si wafer in the group's clean room at the Faculty. The inset shows a electron microscope image of one the sensors.



Scheme explaining the principle of operation of a magnetoelastic sensor for the detection of pathogens. The resonance frequency of the functionalized ME resonator shifts to lower values when the pathogens from a test sample are binded. The contactless detection allows for a remote interrogation of the sensor.

Software Technologies Working Group (GTTS, http://gtts.ehu.es)

Germán Bordel, Mikel Peñagarikano, Luis Javier Rodriguez-Fuentes and Amparo Varona
Department of Electricity and Electronics

KEY WORDS: Automatic Speech Recognition, Automatic Video Subtitling/Captioning, Spoken Term Detection, Information Retrieval for Multimedia Resources, Language and Speaker Recognition/Verification,

Research at GTTS focuses on fundamental software technologies and machine learning applications, in particular those related to speech processing and information retrieval. Our expertise spans speech segmentation, language and speaker recognition/verification, speaker diarization, automatic speech recognition, video subtitling, spoken term detection, etc. Part of our efforts are devoted to develop tools and prototypes for various applications. For example:

> Automatic bilingual video subtitling applied to plenary session videos of the Basque Parliament (http://www.parlamentovasco.euskolegebiltzarra.org/), running from September 2010.

Besides, we also pay special attention to the dissemination of results, both in prestigious publications and through technology transfer to companies in our area, and the collaboration with other research groups. Finally, we also devote great efforts to academic training (PhD and master theses). For the next year, GTTS is especially involved in teaching the Master in Blockchain Technology and Crytoeconomics.

RESEARCH ACTIVITY IN THE LAST FIVE YEARS

- Basque Government Research Group (A): Aholab-GTTS 2019-2022 (100.000 euros)
- Projects, contracts and research fellowship: 6 (200.000 euros)
- Most relevant publications: 12 (5 JCR journals, 7 peer-reviewed conferences)
- Thesis: 2 presented
- Organization of international conferences:
    - Odyssey 2016: The Speaker and Language Recognition Workshop (http://www.odyssey2016.org)
- Organization of international evaluations of technology:
    - MediaEval(1) - Query-by-Example Search on Speech Task (QUESST) (2015)
    - Albayzin Text-to-Speech Alignment Evaluation (2020)
- Participation in international evaluations of technology:
    - NIST(2) Language Recognition Evaluation (2015)
    - NIST(2) Language Recognition Evaluation (2017)
    - Albayzin Search on Speech Evaluation (2018)
    - NIST(2) Speaker Recognition Evaluation (2019)

TECHNOLOGY TRANSFER

- Hitzaldi: tool for audio-text alignment in parliamentary interventions
- Sautrela: software package (free access) for the development of speech processing applications
- Hearch: search tool for audiovisual resources (from automatic transcriptions of speech)
- Kalaka-3: database for the development of language recognition systems
- ICT COST-278: database of TV news in Spanish and Basque for audio segmentation and speaker diarization

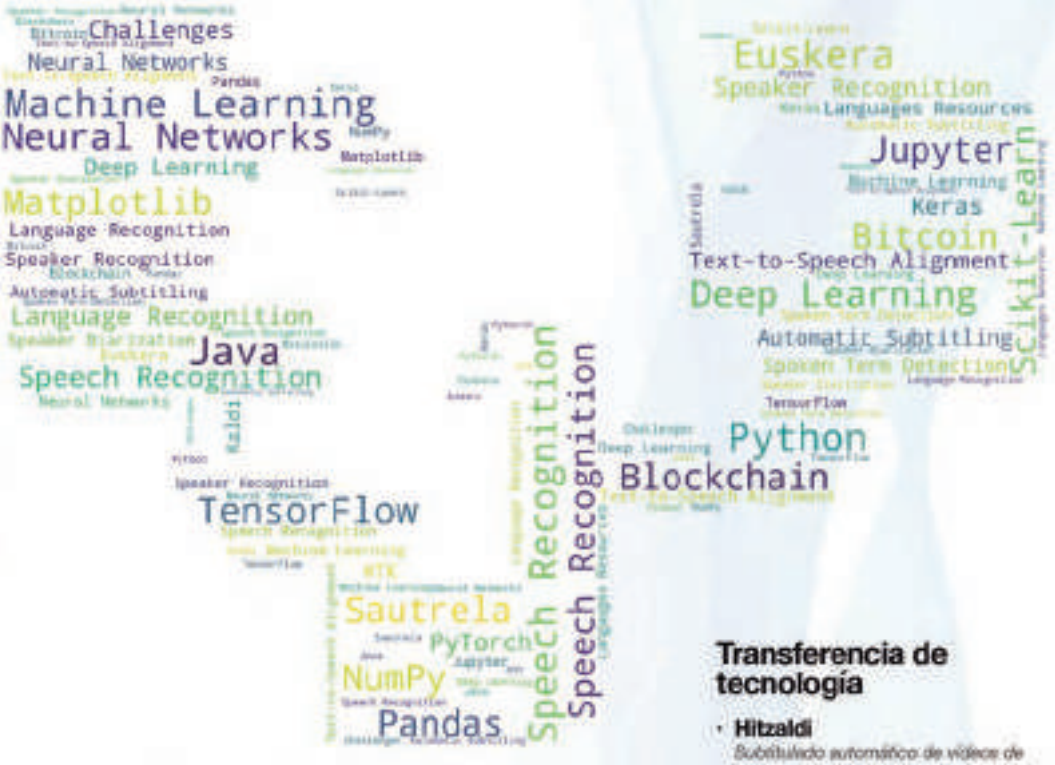
(1) MediaEval Benchmarking Initiative for Multimedial Evaluation
(2) NIST: National Institute of Standards and Technology

Grupo de Trabajo en
Tecnologías Software

GTTS.EHU.EUS

Departamento de Electricidad y Electrónica

Luis Javier Rodríguez Fuentes | Amparo Varona | Germán Bordel | Mikel Peñagarikano



Actividad investigadora (últimos 5 años)

- **Grupo Investigación Gobierno Vasco (A)**
  Aholab-GTTS 2019-2022 (100.000 euros)
- **Proyectos + Contratos + Becas**
  - Total Proyectos: 7 (230.000 euros)
  - Proyecto más reciente (2020-2023): OpenSpeech - MINECOR PID2019-106424RB-I00: Metodologías no supervisadas para el aprovechamiento de datos de dominio público en reconocimiento automático del habla: de la abundancia a la escasez de recursos.
- **Publicaciones más relevantes**
  5 revistas JCR + 7 congresos internacionales (peer reviewed)
- **Tesis doctorales**
  2 presentadas
- **Organización de congresos internacionales**
  Odyssey: The Speaker and Language Recognition Workshop (2016)
- **Organización de evaluaciones internacionales**
  MediaEval Query-by-Example Search on Speech (2015)
  Albayzin Text-to-Speech Alignment Evaluation (2020)
- **Participación en evaluaciones internacionales**
  NIST Language Recognition Evaluation (2015, 2017)
  Albayzin Search on Speech Evaluation (2018)
  NIST Speaker Recognition Evaluation (2019)

Transferencia de tecnología

- **Hitzaldi**
  Subtitulado automático de vídeos de sesiones del Parlamento Vasco usando las actas oficiales
- **Sautrela**
  Paquete de software (de acceso libre) para el desarrollo de aplicaciones de procesamiento del habla
- **Hearch**
  Herramienta de búsqueda en recursos audiovisuales a partir de transcripciones automáticas del habla
- **Kalaka-3**
  Base de datos para el desarrollo de sistemas de reconocimiento de la lengua
- **ICT COST-278**
  Base de datos de noticias de televisión en euskera y castellano para segmentación de audio y diarización de locutores

GTTS Tecnologías Software

Universidad del País Vasco | Euskal Herriko Unibertsitatea

Zientzia eta Teknologia Fakultatea
Facultad de Ciencia y Tecnología

VII Jornadas de Investigación

28-30 de septiembre de 2020

Facultad de Ciencia y Tecnología
UPV/EHU

Theory of Nanophotonics

Mattin Urbieta[1,2], Bruno Candelas[2], Luca Bergamini[1,2], Eduardo Ogando[3] and Nerea Zabala[1,2]
[1]Department of Electricity and Electronics, UPV-EHU, Leioa;
[2]CFM, Centro Mixto CSIC-UPV/EHU and DIPC, Donostia;
[3]Department of Applied Physics II, UPV-EHU, Leioa.

KEY WORDS: light, plasmon, nanoparticle, nanoantenna, metasurface.

We investigate theoretically, and in collaboration with experimental groups, the phenomena taking place at nanostructures excited by light. Metal nanostructures are able to convert Visible–Near-Infrared light into collective excitations of conduction electrons (plasmons), producing evanescent waves with a decay length of nanometer scale. At light wavelengths resonant with plasmons, the metallic structures, often referred to as optical antennas or nanoantennas, feature a remarkable absorption and an intense electromagnetic field enhancement and localization around their surface. Optical antennas boost light-matter interaction by bridging the mismatch in length scales between the size of the propagating radiation (around 500 nm for visible light) and that of the emitter or receiver (around 1 nm for a molecule). This allows to mold the flow of light and control its emission and absorption in the nanometer scale, beating the diffraction limit.

Under illumination, the plasmon-induced intense electromagnetic field is further enhanced in metallic tips (lightning-rod effect) or intermediate gap regions between antennas with nanometric separation, producing the so called hot-spots. When the gaps are shrunk down below the nanometer, phenomena as electron tunneling or atomic-scale features start to play a significant role and a full *Quantum Plasmonics* description is required in order to understand the interaction.

The nanoantennas are often repeated in periodic structures, forming *Metasurfaces*, so that the enhanced field due to the plasmon is significantly modulated by the diffractive coupling introduced by the periodic arrangement. Moreover, plasmon excitations are further exploited in *Plasmonic Hybrid Metasurfaces*, in which plasmonic metallic nanoantennas are merged with materials presenting specific functionalities as metal-insulator phase transitions, ferromagnetism or spintronic properties. These combinations provide a powerful toolset to design new artificial materials and optoelectronic devices for active control, all-optical switches, more accurate molecular spectroscopies, molecular and biological sensors, etc...

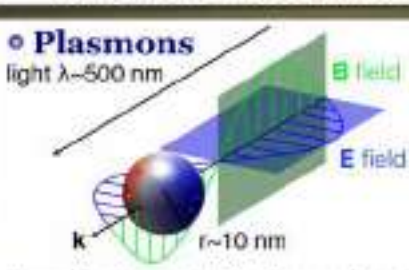
Universidad del País Vasco · Euskal Herriko Unibertsitatea
FACULTY OF SCIENCE AND TECHNOLOGY

Theory of Nanophotonics

Mattin Urbieta, Bruno Candelas, Luca Bergamini , Eduardo Ogando and Nerea Zabala
Department of Electricity and Electronics, Faculty of Science and Technology, UPV-EHU

Nanophotonics: control light on length scales below wavelength (λ~500nm for Vi-NIR light)

Plasmons



Metal nanostructures convert Vi-NIR light (propagating EM waves) into **plasmons** (collective oscillations of conduction band electrons), with a decay length ~10-100nm. They work as **Optical Nanoantennas.**

Theory of Nanophotonics describes phenomena taking place in nanostructures excited by light . We solve Maxwell's equations analytically or numerically with different methods: BEM, DDA, FDTD...

Applications

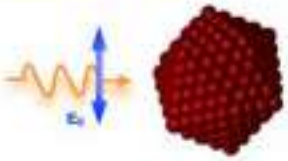
Optoelectronics

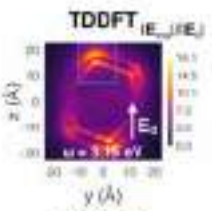
Molecular and biological sensors

Field enhancedspectroscopy and microscopy

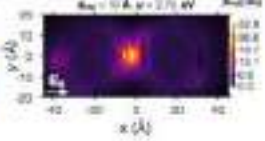
Field enhancement and localization: shape and quantum effects

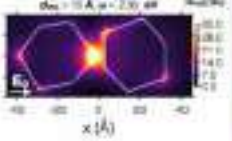
Plasmons excited with light





Plasmonic gap: Tip and facet



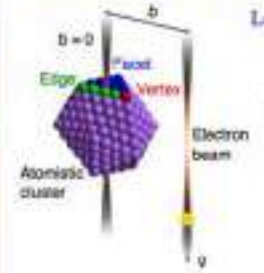


Plasmon-induced intense electromagnetic field is enhanced and localized around metallic tips (**lightning-rod effect**) or gaps between nanoantennas with nanometric separation, creating **hot-spots.**

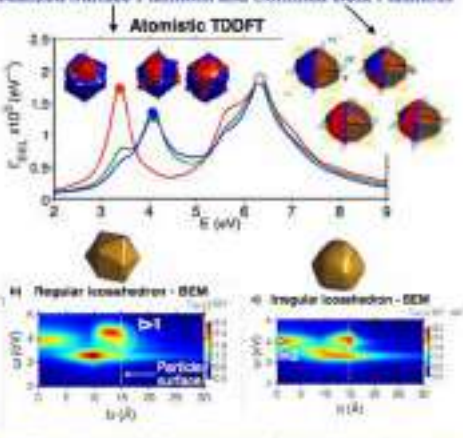
ACS Nano 12, 585–595, (2018)

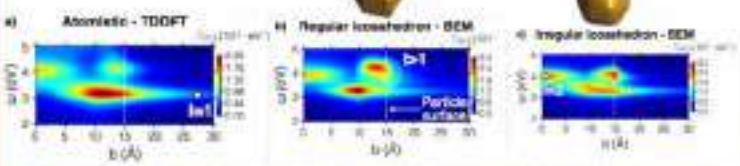
Plasmons excited with electrons

Electron Energy Loss Spectroscopy



Localized Surface Plasmons and Confined Bulk Plasmons

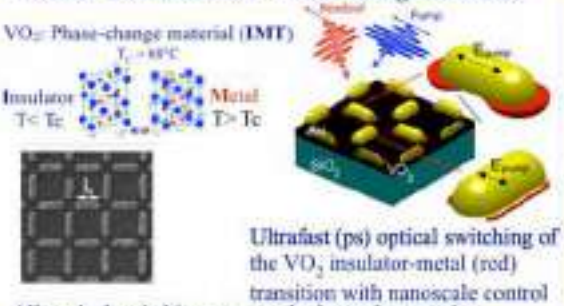




Electrons passing nearby a metallic nanoparticle lose energy by exciting plasmons. We study the electron energy loss probability using quantum atomistic models (TDDFT) and classical approaches (BEM).

Plasmonic metasurfaces

Plasmonic nanoantennas + Phase change materials



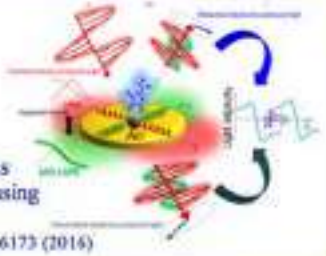
Ultrafast (ps) optical switching of the VO_2 insulator-metal (rod) transition with nanoscale control

All-optical switching, nanoscale thermal memories

Light: Sci. &Appl. **5**, e16173 (2016)

Magneto-optics: plasmons with ferromagnetic materials

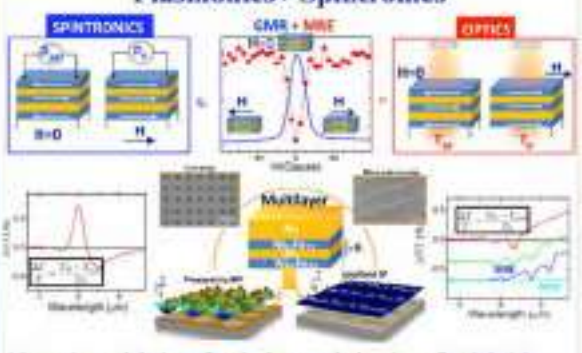
Ni nanodisks (SEM)



Excitations in Ni nanodisks
Aplications: molecular sensing

Nano Lett. **16**, 2533 (2016), e16173 (2016)

Plasmonics+ Spintronics



Magnetic modulation of optical transmission (or reflectivity) in mid-IR with low magnetic fields in metasurfaces with giant Magnetoresistance (GMR) multilayers.
Mechanism: magnetorefractive effect (MRE), different optical response with and without magnetic field due to electron spin.
ACS Photonics **5**, 3956 (2018)

http://cfm.ehu.es/nanophotonics

Financial support
Department of Education of the Basque Government, project ref. No. IT-1164-19,
Department of Industry of the Basque Government project KK- 2018/00001,
MICIN project ref. No. PID2018-101743CB-I00

Zientzia eta Teknologia Fakultateko VII. Ikerkuntza Jardunaldiak -September 28-30, 2020, Leioa (Bizkaia)

Shape memory alloys for aero-space and micro-nano applications: mechanical and microstructural properties

José Fdo. Gómez Cortés[1], Mikel Pérez Cerrato[1], Patricia Lorenzo[1], Isabel Ruíz Larrea[2], Tomasz Breczewski[2], María Luisa Nó[2] and José María San Juan[1]
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KEY WORDS: shape memory, superelasticity, aerospace, micrsotructure, mechanical properties

Shape Memory Alloys (SMA) are a family of intelligent materials exhibiting the exceptional mechanical properties of shape memory and superelasticity. The shape memory effect is produced thanks to a reversible first-order phase transition between two solid phases, the high-temperature austenitic phase, and the low-temperature martensitic phase. The martensite in SMA can be easily deformed to a low-temperature shape, but the whole deformation disappears once the material is transformed back into its austenite form, or high-temperature shape, by heating. This reversible change of shape can be also induced by the application of stress at constant temperature and in this case, the stress-induced martensite gives place to the superelastic effect. The amount of strain recovered is exceptionally high for a metallic alloy (it can be around 10%), as well as the work output per unit volume (1x107 J/m3). These properties allow SMA to have a huge variety of applications, in sectors such as the biomedical (e.g. stents, prosthetics...), robotics, sensors and actuators in cars, aircrafts and satellites, or miniaturization of electro-mechanical devices.

The Research Group on Physical Metallurgy (GIMF) is specialized in the synthesis and characterization of copper-based SMA. In particular, Cu-Al-Ni and Cu-Al-Be ternary alloys and Cu-Al-Ni-X quaternary alloys (where X can be Ga, Mn, Be, Au...), are produced as poli-crystals and single-crystals. The concentration of the alloying elements allows control the properties, but to master the functional properties of SMA, a deep knowledge of the relationship between microstructure and mechanical properties is crucial and consequently, this is one of the main activities carried out in our research group. The microstructural characterization through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) are deeply approached, together with X-ray and Neutron diffraction experiments [1]. In addition, the thermal properties via differential scanning calorimetry (DSC), the mechanical properties by tensile and compression stress-strain measurements are also carefully studied. Finally, nano-compression tests by instrumented nanoindentation techniques allow determining the superelastic and memory behavior of SMA at micro and nanoscale [2-5]

Some of the goals of our research group have already been accomplished, and our materials are being applied in an aerospace actuator REACT, (http://react-space.com), developed in the frame of a European H2020 project. We are proud of our SMA, which are already flying in real space missions, and new space actuators are being developed in our group. At present we are also working on the applications of SMA at micro and nanoscale, being this field a promising one in which we are worldwide pioneers [2,3]. In the poster, a selection of the most outstanding results obtained recently in the frame of the GIMF activities will be presented and discussed.

[1] I. Ruiz-Larrea, et al., Journal of Applied Physics 125 (2019) 082536
[2] J. San Juan, M.L. Nó, C.A. Schuh, Nature Nanotechnology 4 (2009) 415-419.
[3] J.F. Gómez-Cortés, et al., Nature Nanotechnology 12 (2017) 790-796.
[4] J.F. Gómez-Cortés, et al., Acta Materialia 166 (2019) 346-356.
[5] V. Fuster, J.F. Gómez-Cortés, M.L. Nó, J. San Juan, Advanced Electronic Materials 6 (2020) 1900741.

Shape Memory Alloys for Aero-Space and Micro-Nano Applications: Mechanical and Microstructural Properties

José F. Gómez-Cortés, Mikel Pérez-Cerrato, Patricia Lorenzo, Josu Ibáñez, Isabel Ruiz-Larrea, Tomasz Breczewski, María L. Nó and José M. San Juan

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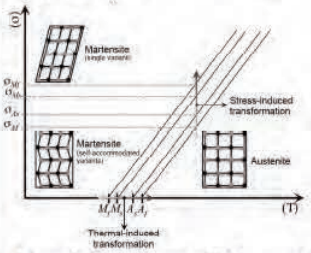
What is a Shape Memory Alloy (SMA)?

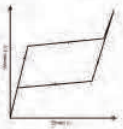
✧An SMA is an active metallic material that exhibits exceptional thermo-elastic properties that offer the highest work-out per unit of volume, in comparison with other functional materials. As a consequence of it, SMAs are incredibly useful as sensors and actuators, and even more when decreasing the size of the device, leading to potential applications in Micro-Electro-Mechanical Systems (MEMS) [1,2].

✧Superelasticity and shape memory effects are the two main thermo-elastic behaviours in an SMA. Their existence is due to a reversible solid-state phase transformation, known as the martensitic transformation (MT). The MT occurs between a high-temperature phase (austenite) and a low-temperature phase (martensite).



Schematic phase diagram of the thermo-elastic martensitic transformation in the stress-temperature field

Scheme of the characteristic line shape of the superelastic response in the stress-strain field. (stress-induced MT)



Scheme of the characteristic line shape of the shape memory response in the stress-strain field. (thermal-induced MT)

Aero-space Applications

Alloys production: We produced polycrystals and single-crystals of copper-based SMA. In particular, Cu-Al-Ni and Cu-Al-Be ternary alloys and Cu-Al-Ni-X quaternary alloys (where X can be Ga, Mn, Be, Au...). Below we can see a single crystal of Cu-Al-Ni grown in our laboratories.

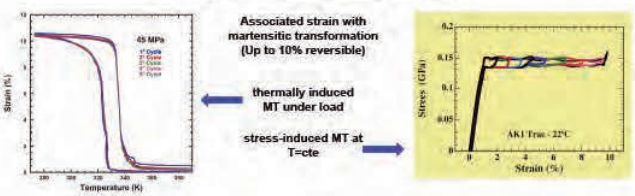
We are currently working on new ways of producing shape memory alloys by new single-crystal technologies, as well as through modern additive manufacturing techniques.

Alloys characterization

The microscopic characterization of the materials is an essential step on the study of SMAs. It allows to properly understand the mechanism of the transformation, homogeneity of the composition, microstructure, thermal stability parameters, etc.

Optical micrograph of a Cu-Al-Ni single-crystal. Both images show the same region of the sample, being the left image in austenite phase, and in martensite on the right one.

Mechanical characterization



The single-crystal SMAs are nowadays being tested as part of a resettable hold-down and release actuator, HDRA, for use in satellites and space missions. This was developed in the frame of the European project H2020 REACT.
Our SMA are already flying in the Space !

What is our Interest and Work?

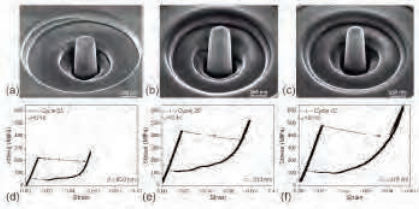
The Research Group on Physical Metallurgy (GIMF) is specialized in the synthesis and characterization of copper-based SMA. In particular, Cu-Al-Ni and Cu-Al-Be ternary alloys and Cu-Al-Ni-X quaternary alloys (where X can be Ga, Mn, Be, Au...), are **produced as polycrystals and single-crystals**.

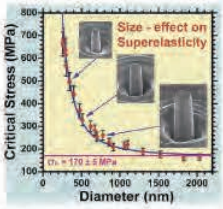
- **The microstructural characterization** through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) are deeply approached [3].
- In addition, **the thermal properties**,via differential scanning calorimetry (DSC), and **the mechanical properties** by tensile and compression stress-strain measurements are also carefully studied [4].
- Finally, **nano-compression tests** by instrumented nanoindentation techniques allow determining the superelastic and memory behavior of SMA at micro and nanoscale [1,2,5,6].

Micro-Nano Applications

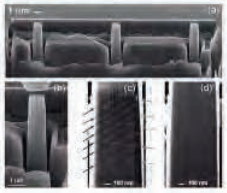
One of the main research areas of our group is the development of SMAs for micro- and nano- actuators. The unusual properties of SMAs are exceed at small volumes, so we build and test samples of very small size. For instance, the left image shows the martensite grains of a *lamella*, a thin film of some few hundred of nanometeres thick.

With the help of a FIB (Focus Ion Beam) one can cut the surface of nearly any material and mill it in the desired shape. It is a tough and time-consuming effort, but it is possible to build small pillars with a cross-section as small as few hundred of nanometers. These pillars are great to conduct mechanical compression experiments, as they give a lot of information about the properties of alloy at the nanoscale, which does differ from the bulk [1, 2, 4].





For example, these graphs show how the critical stress, this is the value at which the transformation takes place, dramatically increases with smaller values of the area of the pillars [1, 2, 6].



The final image shows a superelastic test in one of the pillars during an in-situ nano-compression experiment inside the Scanning Electron Microscope. The head of the nanoindenter pushes the pillar down perpendicular to the surface of the material.(b). After the elastic response, and once the critical stress has been reached, the material transforms into martensite, as shown by arrows in (c). Upon unloading the material fully recovers its original shape (d), [6].

ACKNOWLEDGEMENTS

This work is supported by the Spanish Ministry of Economy, MINECO, projects MAT2017–84069P and CONSOLIDER-INGENIO 2010 CSD2009–00013, as well as by the ELKARTEK-ACTIMAT project from the Industry Department of the Basque Government. J.F. Gómez-Cortés and M. Pérez Cerrato acknowledge the Post-Doctoral Grant (ESPDOC18/37) from the UPV/EHU, and the Pre-Doctoral Grant from the Basque Government (PRE_2019_2_0268), respectively.

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[2] M.L. Nó et al., ***Acta Materialia*** 58 (2010) 6181–6193.
[3] I. López-Ferreño et al., ***J. Materials Research & Technology*** 9 (2020) 9972–9984.
[4] J. San Juan, M.L. Nó, C.A. Schuh, ***Nature Nanotechnology*** 4 (2009) 415–419.
[6] J.F. Gómez-Cortés, et al., ***Acta Materialia*** 166 (2019) 346–356.

Research Group on Thermo-physical Properties of Materials (GI-PTFM)

Iñigo González de Arrieta[1], Telmo Echániz[2], Raquel Fuente[2], Irene Urcelay-Olabarria[1], José M. Campillo[1], Leire Usategui[2], Josu M Igartua[1], Gabriel A López[1]
[1]Applied Physics II, University of the Basque Country UPV/EHU, Leioa, 48940, Spain;
[2]Applied Mathematics, School of Engineering, University of the Basque Country UPV/EHU, P. Ingeniero Torres Quevedo, Bilbao, 48013, Spain.

KEY WORDS: Radiometry, Material Science, Thermo-physical Properties, Materials for Energy.

The members of the Research Group on Thermo-physical Properties of Materials (GI-PTFM) have extensive experience in experimental characterization techniques such as electron microscopy, diffraction, various spectroscopies; and in topics such as physical metallurgy, structural properties, oxidation kinetics in situ, multiferroic materials, materials for thermo-solar and electro-chemical energy.

In the GI-PTFM we are prepared to face important research challenges. Our Group has got a unique facility in Spain, and one of the few around the world, the high precision emissometer (HAIRL), which was designed, built and calibrated completely by the Group. Due to the shortage of laboratories that have instruments to measure spectral/directional emissivity, and thanks to the development of rigorous methods of calibration and calculation of errors, we are a recognized worldwide reference.

The infrared emissivity data of the materials at service temperature are decisive in a broad scientific/technological spectrum; and its use is of special interest in technological applications in which the heat transfer by radiation is critical: design and production of advanced alloys through state-of-the-art processes (additive manufacturing) or in solar-thermal energy collectors.

We address the following topics:

Optimization of materials for alternative energies: We have significant contributions in the optimization of materials to capture and store solar energy, where thermo-optical properties at high temperature are crucial. The efficiency of these applications is closely related to the precise value of the emissivity. We work on multi-layer selective coatings and nanoadhesive absorbent paints, radiative properties of candidate perovskites for photovoltaic generation and energy storage systems; nano-fluids based on molten salts, with usable physical properties.

Instrumentation and methods of measuring emissivity: The current impossibility of measuring infrared emissivity in liquids is an inconvenience in many technological applications, since there is hardly any data in the literature. Our proven experience in the construction of HAIRL will allow us to finish building and calibrating a new radiometer for solids and liquids (up to 1600 ˚C in high vacuum).

Fundamental studies of thermo-optical properties of materials: These properties can be related to other fundamental properties of materials such as electrical conductivity and vibration frequencies of phonons. We study these properties from directional spectral infrared emissivity data as a function of temperature in ceramics and metals.

Industrial application of thermo-optical techniques: We work together with PETRONOR Innovation in a temperature control project using thermography to apply it in reforming furnaces. We are developing a correction algorithm to apply in commercial thermographic measurement equipment.

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[2] *Applied Mathematics, University of the Basque Country UPV/EHU, 48013 Bilbao*

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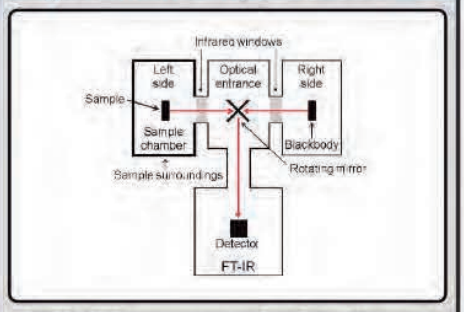
Summary

The members of the **Research Group on Thermo-physical Properties of Materials (GI-PTFM)** have extensive experience in experimental characterization techniques such as electron microscopy, diffraction, various spectroscopies; and in topics such as physical metallurgy, structural properties, *in situ* oxidation kinetics, multiferroic materials, materials for thermo-solar and electro-chemical energy.

In the GI-PTFM we are prepared to face important research challenges. Our Group has got a unique facility in Spain, and one of the few around the world, the **high-accuracy HAIRL emissometer**, which was designed, built and calibrated completely by the Group. Due to the shortage of laboratories that have instruments to measure spectral/directional emissivity, and thanks to the development of rigorous methods of calibration and calculation of errors, we are a recognized worldwide reference.

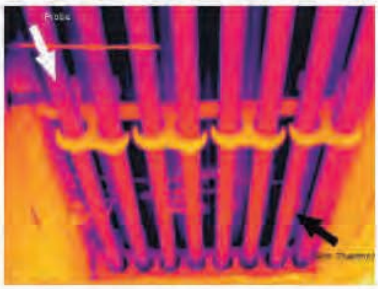
The **infrared emissivity data of the materials at working temperature** are decisive in a broad scientific/technological spectrum; and its use is of special interest in technological applications in which the heat transfer by radiation is critical: design and production of advanced alloys through state-of-the-art processes (additive manufacturing) or in solar-thermal energy collectors. We address these topics below.

Experimental apparatus



The HAIRL emissometer has been in use for more than 14 years. It consists of a Fourier-transform infrared spectrometer (FTIR), a vacuum sample chamber, a commercial blackbody source and an optical entrance box that allows switching between the blackbody and the sample. It can perform measurements up to **1200 °C in high vacuum or a controlled atmosphere** (I. González de Arrieta *et al.*, Metrologia **57**, 045002, 2020).

Industrial applications

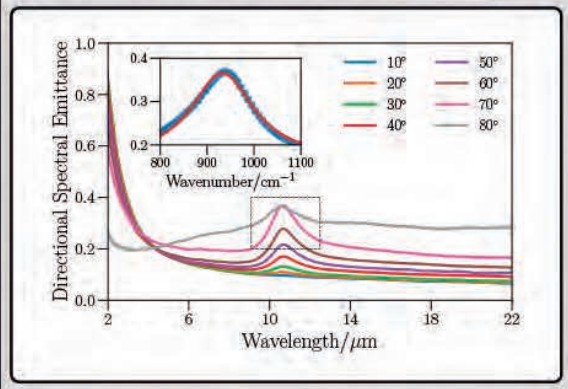


We work together with **PETRONOR Innovación** in a temperature control project using thermography to apply it in reforming furnaces. We are developing a **correction algorithm** to apply in commercial thermographic measurement equipment.

Acknowledgements

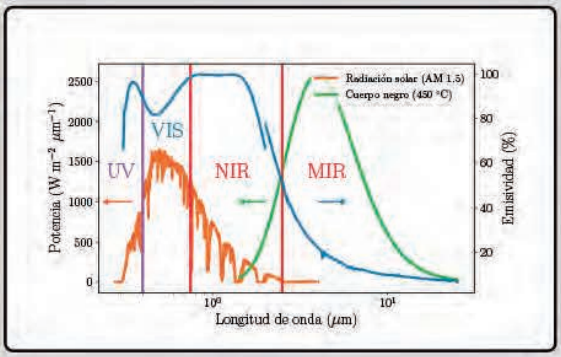
The authors would like to acknowledge the following funding sources: Grupos de Investigación de la UPV/EHU (GIU19/019); Proyectos Universidad/Empresa US19/13; ELKARTEK KK2018/00098; Convocatoria de Infraestructuras de la UPV/EHU INF19/18.

Fundamental studies of thermo-optical properties of materials



The optical and thermal radiative properties of materials can be related to other fundamental properties, such as the **electrical conductivity and phonon frequencies**. We study these properties from directional spectral infrared emissivity data as a function of temperature in ceramics and metals. We have observed that the radiative properties of materials are more complex than they are often assumed (see, for example, the **Berreman effect** in a multilayer solar stack, pictured to the left).

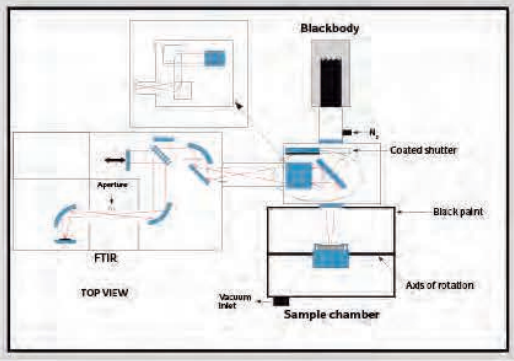
Optimization of materials for alternative energies



We have significant contributions in the optimization of materials to capture and store solar energy, where thermo-optical properties at high temperature are crucial. The **efficiency** of these applications is closely related to the precise value of the emissivity.

We work on multi-layer **selective coatings** and nanoadhesive absorbent paints, radiative properties of candidate **perovskites** for photovoltaic generation and energy storage systems; **nano-fluids** based on molten salts, with usable physical properties.

Instrumentation and methods of measuring emissivity



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Physical and mathematical fundamentals of the structure of the Universe

A. Alonso[1], M. Bouhmadi-Lopez[1,2], D. Brizuela[1], T. Broadhurst[1,2], I. de Martino[1], J. Morais-Viegas[1], F. Fernández-Álvarez[1], I. Garay[1], J. Ibáñez[1], R. Lazkoz[1], I. Leanizbarrutia[1], M. Reyrinck[1,2], M. Ortiz[1], D. Sáez[1], V. Salzano[1], J.M.M. Senovilla[1], B. Reina[1], R. Vera[1], F. Vidotto[1]

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KEY WORDS: Cosmology, General Relativity, Loop Quantum Gravity, Relativistic Astrophysics, neutron stars, black holes, gravitational waves, modified theories of gravity, dark matter, dark energy, gravitational lensing

Einstein's equations of General Relativity (or modifications) link the geometry of spacetime (gravity) with the physics of non-gravitational fields. They constitute the framework for the study of the Universe and relativistic astrophysical objects. A better understanding of the Universe involves deepening the description of its early stages, regimes of high energies, and the principles governing the laws that govern it. Cosmology and physics directed to the description, evolution and emission of gravitational waves of relativistic systems are intimately related to the rest of the aspects of the structure of the Universe, that is to say, with more fundamental aspects, and in general of a more mathematical nature.

These theoretical aspects must also be confronted with phenomenological aspects of the Universe, both in the context of General Relativity and in the wider context of modified theories. This is an area of research in full swing thanks to the arrival of new observational data. Broadly speaking these data provide surprising conclusions about the possible components of the Universe, whose "presence" is manifested in the kinematics of the Cosmos at different scales. One of the most controversial features is the apparent acceleration of the expansion of the Universe.

Main sublines:

1. Dynamics of very compact astrophysical objects and black holes. Emission of gravitational waves, and cosmological gravitational waves. The role of the cosmological constant.
2. Quantum cosmology and loop quantum gravity: dynamics, semiclassical approach and physical consequences.
3. Mathematical relativity; trapped and umbilical submanifolds, computer algebra, initial data characterisations and exact solutions.
4. Dark matter and energy: observational tests and alternative gravity theories.
5. Gravitational lensing, galaxy formation and galactic clusters, panoramic surveys and galactic telescopes.

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Las **ecuaciones de Einstein** de la Relatividad General (o modificaciones) ligan las geometría del espaciotiempo (la gravedad) con la física de los campos no gravitatorios. Constituyen el marco para el **estudio del Universo** y los **objetos astrofísicos relativistas**. Una mejor comprensión del Universo conlleva profundizar en la descripción de sus primeras etapas, regímenes de altas energías, y en los principios que rigen las propias leyes que lo gobiernan. La **Cosmología** y la física encaminada a la descripción, evolución y emisión de **ondas gravitacionales** de sistemas relativistas están intimamente relacionadas con el resto de los aspectos de la estructura del Universo, es decir, con **aspectos más fundamentales**, y en general de naturaleza más matemática si cabe.

Agujeros negros

Los horizontes separan regiones diferenciadas cualitativamente según los caminos que sigue la luz. En particular, un **horizonte de sucesos** encierra una región de donde la luz no puede escapar, y es lo que define un **agujero negro** estático. Los únicos agujeros negros descritos teóricamente son estacionarios (como máximo rotan: tipo **Kerr**).

Nuestro objetivo consiste en **describir agujeros negros en transición**, desde su formación al estado estacionario final. Para ello, el estudio del horizonte de sucesos no es suficiente. El propósito es tratar nuevos tipos de horizontes: atrapados, aislados y dinámicos y a su generalización a tubos marginalmente atrapados.

Fotografía simulada por ordenador de un disco de gas en acreción sobre un agujero negro.
Autor: Interstellar / Paramount Pictures

Propiedades matemáticas del agujero negro de Kerr:

El agujero negro de Kerr es una de las **soluciones** más importantes de las ecuaciones de Einstein de vacío ya que físicamente representa un **agujero negro en rotación**. Principalmente nos centramos en el estudio de caracterizaciones invariantes de la solución de Kerr, que permiten determinar cuando la solución para un conjunto de datos iniciales de las ecuaciones de Einstein de vacío se corresponde con Kerr. También podemos establecer si una solución completa de las ecuaciones "es parecida" a la solución de Kerr. Estas técnicas son importantes a la hora de estudiar la estabilidad de la solución de Kerr o si dicha solución puede ser el "estado final" de un proceso de evolución de un agujero negro dinámico.

Cuerpos en rotación (estrellas, galaxias, cúmulos) en Relatividad General

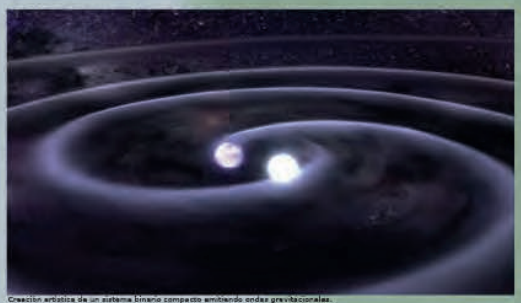
Aunque la mayor parte de los estudios en objetos astrofísicos, como estrellas de neutrones, se han basado en la aproximación Newtoniana, **necesitamos la RG incluso para obtener rasgos cualitativos**. En particular para calcular la emisión de **ondas gravitacionales**.

Estrellas Relativistas:

Hemos demostrado que el conocido **modelo de Hartle-Thorne** (1967) usado en astrofísica relativista es el modelo más general posible para describir **perturbaciones estacionarias y axisimétricas hasta segundo orden** en torno a configuraciones esféricas y estáticas. De aquí hemos podido demostrar un **resultado de existencia y unicidad** de las perturbaciones bajo suposiciones muy generales de regularidad: la solución del problema a segundo orden depende únicamente de dos variables, e.g. la densidad central y la velocidad angular.

Por otro lado, **hemos corregido el cálculo original de Hartle-Thorne de la masa de la estrella rotante en función de su radio**. La corrección conlleva un término proporcional a la desidad de materia-energía en la superfice de la estrella. En modelos recientes de estrellas de "strange" quarks ese término resulta ser importante.

Creación artística de una estrella de neutrones.
Autor: Kevin M Gill con licencia CC



Creación artística de un sistema binario compacto emitiendo ondas gravitacionales.
Autor: NASA

Ondas gravitacionales en sistemas binarios compactos:

Recientemente se había comprobado que una corrección ad-hoc en el cálculo del parámetro "Love" **(fuerzas de marea)** permite encontrar relaciones universales entre el **Love, I (momento de inercia)** y **Q (momento cuadrupolar)**. Por "universales" se entiende que no dependen de la ecuación de estado para la materia en la estrella.

Demostramos **1)** que esas correcciones vienen dadas por aplicación directa del marco matemático desarrollado para estrellas relativistas) **2)** la corrección al cálculo de la masa nos permite encontrar **otra serie de relaciones universales incluyendo la masa**. Estas últimas relaciones representan un avance significativo en la descripción de binarias compactas, ya que el conjunto de relaciones (completadas ahora con la masa) permiten deducir los parámetros de la perturbación directamente a partir de datos observacionales (mediante la observación de ondas gravitacionales emitidas, en particular).

Gravedad Cuántica:

La búsqueda de una descripción cuántica de la gravedad sigue siendo uno de los problemas principales de la física teórica. La **Gravedad Cuántica de Lazos** presenta resultados físicos relevantes a este respecto: posible explicación del origen de la **entropía de agujeros negros**; alternativa al Big-Bang reemplazándolo por un rebote a escalas cuánticas (**Big-Bounce**)...

Objetivos: construir modelos sencillos que nos permitan mejorar las bases de la teoría, concretamente la implementación de la **dinámica** y la búsqueda de un **sector semiclásico**, y que nos permitan extraer consecuencias físicas.

Fotografía simulada por ordenador de la estructura cuántica del espacio-tiempo.
Autor: Max Planck Institute for Gravitational Physics

Fondo cósmico de microondas (CMB): ¿una ventana a la gravedad cuántica?

El CMB puede ser un laboratorio natural donde **comprobar experimentalmente** cualquier teoría de gravedad cuántica. Según la teoría de la inflacción, en los primeros instantes de nuestro universo, se produjo una expansión enorme y repentina que funciona como una lupa, pudiendo convertir efectos minúsculos e indetectables en medibles. Nuestro objetivo, por tanto, es estudiar si los **efectos gravito-cuánticos** dejan algún rastro visible en el CMB.

Enlaces de espaciotiempos en gravedad cuadrática:

teorías de gravedad que generalizan la RG mediante la inclusión de términos cuadráticos de la curvatura en el Lagrangiano. Conforman teorías efectivas de marcos teóricos de **gran unificación**, como teorías de cuerdas. El resultado más notable es la aparición de **capas dobles**, en analogía a las **capas dipolares** (+ y -) en electromagnetismo. Estas capas no existen en RG, debido a que sólo hay masas positivas.

Early Universe Cosmology and Fundamental Physics

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Cosmology, General Relativity, Inflation, String Theory, Multiverse, Cosmic Strings

We are currently investigating several aspects of some of the most interesting topics in Theoretical Cosmology. Here is just a short summary of some of these topics.

- **Cosmic Strings.**
  Cosmic strings are topological defects that may have been created in the early universe. They typically form in a phase transition that gives rise to a complicated network of long strings that stretch across the horizon. One of the most important questions that one needs to address in order to extract predictions on these theories is to understand the cosmological evolution of these networks and its statistical properties. One of the most interesting methods to tackle these questions is the use of computer simulations that evolve the strings from some initial conditions. We are one of the leading research groups on cosmic strings simulations being involved in the largest simulations of a network of strings ever performed.

- **Cosmological Inflation**
  Several cosmological observations suggest that our universe underwent a period of accelerated expansion in its early stages. On the other hand the precise underlying physics of inflation and in particular its embedding within a fundamental theory are still a mystery. In many models inflation is in fact eternal. This would lead to the formation of "pocket universes" that would rise to universes like ours. This view of the universe give some interesting predictions for cosmological observables that allow us to distinguish this scenario from other ones. We are currently following several lines of research to further investigate these issues.

- **String Theory Cosmology.**
  String Theory is today one of the leading candidates for a fundamental theory. It is therefore natural to look for ways to link String Theory and Cosmology. Recent avances on String Theory compactification have allowed us to find some of the most detailed descriptions of Inflation in String Theory. Our group is mainly interested in extracting the observational consequences of the novel ways inflation can occur in String Theory.

- **The Landscape of String Theory.**
  String Theory suggests that there is a large number of ways that one can compactify the original 10d spacetime down to four dimensions. This compactification process gives rise to a complicated multidimensional potential that fixes all the possible degrees of freedom that specify, for example, the geometry of the internal space. Some of the minima of this potential would have a positive value of the cosmological constant and therefore one would expect to have patches of an eternally inflating spacetime. This is an interesting new take on the idea of cosmology within string theory and it is paramount to extract the observational consequences of a multiverse of this kind.
  Our group is currently working on several avenues to explore the consequences of this radical new picture of the spacetime suggested by the existence of a String Theory Landscape.

COSMIC SUPERSTRINGS

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ikerbasque

Cosmic Super-Strings are line-like structures that may have been produced in the early universe when the average energy density in the universe was very high. They are formed at phase transitions as topological defects that trapped this high energy density in their cores.

They can also be produced in cosmological models of the Early Universe that rely on String Theory. In this cases these cosmic strings are nothing more that blown up versions of the fundamental strings of String Theory, hence the name of Cosmic SuperStrings.

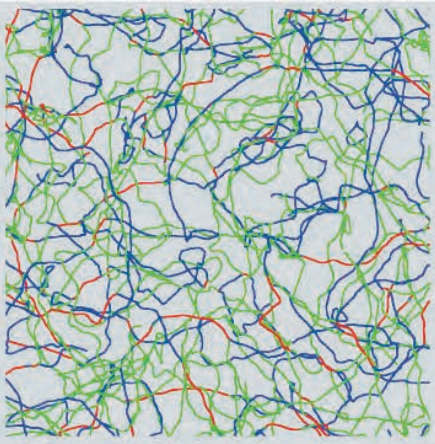
Their discovery would open up a new window on the high energy frontier in Cosmology and Particle Physics

Lattice Field Theory Simulations

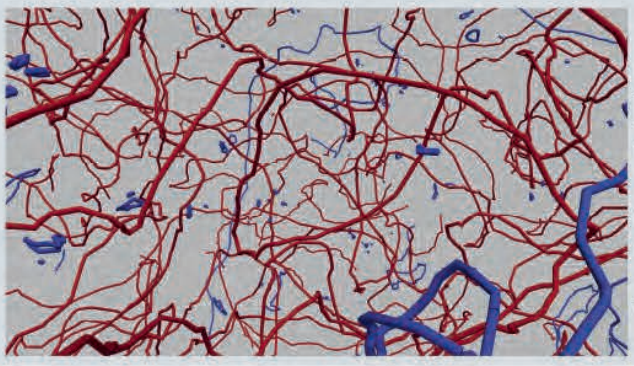
Cosmic Strings can appear as solitonic solutions of high energy field theory models that could control the evolution of the primordial universe. One can therefore study their dynamics in classical lattice field theory simulations.

In these simulations one can understand the microphysical processes that are relevant for the evolution of the string networks. Using high performance supercomputers one can simulate the evolution of these networks of strings in an expanding universe. The network of strings reaches a scaling solution that allows us to use the information from the simulation and extrapolate to cosmological sizes.

We show, on the figure on the right, a snapshot of a simulation of pq-strings a field theory model that mimics the properties of superstrings networks in the early universe.



Nambu-Goto Simulations



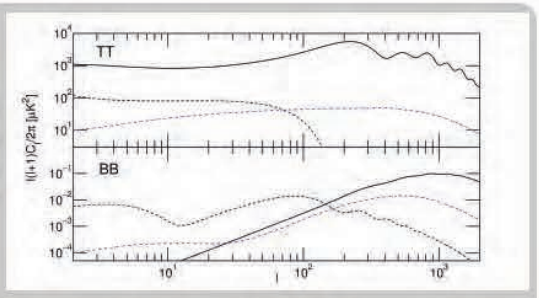
Cosmic Strings can also be simulated using the relativistic string equations of motion; the Nambu-Goto action. This approximation disregards all the effects at the scale of the string thickness. One can therefore simulate networks with a much larger dynamic range than in the field theory case. In this type of simulations the only interactions of the strings occur at intersections where loops of strings can be produced.

Using these simulations we have been able to show that there is a scaling population of non-self intersecting loops. Due to the string tension once formed these loops oscillate emitting gravity waves (GW).

We show, on the figure on the left, a snapshot of one of these Nambu-Goto simulations where we show in blue the loops and the long strings in red.

Imprint on the Cosmic Microwave Background:

The high energy scale of the tension of the cosmic strings gives rise to a distortion of the Cosmic Microwave Background (CMB). These distortions could have an observable effect on the Temperature (and Polarization) Power Spectrum of the CMB. We show, on the left, the best fit model for the Temperature and Polarization Power Spectrum with the contributions from strings in blue. Using this type of measurement one can impose an upper limit on the tension of the strings that is allowed by the CMB data observed by the Planck satellite.

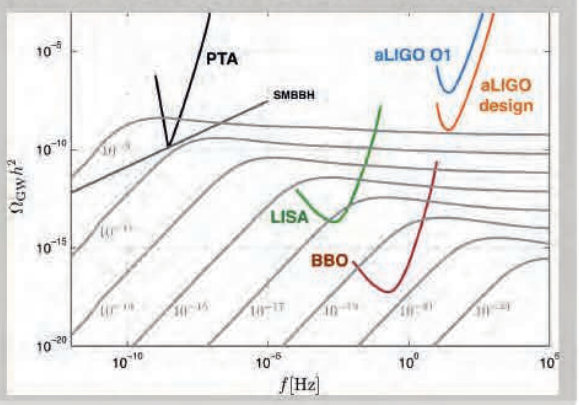


Stochastic Gravitational Wave Background:

A network of cosmic strings continuosly generates loops. Some of these loops will end up in non-selfintersecting trajectories that survive for a long time oscillating due to their tension. During all this time the loops emit a spectrum of gravitational waves that depends on the shape of the string. The contribution from all these loops over the cosmological history leads to a stochastic background of gravitational waves that could be detected by current and future GW obsevatories such as PTA, LIGO, LISA, etc...

We have used the numerical simulations described above to compute the density of loops at all times as well as their typical shape. This has allowed us to compute the average spectrum of gravitational waves produced by these loops.

Using this information we can estimate the spectrum of gravitational waves from string networks of different tensions and identify their potential observability by all the current gravitational wave observatories. (See the Figure on the right).



MATEMATIKA

MATEMÁTICAS

Klima-aldaketa
Cambio Climático

Mathematical techniques and operations research tools to improve industrial processes

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KEY WORDS: Optimization. Linear programming. Industrial Mathematics. Call center. Job shop problem. Inventory replenishment.

A wide variety of mathematical techniques has been used for finding coherent solutions in many different scientific fields. Here we will give a brief description of four optimization models developed in different backgrounds and carried out in collaboration with institutions and enterprises.

SUBTITLE

Here we will briefly describe four optimization models, each one developed in collaboration with different institutions or enterprises. The models have been designed for solving practical problems in real scenarios. The operating profits in all cases has been significative.

The first model concerns the call center service that manages the internal incidences of a big distribution company like Eroski S. Coop. The service is made up of three levels. The first two levels are managed by own agents and the third one by subcontracted people. The first level agents are dedicated to manage incoming calls, which arrive randomly to a general server. The time between two arrivals follows approximately an exponential distribution. A classical escheme in queuing theory is the Erlang-C model. It matches properly the dynamic of the first stage. Otherwise, when the conditions are far from the ideal ones, then, few theoretical results can be used in order to build an analytical model. This is the case at the second level, where the arrivals are cathegorized and distributed in several queues. In this scenario the incorporation of multi-skill agents and the use of routing algorithms emerge as essential for improving the management of the service.

The second model concerns the optimal management of the stock of certain components of the blood produced for medical uses in order to reduce outdated units of products. The project has been developed in collaboration with the Basque Centre for Transfusion and Human Tissues and the Blood and Tissues Bank of Aragón. Specifically, the blood platelet is a very sensible product due to the short expiry date, 5-7 days from donation to transfusion. However, these components are mostly used in programmed treatments and statistical predictive models are useful for accurately forecasting demand. Consequently, avery day a calculus of a safety stock can be made guaranteeing the supply and minimizing the loss by outdating.

The target of the third project is to design an efficiently scheduling of the rubber components manufacturing of a tire production plant. A mathematical formulation followed by a computational code have to be found in order to optimize the assignment of the tasks to the machines. The complexity of the problem lies in the large number of different components to be considered together with the limitations in the compatibility between some machines and components. In addition, the production flow depends on several sequentially ordered sets of products that comprise from grinding the raw material until manufacturing the final product ready to be assembled. Occasionally, urgent incoming demand of products can cause a sudden change in the factory environment that needs a fast answer. In this scenario, operations research tools and optimization models become crucial for calculating at any given moment a feasible solution that reaches the new constraints.

In the fourth project, we analyze mathematically the optimal scheduling of promissory notes issued. This type of financial product is a very effective mechanism for guaranteeing the flow of cash as well as the reserves of big companies. The issuances have to reach certain conditions regarding the lead time and the amount limits. These restrictions are imposed by the market regulator and the operational reality of the company. An optimum scheduling of the promissory notes issuance can be found by integer linear programing methods.

Optimización de procesos industriales mediante tecnología matemática e investigación operativa.

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Optimización de un call-center multicola

Este proyecto se esta realizando en colaboración con la compañía Eroski S. Coop.

Los call center están compuestos por un equipo de k agentes que atienden incidencias con una tasa de llegada λ y procuran resolverlas o canalizarlas a un especialista con una tasa de salida $k\mu$. La densidad de la cola $\rho = \lambda/k\mu$ debe ser < 1 para evitar el colapso. Con una única cola y respuesta idéntica de todos los agentes, se formula el clásico modelo de flujo Erlang-C de *teoría de colas*. Ahí se considera que el tiempo de separación entre dos llegadas y el de resolución de la incidencia siguen distribuciones exponenciales aleatorias con función de densidad $f(t) = \lambda e^{-\lambda t}$, $t \geq 0$ y $g(t) = \lambda e^{-k\mu t}$ respectivamente.

Dados W (variable aleatoria correspondiente al tiempo de espera en cola) y AWT (tiempo máximo aceptable de espera), la calidad del servicio está determinada por los siguientes indicadores:

- Service Level: $SL = P(W < AWT)$,
- Average Speed of Answer: $E(W)$,
- Ocupación del servicio: $\sum_{i=1}^{Agentes} \frac{\text{Tiempo agente } i \text{ realizando servicios}}{\text{Tiempo agente } i \text{ en el call center}}$.

Los modelos se complican cuando las entradas y salidas se distribuyen irregularmente, hay diversas colas y perfiles de agentes o cuando se consideran abandonos y bloqueos. Entonces es necesario recurrir a la simulación numérica dada la dificultad para proponer modelos analíticos.
En este proyecto se ha diseñado un algoritmo de asignación de llamadas a los agentes del segundo nivel, distribuidos en 4 colas según categorías. La solución a este problema requiere de un algoritmo de ruteo eficiente que elija una optima asignación agente-incidencia en el momento que el sistema registre un evento: (1) *llamada entrante con agentes libres* o (2) *agente que se desocupa con llamadas en cola*. El algoritmo gestiona el flujo de llamadas optimizando el rendimiento según una ponderación entre la urgencia de la llamada para cumplir el AWT y las entradas de una matriz numérica de idoneidades entre agentes y categorías de llamadas. El algoritmo y la incorporación de agentes con habilidades multiples incrementan sustancialmente los indicadores de calidad.

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Gestión de la financiación mediante pagarés

Este proyecto se esta realizando en colaboración con la compañía Attest

Las grandes empresas planifican su flujo de financiación con un horizonte anual. Dependiendo de las necesidades económicas y previsión de ingresos, cada semana se realizan operaciones. El producto más flexible y barato para garantizar la financiación es la emisión de pagarés con vencimiento a futuro. Cada semana las compañía emiten ciertos pagarés con un límite de capital, mientras s devuelve a los inversores prestatarios el depósito correspondiente al pagaré vencido. El objetivo de este flujo de capitales es que la liquidez se mantenga en los límites previstos.
La emisión de pagarés son gestionados por un empresa financiera que diseña un calendario anual de emisiones optimizando la rentabilidad y teniendo en cuenta circunstancias legales o comerciales que se traducen en restricciones. La solución óptima en términos de incentivar las emisiones con un corto plazo de vencimiento se puede modelizar mediante programación lineal entera donde $P_{i,j}$ son las variables enteras que simbolizan el capital acumulado en la semana j en el pagaré que vence en la semana i y $E_{i,j}$ son las variables binarias que indican si en la semana j se emite el pagaré i.
Algunas de las restricciones del modelo son las siguientes:

- No se puede emitir un pagaré que venza antes de 4 semanas: $P_{i,j} - P_{i,j-1} = 0,\ \forall j \leq i-3$,
- Cotas emisión y capital acumulado: $UE_i \leq P_{i,j} - P_{i,j-1} \leq LE_i,\ U_i \leq P_{i,i-1} \leq L_i,\ \forall i, j$,
- Emisión $\Leftrightarrow$ aumento de capital: $P_{i,j} - P_{i,j-1} \geq E_i,\ 1000E_i \geq P_{i,j} - P_{i,j-1},\ \forall i, j$,

Por otra parte, por cuestiones comerciales, la función objetivo de la optimización penaliza la emisión de pagarés con vencimientos a largo plazo, así como la acumulación de emisiones similares en vencimiento.

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Optimización del flujo en la producción

Este proyecto se esta realizando en colaboración con la compañía Bridgeston Hispania

Un neumático se elabora ensamblando diferentes capas de compuestos que le dotan de firmeza, flexibilidad y resistencia. Posteriormente se procede al vulcanizado. Dichos compuestos previamente son procesados en secuencias ordenadas de entre 3 y 6 componentes, desde uno de fase inicial hasta llegar a los de fase final. Estos últimos son los que se ensamblan. La producción de compuestos se realiza en una planta con varias máquinas, cada una de ellas habilitada para fabricar sólo algunos compuestos. Las capacidades de cada máquina junto con las cantidades de compuesto fabricado en cada sesión y la duración del proceso está registrado en un catálogo o base de datos. Esta información sirve para el diseño de un diagrama de flujo o grafo que comunica los nodos (compuestos) mediante arcos (máquinas).

El objetivo es programar una asignación optima de los compuestos a las máquina activas, garantizando el suministro de compuestos final demandados. Para ello se plantea un modelo de optimización de flujo en redes con restricciones, expresado en términos de programación lineal entera-binaria, donde el tiempo es fraccionado en intervalos. Las variables de decisión son

$$M_{ijk} = \begin{cases} 1 & \text{si en el instante } k \text{ la máquina } i \text{ comienza a procesar el compuesto } j \\ 0 & \text{si en el instante } k \text{ la máquina } i \text{ NO comienza a procesar el compuesto } j \end{cases}$$

Algunas de las restricciones del modelo son las siguientes:

- una máquina no puede comenzar más de un trabajo al mismo tiempo: $\sum_j M_{ijk} \leq 1,\ \forall i, k$,
- se garantiza el flujo de producción, es decir, un compuesto se fabrica si hay materia prima,
- se debe garantizar la producción de compuestos finales demandadados cada día.

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Gestión del stock de componentes sanguíneos

Este proyecto se esta realizando en colaboración con el Banco de Sangre y Tejidos de Aragón

Algunos tratamientos en centros hospitalarios requieren de transfusiones de componentes sanguíneos. Los concentrados de plaquetas son los más delicados debido a su corta caducidad, entre 5 y 7 días. Los centros de transfusiones procesan y almacenan la sangre de los donantes. Se debe de garantizar el abastecimiento y por cuestiones éticas y económicas, hacer una buena gestión del inventario.

Para una correcta gestión del stock se estima la demanda de cada día de la semana, que en este caso se ajusta a una distribución normal y se incorpora al modelo los detalles de la operatividad del centro, como por ejemplo que los domingos no se producen unidades o que en Semana Santa, Navidad, etc, la demanda y la producción son irregulares.
Se considera una política de distribución FIFO (first in first out). Una estrategia práctica que ahorra un porcentaje importante de unidades procesadas innecesariamente, es la de reponer el inventario según el consumo estimado, el margen de seguridad, las unidades caducadas estimadas y el stock actual. Como intervalo temporal se toma el tiempo transcurrido desde la toma de decisiones de producción hasta el siguiente instante de reposición que, por ejemplo, en el caso de un jueves, puede ser hasta el domingo.
La producción de un jueves sería $p_4 = \mu_{4567} + 3\sigma_{4567} + k_4 - s_4 + w_6$ donde μ es la media de demanda de jueves a domingo, σ es la desviación típica, k_4 es una cantidad fija, s es el stock existente y $\int_{-\infty}^{s_{4,3}} (s_{4,3} - x_{456}) f_{456}(x_{456}) \mathrm{d}x_{456}$ es la caducidad que se produciría el sábado.

Bibliografía

[1] MA Pérez Vaquero, C Gorria, M Lezaun, FJ López, J Monge, C Eguizabal and MA Vesga, Optimization of the management of platelet concentrate stocks in the Basque Country, *Vox Sanguinis (2016)*.

[2] C Gorria, G Labata, M Lezaun, FJ López, AI Pérez Aliaga and MA Pérez Vaquero, Impact of implementing pathogen reduction technologies for platelets on reducing outdates, *Vox Sanguinis (2019)*.

Proyectos

Consolidated Research Group Grant IT649-13; MTM2016-76329-R (AEI/FEDER, EU); H2020 RISE (MATHROCKS); KK-2019/00085 Elkartek 2019. Investigador Principal: David Pardo.

Stochastic network optimization for intelligent transport and logistics

Unai Aldasoro[3], Larraitz Aranburu[1], Isabel Eguía[3], Laureano F. Escudero[4], M. Araceli Garín[2], I. Gago[6], Gorka Kobega[6], María Merino[1], Gloria Pérez[1,6], Celeste Pizarro[5] and Aitziber Unzueta[3]
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[2]Department of Applied Economics III (Econometrics and Statistics), UPV/EHU;
[3]Department of Applied Mathematics, UPV/EHU;
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[5]Applied Mathematics, Materials Science and Engineering and Electronic Technology, URJC;
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KEY WORDS: stochastic optimization, network applications, risk management.

There is no doubt that quantitative methods, such as modeling techniques, massive data processing and mathematical optimization, they are a powerful tool that helps to expand knowledge in many fields. In particular, the Group of Stochastic Optimization (GOE) is centered nowadays in the Transport and Logistics sector, in which these methods can provide results that significantly promote intelligent and sustainable decision-making.

As stated in the National Plan for Scientific and Technical Research and Innovation 2017-2020, its fourth challenge is focused on sustainable, intelligent, connected and integrated transport. The main objective of this research group is the use of modeling, data management and optimization to solve intelligent transport and logistics challenges. That is, to enable making optimal decisions in terms of sustainability (resource optimization), security (risk management), connection and integration (integral network models).

The specific objectives are:

1. The study of stochastic network applications: problems of transport routing, energy, facility location and logistics distribution;
2. Risk management: control of the worst scenarios, such as situations of call collapse in the healthcare system or situations of natural disasters, through risk measures like stochastic dominance; and
3. The development of methodologies: exact, heuristic and hybrid algorithms that obtain quality solutions in competitive times, such as decomposition methods adapted to the new challenges.

The group is working currently in four case studies:

A. Routing optimization for intelligent transport;
B. Topology determination of an integrated electricity network;
C. Analysis and design of a connected emergency healthcare system and
D. Optimization of humanitarian logistics for sustainable disaster relief.

These four cases are linked to the 2030 Agenda and the Sustainable Development Goals 3 of health and well-being, 7 of affordable and non-polluting energy, 11 about sustainable cities and communities and 13 of climate action (climate change).

The applications are part of a close collaboration with:

- Basque Center for Applied Mathematics (BCAM);
- ZIV Aplicaciones y Tecnología S.L., a leading company in intelligent systems for low, medium and high voltage power network;
- Basque Public Health Service-Osakidetza (Emergencies);
- Intelligent System Group (ISG) of the UPV/EHU;
- Energy Research in Building (ENEDI) group of the Bilbao School of Engineering (UPV/EHU);
- Statistics and Optimization group (IT1252-19) recognized by the Basque Government;
- Decision Aid Models for Logistics and Disaster Management (Humanitarian Logistics) group of the University Complutense of Madrid.

STOCHASTIC NETWORK OPTIMIZATION FOR INTELLIGENT TRANSPORT AND LOGISTICS

UPV EHU

bcam basque center for applied mathematics

GOE
www.ehu.es/es/web/goe

EWGSO

STOCHASTIC OPTIMIZATION

Stochastic Optimization (SO) is a field of Operations Research (OR) that appeared as a response to the need to incorporate uncertainty into mathematical optimization models and it is broadly employed in real-world applications.

APPLICATIONS TREE

STOCHASTIC NETWORK OPTIMIZATION

- INTELLIGENT TRANSPORT
  - **ROUTING**
    The development of exact and hybrid methodologies for solving routing problems in order to guarantee connected and sustainable transport.
  - **ENERGY**
    •Determination of the topology of integrated electricity network.
    •Energy supply systems of buildings.
- INTELLIGENT LOGISTICS
  - **LOCATION**
    Connected Network for Emergency Healthcare System. Ambulance location, resource optimization and guaranteeing the highest risk demands.
  - **DISTRIBUTION**
    Sustainable Logistics for the Humanitarian Emergencies. Humanitarian logistics for disaster relief in catastrophic events, facility location, distribution and transport of basic products.

SPS · EURO · SEIO · Mathematical Optimization Society

NTNU

ALGORITHM

Risk averse?

- Optimal ?
  - **MATHEURISTICS**
    ALGORITHMS:
    CLD-MS
    FRC
    HBFC
    EA4OP
  - **EXACTS**
    ALGORITHMS:
    CBD
    BFC-MS
    BC4OP
- Time consistent?
  - **TIME STOCHASTIC DOMINANCE**
    ALGORITHMS:
    FRC-TSD
    CLD-TSD
    BFC-TSD
  - **EXPECTED CONDITIONAL STOCHASTIC DOMINANCE**
    ALGORITHMS:
    FRC-ESD
    BFC-ESD
    RCPA-ESD
    RCSD-ESD

High Performance Computing (HPC)

- ARINA cluster by IZO-SGI, SGIker of UPV/EHU & European funding (3728 cores, 16-512Gb RAM)
- HIPATIA cluster provided by BCAM (624 cores, 4TB RAM)
- LEC Laboratory of Quantitative Economics from UPV/EHU directed by fernando.tusell@ehu.es
- Workstations Dell Precision T7500 u. windows 7 and Linux (8 cores, 12Gb RAM)

PUBLICATIONS:

Matrix analysis and applications group

Agurtzane Amparan[1], Gorka Armentia[1], Itziar Baragaña[2], María Asunción Beitia[3], Juan Miguel Gracia[1], Inmaculada de Hoyos[1], Silvia Marcaida[1], Alicia Roca[4], Francisco Enrique Velasco[1] and Ion Zaballa[1]
[1]Departamento de Matemática Aplicada y Estadística e Investigación Operativa (UPV/EHU); [2]Departamento de Ciencia de la Computación e Inteligencia Artificial (UPV/EHU); [3]Departamento de Didáctica de la Matemática y de las Ciencias Experimentales (UPV/EHU); [4]Departamento de Matemática Aplicada (Universidad Politécnica de Valencia).

KEY WORDS: matrix analysis, control theory, linear systems, structure invariants, perturbation, numerical linear algebra, inverse problems, canonical forms, eigenvalues, singular values.

The Group of Matrix Analysis and Applications (GAMA) of the University of the Basque Country UPV/EHU is the result of the evolution of a team that has been working uninterruptedly in research since 1981. The main research areas of this group are:

- Theory of matrices.
- Mathematical control theory.
- Perturbation theory.
- Numerical linear algebra.

The aim of our research is to gain insight into the structure of the linear control systems and matrices and to develop mathematical techniques in order to solve problems in these areas. The following research lines have been designed:

- Study of the structure of control systems and matrices.
- Spectral perturbation of matrices and linear systems.

These research lines are closely related. Nevertheless, in order to clarify the problems that we are interested in, we will state, in a general manner, some of them:

1. Construct spectral filters for matrix polynomials having the same finite and infinite elementary divisors.
2. Parametrize the spectral filters of general quadratic systems, characterize the eigenvectors of classically damping systems and generalize the phase synchronization method.
3. Design a procedure to effectively construct vibrating and gyroscopic systems with prescribed dynamic behaviour.
4. Construct new classes of structure preserving strong linearizations for rational matrices, find a procedure to recover the minimal bases of rational matrices out of their strong linearizations and make a backward error analysis of algorithms based on linearizations for rational eigenvalue problems.
5. Progress on the characterization of the assignment of invariants under state feedback and output injection, for linear control singular systems.
6. Complete the study of the hyperinvariant and characteristic subspace lattices.
7. Generalize Berlekamp-Massey algorithm to obtain matrix generators of minimal length for a given sequence of matrices.
8. Study the regularity of the stratified manifold of controllable and observable linear systems with fixed controllability and observability indices.
9. Obtain a general characterization of the stable (A,B)-invariant subspaces.
10. Analyse the geometry of the connected components of the pseudospectra and compute their derivatives in the sense of the Hausdorff metric.
11. Provide conditions for the reduction of a non-analytic matrix function of real variable to its Jordan form under global similarity.

The methods and techniques to be used run over almost all fields of mathematics: from Linear Algebra and Matrix Analysis or Combinatorics to Differential Geometry or Commutative Algebra.

Weekly seminars are kept where the progression of the subgroups' work is shown, the difficulties are discussed and other researchers' work related to our problems is explained. This and the individual study of papers are the main methodological tools. The results are published in the most important specialised journals: Linear Algebra and its Applications, SIAM Journal of Control and Optimization, SIAM Journal on Matrix Analysis and Applications, International Journal of Control, Linear and Multilinear Algebra, Electronic Journal of Linear Algebra, etc.

More information in: http://www.ehu.eus/gama

GRUPO DE ANÁLISIS MATRICIAL Y APLICACIONES

http://www.ehu.eus/gama

EQUIPO

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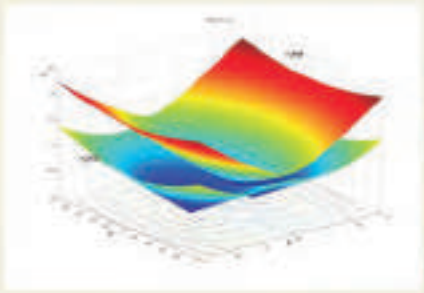
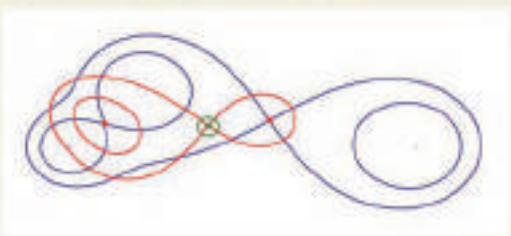


LÍNEAS DE INVESTIGACIÓN

- Estudio de la estructura de sistemas de control y matrices
- Perturbación espectral de matrices y sistemas lineales

OBJETIVOS

- Investigar las propiedades algebraicas de sistemas lineales y cuadráticos, en particular, de modelos polinomiales y racionales
- Innovar en técnicas para la resolución numérica de problemas no lineales de valores propios
- Estudiar el comportamiento de invariantes estructurales frente a pequeñas perturbaciones en una matriz
- Obtener soluciones que sean susceptibles de implementarse prácticamente
- Aplicar la teoría de sistemas lineales de control a problemas de Criptografía y Codificación
- Contribuir a la formación de estudiantes



ACTIVIDADES

- Proyectos de investigación
- Seminarios semanales
- Revistas en las que publicamos:
  - ✓ Linear Algebra and its Applications
  - ✓ SIAM Journal on Matrix Analysis and Applications
  - ✓ SIAM Journal on Control and Optimization
  - ✓ Linear and Multilinear Algebra
  - ✓ Automatica
  - ✓ International Journal of Control
  - ✓ Systems and Control Letters
  - ✓ Mathematics of Control, Systems and Signals
- Congresos en los que participamos:
  - ✓ ILAS Conferences
  - ✓ IFAC Conferences on System Structure and Control
  - ✓ MTNS (Mathematical Theory for Networks and Systems)
  - ✓ SIAM (Society for Industrial and Applied Mathematics)
  - ✓ CEDYA+CMA (Congreso de Ecuaciones Diferenciales y Aplicaciones + Congreso de Matemática Aplicada)
  - ✓ ALAMA Encuentro de Álgebra Lineal, Análisis Matricial y Aplicaciones
- Congresos organizados:
  - ✓ Encuentro Internacional de Álgebra Lineal y Aplicaciones, 1983
  - ✓ Encuentro de Análisis Matricial y Aplicaciones, EAMA, 1994
  - ✓ XXV Aniversario del Grupo de Álgebra Lineal de la UPV/EHU, 2006
  - ✓ Encuentro ALAMA, 2008
- Dirección de tesis doctorales
- Profesores invitados
- "Referee" para revistas del área
- Estancias en otras Universidades
- Becas de colaboración

COLABORACIONES

- Proyectos coordinados con grupos de la Universidad Politécnica de Cataluña, Universidad Carlos III y Universidad de Barcelona
- Integrado en la Red Temática ALAMA (Álgebra Lineal, Análisis Matricial y Aplicaciones), reconocida como Red de Excelencia

Mathematical analysis and applications

N. Accomazzo[1], J. Apraiz[1], N. Arrizabalaga[1], B. Badreddine[1], J.B. Bru[1], J. Canto[3], J. Cayama[1], C. Cuesta[1], X. Diez[1], F. de la Hoz[2], J. Duoandikoetxea[1], D. Eceizabarrena[3], L. Escauriaza[1], M. Escobedo[1,3], A. Fernández[1], S. Kumar[3], J. Martínez-Perales[1], M. Mourgloglou[1,4], O. Oruetxebarria[1], I. Parissis[1,4], C. Pérez[1,3,4], J. Rivas[1], L. Roncal[3,4], F. Vadillo[2], L. Vega[1,3], A. Zacharopoulos[1].

[1]Depto. De Matemáticas-UPV/EHU;
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[4]IKERBASQUE, Basque Foundation for Science.

KEY WORDS: PDEs, Dynamics, Harmonic Analysis, Quantum Mechanics, Numerical Analysis.

Our group focuses on several branches of Mathematical Analysis and Mathematical Physics. Some of the topics in which our group works are the study of: uncertainty principles and their applications; different properties of a variety of equations (Dirac Equation, Schrödinger Equation and the Vortex Filament Equation, among others) and related problems, in connection with some physical phenomena; unique continuation and Control Theory; properties of maximal operators in different situations; free boundary regularity of harmonic measure; operators which arise from Fourier theory and the study of solutions of elliptical equations such as singular integral operators and their weighted versions, in a quantitative way; the extension problem for the sublaplacian in the Heisenberg group; the analysis on the infinite dimensional torus; discrete harmonic analysis; generalized spherical means acting on radial functions and their relation to the solution of Euler-Poisson–Darboux equations; fractional and classical Poincaré-Sobolev type inequalities in relation with elliptic partial differential equations, and the study of fractional differential equations, in both the mathematical and the numerical settings.

Our main projects are the ones listed below:

- ***"Mathematical and Numerical Analysis of some Partial Differential Equations and their Applications"*** *(PGC2018-094522-B-I00; PI: Carlota Cuesta and Luis Vega).*
- **"Analisis Armónico, Mecánica Cuántica y Aplicaciones a las EDP"** *(MTM2017-82160-C2; Coordinator: Carlos Pérez Moreno; Coordinated Project with two subprojects with PIs: Carlos Pérez Moreno and Luz Roncal, and Mihalis Mourgoglou).*

- **"Control y Estabilidad de Redes Eléctricas Híbridas AC/DC: Ecuaciones Diferenciales y Ecuaciones en Derivadas Parciales para el Análisis de Estabilidad en Redes"** *(MTM2017-82996-C2-1-R, PIs: Miguel Escobedo and Enrique Zuazua).*

- **"Fourier Analysis and Partial Differential Equations"** *(IT1247-19, PI: Carlos Pérez Moreno).*

- **"Harmonic Analysis and Differential Equations: New Challenges"** *(ERC Advanced grant 2014 669689HADE, PI: Luis Vega).*

- **"Interplays between Harmonic Analysis and Inverse Problems"** *(PGC2018-094528-B-I00, PIs: Pedro Caro and Ioannis Parissis).*

Mathematical Analysis and Applications

N. Accomazzo[1], J. Apraiz[1], N. Arrizabalaga[1], B. Baddredine[1], M. Bravin[3], J.B. Bru[1,3,4], J. Canto[3], J. Cayama[1,3], C.M. Cuesta[1], F. de la Hoz[2], X. Diez[1], J. Duoandikoetxea[1], D. Eceizabarrena[3], L. Escauriaza[1], M. Escobedo[1], A. Fernández[1], S. Iakunin[3], S. Kumar[3], R. Lucà[3], J. Martínez-Perales[3], M. Mourgoglou[1,4], O. Oruetxebarria[1], I. Parissis[1,4], C. Pérez[1,3,4], C.V. Pohjola[3], E.F. Ponce[3], J. Rivas[1], L. Roncal[3,4], F. Vadillo[2], L. Vega[1,3], A. Zacharopoulos[1], A. Zarnescu[3], C. Zillinger[3].

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Universidad del País Vasco — Euskal Herriko Unibertsitatea

Extension of John–Nirenberg inequality

Javier Canto and Carlos Pérez

Functions of Bounded Mean Oscillation (BMO) are functions satisfying

$$\|f\|_{BMO} := \sup_{B \text{ ball}} \frac{1}{|B|} \int_B |f - f_B| < \infty,$$

where $f_B = \frac{1}{|B|}\int_B f$ denotes the average of f in the ball B.
John–Nirenberg inequality bounds the size of level sets of such functions, more precisely, there exists $c > 0$ such that for any $f \in \text{BMO}$,

$$|\{x \in B : |f(x) - f_B| > \lambda\}| \leq c e^{-\frac{c}{\lambda \|f\|_{\text{BMO}}}} |B|, \quad \lambda > 0.$$

Define the Hardy–Littlewood maximal operator M as

$$Mf(x) = \sup_{\substack{B \text{ ball} \\ x \in B}} \frac{1}{|B|} \int_B |f(y)| dy$$

and the Fefferman–Stein sharp maximal operator $M^\sharp$ as

$$M^\sharp f(x) = \sup_{\substack{B \text{ ball} \\ x \in B}} \frac{1}{|B|} \int_B |f(y) - f_B| dy.$$

The following is an extension of the classical John–Nirenberg inequality.

Theorem (C., P., 2019). *For any function $f \in L^1_{loc}(\mathbb{R}^n)$, the following holds:*

$$\left| \left\{ x \in B : \frac{M(f - f_B)(x)}{M^\sharp f(x)} > \lambda \right\} \right| \leq 4^n e^{\frac{-1}{4\lambda}} |B|.$$

Generalized Poincaré inequalities

Javier C. Martínez-Perales

The classical Poincaré inequality states, for some $q > p \geq 1$, the existence of a constant $c > 0$ s.t. for good enough functions f,

$$\left(\frac{1}{|B|} \int_B |f(x) - f_B|^q \, dx \right)^{1/q} \leq c\, r(B) \left(\frac{1}{|B|} \int_B |\nabla f(x)|^p \, dx \right)^{1/p},$$

where B is any ball of radius $r(B)$ in the Euclidean space.

Generalized Poincaré inequalities are inequalities in which uniform local bounds for the oscillations of a function under certain norm are given. This includes the above classical Poincaré inequalities, fractional Poincaré inequalities, the inequalities defining functions of BMO and also their weighted counterparts.

In general, we can write, for a weight function $w \in L^1_{\text{loc}}(\mathbb{R}^n)$, a positive exponent $q > 0$ and a function $f \in L^1_{\text{loc}}(\mathbb{R}^n)$, the generalized Poincaré inequality

$$\left(\frac{1}{w_r(B)} \int_B |f(x) - f_B|^q \, w(x) dx \right)^{1/q} \leq c\, a(f, B), \tag{1}$$

for every ball B, where $w_r(B) = |B| \left(\frac{1}{|B|} \int_B w(x)^r \, dx \right)^{1/r}$, $r > 1$, and $a(f, \cdot)$ is some positive functional which depends on f and is defined for every all ball in the space.

Theorem (M. 2019). *Let v be a weight and $f \in L^1_{\text{loc}}(\mathbb{R}^n)$. Let $p > 0$, $s > 1$. If the functional $a(f, \cdot)$ satisfies certain mild geometric condition w.r.t. p, s and v, then one can obtain an improvement from inequality* (1) *with $w, q, r, c = 1$ to the same inequality with $w = v$, $q = p$ and $r = s$, and $c > 1$ a constant which can be quantitatively controlled.*

This improves a recent very general theorem by C. Pérez and E. Rela which relies in the well known A_∞ condition. Our variant allows to get classical and fractional weighted improved Poincaré inequalities without the A_∞ condition on the weight.

Some members of our group

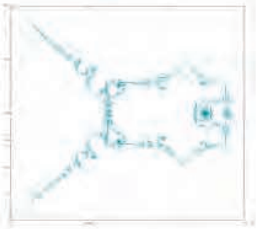
Riemann's non-differentiable function

Daniel Eceizabarrena

The image in the complex plane of the following physical variant of Riemann's non-differentiable function

$$\phi(x) = \sum_{k \in \mathbb{Z}} \frac{e^{-4\pi^2 i k^2 x} - 1}{-4\pi^2 k^2},$$

which appears as a temporal trajectory in an experiment of vortex filaments evolving according to the Binormal Flow equation, looks as follows:

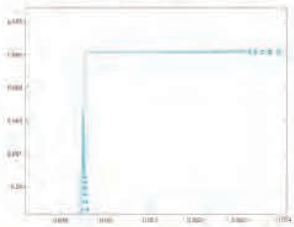


Theorem (E. 2019). *The following geometric results for ϕ hold.*

- *We have the bounds for the Hausdorff dimension:*

$$1 \leq \dim_{\mathcal{H}} \phi(\mathbb{R}) \leq \tfrac{4}{3}.$$

- *ϕ does not have a tangent at any point. More precisely,*
  - *$\phi(\mathbb{R})$ has two perpendicular side-tangents at points $\phi(p/q)$ when $q \equiv 0, 1, 3 (mod 4)$, see below left.*
  - *$\phi(\mathbb{R})$ spirals around $\phi(p/q)$ when $q \equiv 2 (mod 4)$, see below right.*
  - *If ρ is irrational, there is an open set of directions from which $\phi(\mathbb{R})$ approaches $\phi(\rho)$.*



Research Projects

PGC2018-094522-B-I00; PIs: Carlota Cuesta and Luis Vega. **MTM2017-82160-C2**; Coordinator: Carlos Pérez. Two subproyects; PIs: Carlos Pérez and Luz Roncal, and Mihalis Mourgoglou. **MTM2017-82996-C2-1-R**; PIs: Miguel Escobedo and Enrique Zuazua. **IT1247-19**; PI: Carlos Pérez Moreno. **ERC Advanced grant 2014 669689HADE**; PI: Luis Vega. **PGC2018-094528-B-I00**; PIs: Pedro Caro and Ioannis Parissis.

GEOLOGIA

GEOLOGÍA

Klima-aldaketa
Cambio Climático

Late Quaternary Record of Climate Change in the Basque Basin (S Bay of Biscay)

Alejandro Cearreta, Julio Rodríguez Lázaro, Ana Pascual, María Jesús Irabien, Ane García-Artola, Humberto Serrano, Zeltia Varela, Blanca Martínez-García, Aitor Fernández-Martín Consuegra
Geología UPV/EHU

KEY WORDS: environmental transformation, natural processes, anthropogenic impact.

The Harea-Coastal Geology research group (www.ehu.eus/harea-geologialitoral) develops a multidisciplinary approach (sedimentology, geochemistry, micropalaeontology, topography, radiometric chronology) to characterize natural and anthropogenic processes responsible for the environmental transformation of the coastal zone during the last climate cycle (Pleistocene, Holocene and Anthropocene). Its activities can be summarized into the following research lines and recent publications:

1. **Environmental transformation of polluted and regenerated ecosystems.** The coastal area has experienced an intense human pressure that provoked its physical destruction and a significant chemical and biological transformation. The development of environmental conservation and regeneration schemes makes necessary to carry out geological studies to evaluate their modern characteristics, historical alteration processes and the feasibility of improvement proposals (Irabien, M.J.; Cearreta, A.; Gómez-Arozamena, J.; Serrano, H.; Sánchez-Cabeza, J.A. and Ruiz-Fernández, A.C. 2019. Geological record of extreme floods and anthropogenic impacts on an industrialised bay: the inner Abra of Bilbao (northern Spain). *Science of the Total Environment* 696: 1-10).
2. **Holocene relative sea-level (RSL) variations.** An increase in sea-level rise rate is potentially one of the most devastating impacts of the future climate change on coastal areas. Climate change influences the coastline at decadal and centennial scales, and these variations of the RSL are registered in the coastal sedimentary sequences. The reconstruction of Holocene RSL evolution from coastal sedimentary sequences provides a background upon which to compare modern rates of RSL rise, especially the early Holocene period of rapidly rising RSL (García-Artola, A; Stéphan, P.; Cearreta, A.; Kopp, R.E.; Khan, N.S. and Horton, B.P. 2018. Holocene sea-level database from the Atlantic coast of Europe. *Quaternary Science Reviews* 196: 177-192).
3. **Quaternary environmental evolution due to natural processes.** Due to the frequent, rapid and intense climate changes that characterize the late Quaternary, coastal and marine environments have experienced dramatic variations and contain a complete record of the processes and events occurred during this interval. The high-resolution multiproxy study of the sedimentary record allows reconstruction of the past features, to understand the present conditions and to deduce the future environmental variability (Rodriguez-Lazaro, J., Pascual, A., Cacho, I., Varela, Z. and Pena, L. D. 2017. Deep-sea benthic response to rapid climatic oscillations of the last glacial cycle in the SE Bay of Biscay. *Journal of Sea Research* 130: 49-72).
4. **Sedimentary processes with social and economic consequences.** Sedimentary processes in the estuarine areas are frequently altered by human-induced activities (dredgings, dumpings, reclamation, channelling) which can lead to undesirable repercussions. Sedimentological studies contribute to understand the role of the anthropogenic influence and to establish suitable strategies for sustainable development (Irabien, M.J.; Cearreta, A.; Serrano, H. and Villasante-Marcos, V. 2018. Environmental regeneration processes in the Anthropocene: The Bilbao estuary case (northern Spain). *Marine Pollution Bulletin* 135: 977-987). Pascual, A.; Martínez-García, B. and. Mendicoa, J. 2019. Benthic foraminifers as a proxy of the range of the tidal wave in the Oyambre Estuary (Cantabria, Spain). *Continental Shelf Research* 176: 1-18.
5. **Anthropocene: a new epoch in the geological scale?** Human activity is leaving a pervasive and persistent signature on Earth. Numerous anthropogenic markers of functional changes in the earth system have been found through the stratigraphic record. These signals render the Anthropocene stratigraphically distinct from the Holocene (Waters, C.N.; Zalasiewicz, J.; Summerhayes, C.; Barnosky, A.D.; Poirier, C.; Galuszka, A.; Cearreta, A.; et al. 2016. The Anthropocene is functionally and stratigraphically distinct from the Holocene. *Science* 351 (6269): aad2622.1-aad2622.10).

This research group has a leading role in the Postgraduate Programmes (Master and Doctorate) and the UFI on Quaternary: Environmental Changes and Human Footprint (www.ehu.eus/mastercuaternario, www.ehu.eus/doctoradocuaternario, www.ehu.eus/uficuaternario). **Acknowledgements:** IT976-16 (Basque Government) and UFI 11/09 (UPV/EHU).

LATE QUATERNARY RECORD OF CLIMATE CHANGE IN THE BASQUE BASIN (S BAY OF BISCAY)

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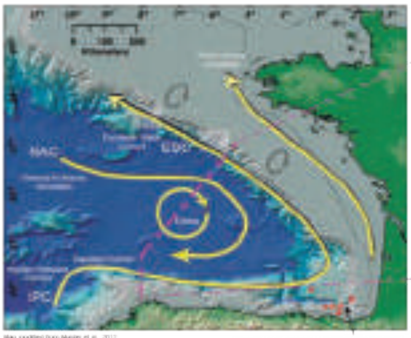
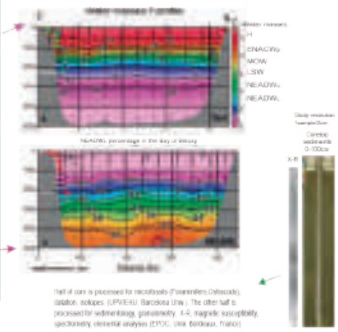
ABSTRACT

Earths' climate during the last 150000 years (Last Glacial Cycle; MIS5 to MIS1) is characterised by sudden oscillation of cold and warm periods known as Dansgaard-Oeschger (D-O) events, with a 1470-year periodicity (lunisolar tidal cycle?). The oscillation is asymmetric, with rapid warming (8°-10°C within decades) and more lasting cooling stages from centuries to a millennium. Each D-O oscillation is preceded by North Atlantic sea surface cooling and massive iceberg discharges (Heinrich events HE). D-O oscillations represent sea level between 45m and 90m below present. D/O and Greenland stadials/interstadials (GI/GS) events are the atmospheric response and HE (Heinrich events) the oceanic response to millennial climate variability. This millennial variability is the abrupt change of atmospheric T in high latitudes of NH with no apparent insolation or external (astronomical) forcings. Causes of global D/O and HE are changes in AMOC (Atlantic Meridional Overturning Circulation) by fresh water influx, solar irradiance, ice-sheet thickness and Arctic sea-ice cover. Two hypotheses explaining the causes for these changes are in discussion: 1) The shutdown of AMOC caused by dilution of N Atlantic water mases due to melt water pulses, and 2) Abrupt warming produced by stratified warm subsurface waters below the halocline and sea ice in Norwegian and North Atlantic seas. It is worth to mention that since methane is very sensitive to D/O cycles, greenhouse gas CO_2 has no role, and its levels are neither cause nor consequence of the most frequent and most abrupt climate changes of the recent past.

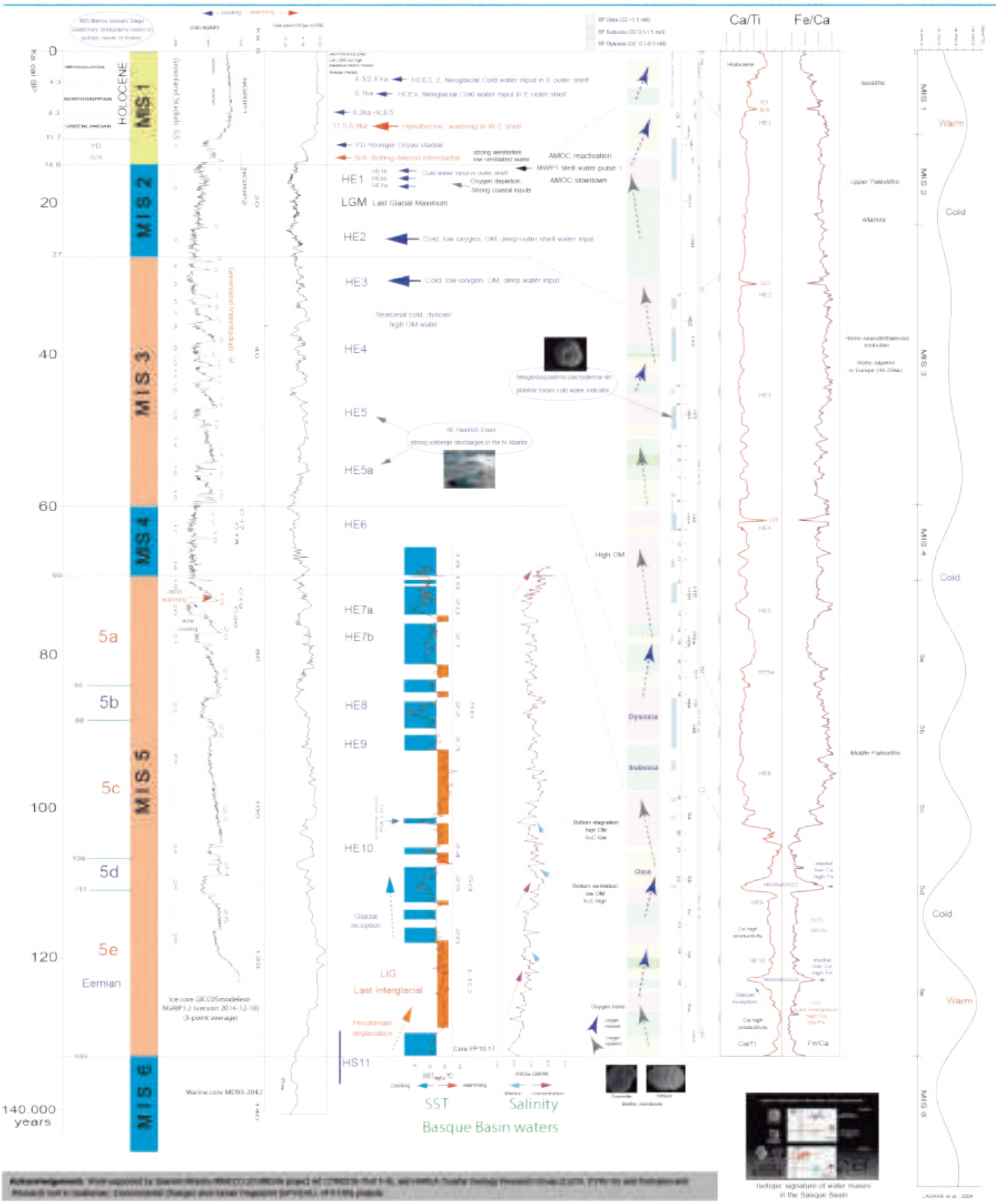
We present results of palaeoceanographic and palaeoclimatic reconstructions from the MIS-5 to Holocene time interval from marine cores of the S Bay of Biscay. Based on detailed analyses of faunal distributions of benthic and planktonic foraminifers and benthic ostracods as palaeo-indicators, together with the results of the chronology, isotopic geochemistry and sedimentological proxies (granulometry, magnetic susceptibility, spectrometry, elemental analyses), we characterise main events in the palaeoenvironmental evolution of this region of the Bay of Biscay during the last 140 ka.

CORE LOCATIONS AND SAMPLING



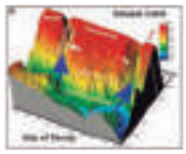


PALAEOCEANOGRAPHIC EVOLUTION BASQUE BASIN

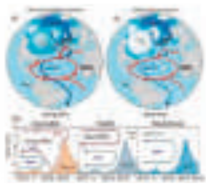


Interpretation

Water masses input in the Basque Basin shelf (Martínez-García, 2012)

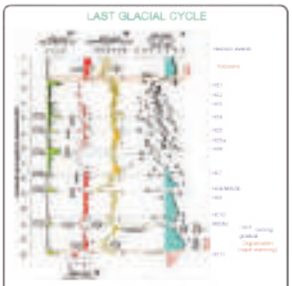


Cold water input into the Basque Basin shelf (diagram from Cremer EPOC)



AMOC (Atlantic Meridional Overturning Circulation) and slowdown/shutdown during HE

LAST GLACIAL CYCLE



Mediterranean evolution 130 ka deep-water
Model from Martrat et al., Science, 2007

Stadials

Bottom poor ventilation, high OM, $\delta_{13}C$ low → AABW (Antarctic Bottom Waters) major influence

Strong and dry westerlies in S Europe

Interstadials

Bottom ventilation, low OM, $\delta_{13}C$ high → NADW (North Atlantic Deep Water) major influence

No Precessional signal in Basque Basin during MIS5e

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TORNER et al., 2019. Quaternary Science Reviews 226: 106037.

Palaeontology, geology and heritage from the mesozoic and cenozoic of the western Pyrenees

Erik Isasmendi[1], Leire Perales-Gogenola[1], Mikel Arlegi[1,2], Humberto Astibia[1], Ainara Badiola[1], Oscar Bonilla[1], Andrea García Sagastibelza[1,2], Asier Gómez-Olivencia[1,3,4], Mikel López-Horgue[1], Xabier Pereda Suberbiola[1], Nathalie Bardet[5], Ana Berreteaga[1], J. Carmelo Corral[6], Ester Díaz Berenguer[7], Ignacio Díaz Martínez[8], Javier Elorza[1], Diego Garate[9], Joseba Rios-Garaizar[10].

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[3]Sociedad de Ciencias Aranzadi, Donostia; [4]Centro UCM-ISCIII de Investigación sobre Evolución y comportamiento Humanos, Madrid; [5]Biogenarium S.C.-Museo de Ciencias Naturales de Álava; [6]Departamento de Ciencias de la Tierra. Universidad de Zaragoza; [7]Research Institute of Paleobiology and Geology. Universidad nacional de Río Negro; [8]Geologia saila; [9]Ikerbasque. Basque Foundation for Science. [10]Centro Nacional de Investigación sobre la Evolución Humana-CENIEH, Burgos.

KEY WORDS: Paleontology, Palaeodiversity, vertebrates, invertebrates, Geology, Geodiversity, Mesozoic, Cenozoic, western Pyrenees, Palaeontological heritage.

This group includes researchers from different fields (palaeontologists and geologists) from the Universidad del País Vasco/Euskal Herriko Unibertsitatea, in collaboration with researchers from other centres and institutions, both national and foreign. Research group IT1418-19 from the Basque Government / EJ and PPG17/05 from the Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU).

The main goal of our research is to contribute to the better understanding of the palaeobiodiversity of western Pyrenees throughout the study of rocks and fossils of invertebrates, vertebrates and associated biota from the Mesozoic and Cenozoic deposits of the Basque-Cantabrian region and nearby sedimentary basins. This knowledge is of utmost importance to understand the geological processes that occurred during the history of these basins and the Earth. The fossil record, which indeed is part of the geological record, is a non-renewable historical archive and constitutes the main tool for the study of biodiversity of the past and the changes in the biosphere.

For this purpose, our main lines of research are:

1. Vertebrate faunas from the Mesozoic and Cenozoic deposits of the western Pyrenees and related biota: geology, taphonomy, palaeobiology and biocronology.
2. Theropod dinosaurs of eastern Cameros Basin and related biota.
3. Palaeodiet of Early and Late Eocene perissodactyls from the Iberian Peninsula and Central Europe: mesowear and microwear using Dental Microwear Textural Analysis (DMTA).
4. Human evolution and palaeocology of the Quaternary. Evolution of the thorax and axial skeleton of *Homo* genus. First human populations of the Basque Country and their environment.
5. Cretaceous sinsedimentary tectonic, hidrotermalism and biotic changes occurred in the sea.
6. Geological heritage and geoconservation of paleontological sites and fossil associations from the western Pyrenees.

Therefore, the activities of the research group can be summarized into three: a) Research; b) Dissemination of scientific and educational findings; and c) Geoconservation.

Recent publications:

Arlegi, M., Veschambre-Couture, C., Gómez-Olivencia, A. (2020). Evolutionary selection and morphological integration in the vertebral column of modern humans. *American journal of physical anthropology*, 171(1), 17-36.

Astibia, H., Merle, D., Pacaud, J. M., Elorza, J., Payros, A. (2018). Gastropods and bivalves from the Eocene marly formations of the Pamplona Basin and surrounding areas (Navarre, western Pyrenees). *Geodiversitas*, 40(2), 211-257.

Badiola, A., Arlegi, M., Astibia, H., Bardet, N., Berreteaga, A., Corral, J. C., Díaz-Martinez, I., Gómez-Olivencia, A., López-Horgue, M.A., Perales-Gogenola, L., Pereda-Suberbiola, X. (2019). The most representative vertebrate fossil record and palaeontological heritage from the western Pyrenees. *Spanish journal of palaeontology*, 34(1), 103-120.

Ősi, A., Pereda-Suberbiola, X. (2017). Notes on the pelvic armor of European ankylosaurs (Dinosauria: Ornithischia). *Cretaceous Research*, 75, 11-22. Doi: 10.1016/j.cretres.2017.03.21.

Piriniar mendebaldeko Mesozoiko eta Zenozoikoko Paleontologia, Geologia eta Ondarea

Erik Isasmendi[1], Leire Perales-Gogenola[1], Mikel Arlegi[1,2], Humberto Astibia[1], Ainara Badiola[1], Oscar Bonilla[1], Andrea García Sagastibelza[1,2], Asier Gómez-Olivencia[1,3,4], Mikel López-Horgue[1], Xabier Pereda Suberbiola[1], Nathalie Bardet[5], Ana Berreteaga[1], J. Carmelo Corral[6], Ester Díaz Berenguer[7], Ignacio Díaz Martínez[8], Javier Elorza[1], Diego Garate[9], Joseba Rios-Garaizar[10].

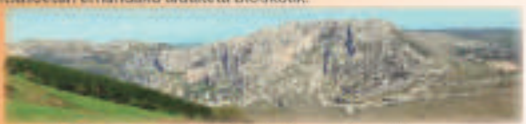
[1]Geologia saila, Euskal Herriko Unibertsitatea. [2]Sorbonne Universités, CR2P-CNRS-MNHN-UPMC Paris 6, Département Histoire de la Terre, Muséum national d'histoire naturelle. [3]Sociedad de Ciencias Aranzadi, Donostia. [4]Centro UCM-ISCIII de Investigación sobre Evolución y comportamiento Humanos, Madrid. [5]Biogenarium S.C.-Museo de Ciencias Naturales de Álava. [6]Departamento de Ciencias de la Tierra, Universidad de Zaragoza. [7]Research Institute of Paleobiology and Geology, Universidad nacional de Rio Negro. [8]Geologia saila. [9]Ikerbasque. Basque Foundation for Science. [10]Centro Nacional de Investigación sobre la Evolución Humana-CENIEH, Burgos.

IKERKUNTZA LERROAK

1) Pirinio mendebaldeko Mesozoiko eta Zenozoikoko ornodun fauna eta erlazionatutako biota: geologia, tafonomia, paleobiologia, eta biokronologia.

2) Pirinioetako mendebaldeko ondare geologikoa eta aztarnategi paleontologiko eta fosil-elkarteen geokontserbazioa.

3) Kretazeoko tektonika sinsedimentarioa, hidrotermalismoa eta itsasoetan emandako aldaketa biotikoak.



Raneroko (Karrantza) karbonatozko plataforma. Behe Albiarra (Behe Kretazeoa).

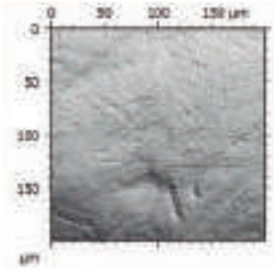
4) Kameros arroko ekialdeko dinosaurio teropodoak eta erlazionatutako biota.

5) Iberiar Penintsulako Goi eta Behe Eozenoko paleodietak: mesohigatze eta mikrohigatzearen ikerketa.

6) Giza eboluzioa eta Kuaternarioko peloekologia.

6.1- *Homo* generoaren bizkarrezurra eta toraxaren eboluzioa.

6.2-Euskal Herriko lehenengo giza populazioak eta haien ingurunea.



Mikrohigatze markak Eozenoko ugaztunen hortzetan

AZTARNATEGIAK

GAUR EGUN — 66 Mu — 145.5 Mu

FANEROZOIKOA — ZENOZOIKOA — MESOZOIKOA

KUATERNARIOA

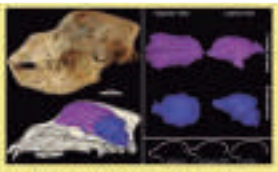
Punta Lucero (Bizkaia)

Homotherium latidens feline handiaren baralaren fosilak.

0.4-0.8 milioi urte, Erdi Pleistozenoa. Ingurune kontinentala.

Santa Isabel (Bizkaia)

0.3 milioi urte, Erdi Pleistozenoa. Ingurune kontinentala.



Ursus spelaeus hartzaren garezur eta burmuinaren errekonstrukzio birtuala.

Monte Carmelo (Israel)

Kebara 2 Neandertalaren bizkarrezurraren eta toraxaren berreraikitze birtuala.

NEOGENOA

PALEOGENOA

Zambrana (Araba)

36-37 milioi urte, Goi Eozenoa. Ingurune kontinentala.

Iberolophus araensis perisodaktilo espezie berriaren buruhezurra, barala eta hortzak.

Castejón de Sobrarbe (Huesca)

Sobrarbesiren cardieli, sirenio espezie berriaren garezurraren 3D berreraikitze birtuala.

41-40 milioi urte. Behe Eozenoa. Ingurune-deltaikoa.

Iruñeko arroko fosil-elkarteak (Goi Nafarroa)

Iruñeko arroan aurkitutako bibalbioa (*Spondylus cisalpinus*) eta gasteropodoa (*Athleta (Volutospina) delvalei*).

41.3-33.9 milioi urte, Erdi-Goi Eozenoa. Ingurune itsastarra eta deltaikoa.

GOI KRETAZEOA

Laño (Trebiño)

73-72 milioi urte, Goi Kretazeoa. Ingurune kontinentala.

Lañon aurkitutako dinosauroen berreraikitzea.

Lañoko dinosauro teropodoen hortzak.

Laño aztarnategiko ornodunen fosilak: dordoka, sugeak, ugaztunak, eta krokodiloak.

BEHE KRETAZEOA

Igea (Errioxa)

125 milioi urte, Behe Kretazeoa, Ingurune lakutarra.

Enciso Taldeko esanosauro hortza

Mutriku (Gipuzkoa)

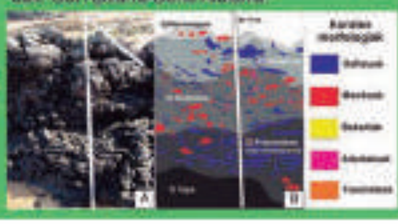
100 milioi urte, Behe Kretazeoa. *Mortoniceras arietiforme* ammonitea.

Arratiako arrain fosilak (Bizkaia)

140 milioi urte, Behe Kretazeoa. Ingurune deltaikoa eta kostaldeko aintzirak.

Ezkutuberezi carmeni arrain klupeomorfoa. Arratiako arroan aurkitutako fosilekin deskribatutako espezie berria.

Euskokantauriar arroko iparraldeko koral segidak. Goi Aptiarra-Behe Albiarra.



DIBULGAZIOA

Arlanpe: Bizkaiko historiaurrea ulertzeko lau leiho

Pirinio mendebaldeko emagatiro fosila; ondare paleontologikoa eta geokontserbazioa (liburua, 2018)

AZKENENGO ARGITALPENAK

The Late Lutetian Thermal Maximum (C19r hyperthermal event, 41.5 Ma): insights from a continental margin section (Cape Oyambre, N Spain)

A. Payros (a), B. Intxauspe-Zubiaurre (a), N. Martínez-Braceras (a), S. Ortiz (b), J. Dinarès-Turell (c), J.A. Flores (d)

(a) Stratigraphy-Paleontology, Univ. Basque Country (UPV/EHU), P.O. Box 644, E-48080 Bilbao, Basque Country (a.payros@ehu.eus). (b) PetroStrat Ltd., Tan-y-Graig, Parc Caer Seion, LL328FA, Conwy, Wales. (c) Istit. Naz. Geofisica e Vulcanologia, Via Vigna Murata 605, I-00143 Rome, Italy. (d) Geologia, Univ. Salamanca, Plaza de los Caidos s/n, E-37008 Salamanca, Spain.

Hyperthermal events were short-lived, intense global warming events driven by the rapid release of greenhouse carbon gases into the atmosphere/ocean system in Paleogene times (66-40 Ma -million years ago-). These events have commonly been regarded as the best geological analogues of ongoing global warming and are therefore taken as reference models to forecast future climate evolution. The most recent hyperthermal event, the Late Lutetian Thermal Maximum or Chron C19r event, took place at ~41.5 Ma. This paleoclimatic event was first identified in sediments from the Atlantic Ocean, but many issues remained unsolved. Using magnetostratigraphic and biostratigraphic information, the astronomically tuned cyclo-stratigraphic record from the Oyambre section was accurately correlated with the Atlantic sites. This, combined with stable isotope data, allowed identification of the C19r event in a conspicuous dark marl bed. Given that the associated negative carbon isotope excursion extends for 2/3 of a precession-driven hemicouplet, a 7–11 kiloyear duration was estimated. Exceptional insolation conditions were found to have accelerated the hydrological cycle, increasing rainfall and runoff on land and terrestrial sediment input to the sea, which resulted in relatively low carbonate content in the deep-sea sediments. The terrestrial input also caused seawater eutrophication and freshening, leading to low $\delta_{13}C$ and $\delta_{18}O$ values, increased abundance of autochthonous and reworked calcareous nannoflora taxa, peaks in the abundance of opportunistic Reticulofenestra <5µm and opportunistic benthic foraminifera, and a reduction in the abundance of oligotrophic calcareous nannofossils.

Acknowledgements: Research funded by the Spanish Government (CGL2015-65404-R and PID2019-105670GB-I00, MINECO/FEDER, EU) and the Basque Government (IT-930-16). BI-Z and NM-B received pre-doctoral grants from the UPV/EHU and the Basque Government, respectively. NM-B received a post-doctoral Dokberri grant from the UPV/EHU.

University of the Basque Country

petrostrat

INGV Istituto Nazionale di Geofisica e Vulcanologia

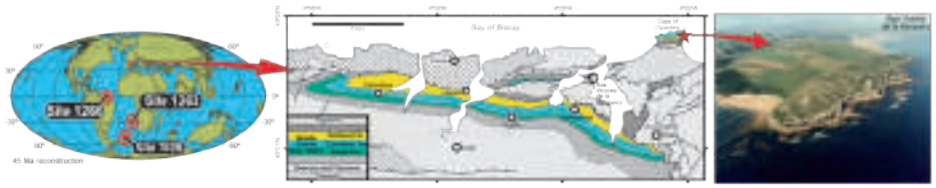
VNiVERSiDAD D SALAMANCA

The Late Lutetian Thermal Maximum (C19r hyperthermal event, 41.5 Ma): insights from a continental margin section (Cape Oyambre, N Spain)

A. PAYROS [a], B. INTXAUSPE-ZUBIAURRE [a], N. MARTÍNEZ-BRACERAS [a], S. ORTIZ [b], J. DINARÈS-TURELL [c], J.A. FLORES [d]

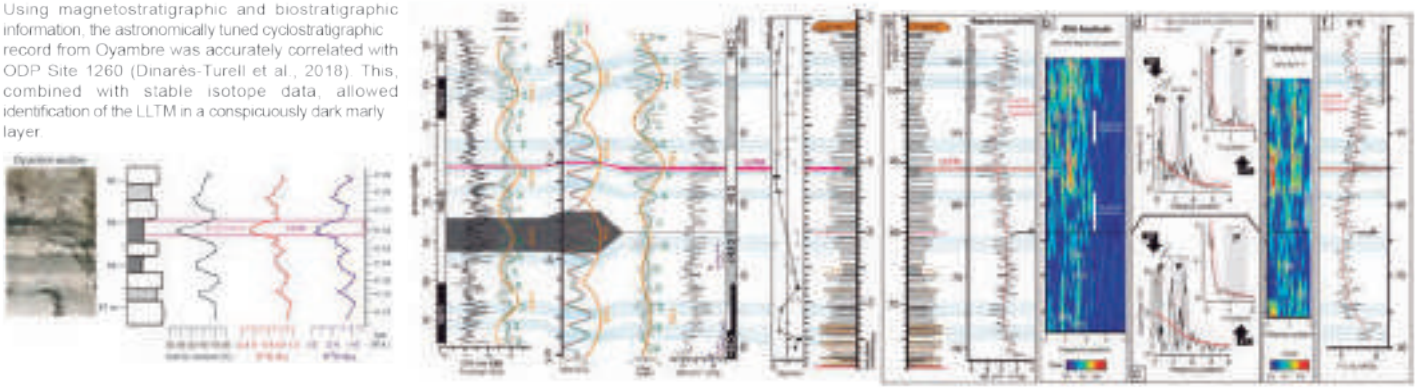
[a] Stratigraphy-Paleontology, Univ. Basque Country, P.O. Box 644, E-48080 Bilbao, Basque Country (a.payros@ehu.eus). [b] PetroStrat Ltd., Tan-y-Graig, Parc Caer Seion, LL328FA, Conwy, Wales. [c] Istit. Naz. Geofisica e Vulcanologia, Via Vigna Murata 605, I-00143 Rome, Italy. [d] Geología, Univ. Salamanca, Plaza de los Caídos s/n, E-37008 Salamanca, Spain.

The last Eocene hyperthermal event, the Late Lutetian Thermal Maximum (LLTM) or Chron C19r event, took place at 41.5 Ma during a long-term cooling phase. This event was first identified in the Equatorial Atlantic ODP Site 1260 as an abrupt peak in bulk Fe content and a short-lived decline in stable isotope values. Additional studies have recently been completed in the Southern Atlantic ODP sites 702 and 1263. However, many issues were not addressed at these sites and no land-based record of the event had been studied. Therefore, the beach cliff at Cape Oyambre (N Spain) was analyzed with the aim of identifying the LLTM and investigating its paleoenvironmental impact (Intxauspe-Zubiaurre et al., 2018).

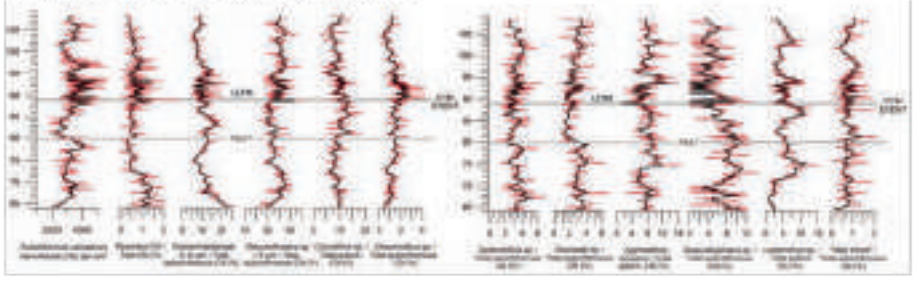


Location of the study area (Cape Oyambre, N Spain) and ODP sites in which the LLTM had previously been identified.

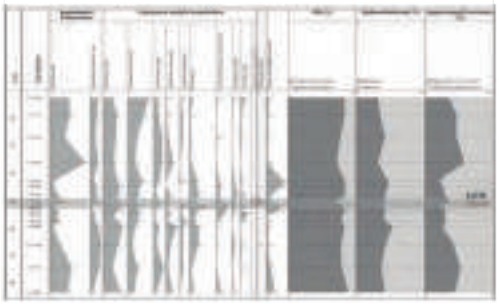
Using magnetostratigraphic and biostratigraphic information, the astronomically tuned cyclostratigraphic record from Oyambre was accurately correlated with ODP Site 1260 (Dinarès-Turell et al., 2018). This, combined with stable isotope data, allowed identification of the LLTM in a conspicuously dark marly layer.



Variations in calcareous nannofossil assemblages along the studied section, including the number of autochthonous calcareous nannofossils per mm², the relative abundance of reworked taxa in proportion to the whole assemblage, and the relative abundance of environmentally significant autochthonous taxa in proportion to total amount of autochthonous taxa. The red lines show actual results, whereas the black lines show 5-point running mean values and illustrate general trends. Note that scale-bars are different for each case.



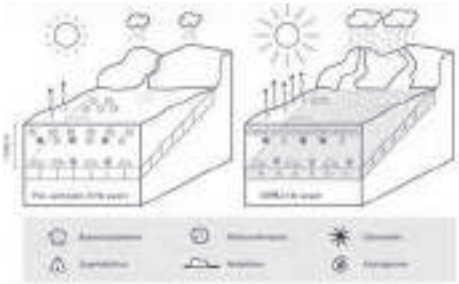
Stratigraphic distribution and relative abundance of selected benthic taxa and benthic foraminiferal indices. Percentages of planktic foraminifera (P/B ratio), epifaunal/infaunal morphogroups and agglutinated/calcareous tests are also shown.



DISCUSSION

Exceptional insolation conditions were found to have accelerated the hydrological cycle during the LLTM, increasing rainfall and runoff on land and terrestrial sediment input to the sea, which resulted in relatively low carbonate content in the deep-sea sediments. The terrestrial input also caused seawater eutrophication and freshening, leading to low $\delta^{13}C$ and $\delta^{18}O$ values, increased abundance of autochthonous and reworked calcareous nannofossil taxa, peaks in the abundance of opportunistic *Reticulofenestra* <5 µm and opportunistic benthic foraminifera, and a reduction in the abundance of the oligotrophic calcareous nannofossil *Zygrhablithus bijugatus*.

Given that the C19r negative carbon isotope excursion extends for 2/3 of a precession-driven hemicouplet, a 7-11 kyr duration was estimated, which agrees with recent estimates from the Atlantic deep-sea sites. However, neither intensified carbon-gas driven greenhouse effect nor warming over and above natural fluctuations could be demonstrated from the Oyambre data.



Environmental model for the LLTM at Oyambre (right), compared to previous and subsequent conditions (left). Increased insolation intensified the hydrological cycle, leading to greater continental sediment and water input into the sea, which caused ecological changes.

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Dinarès-Turell J., Martínez-Braceras N. & Payros A. 2018. High-resolution integrated cyclostratigraphy from the Oyambre section (Cantabria, N Iberian Peninsula): constraints for orbital tuning and correlation of middle Eocene Atlantic deep-sea records. Geochem. Geophys. Geosyst., 19, 2017GC007367.

Intxauspe-Zubiaurre B., Martínez-Braceras N., Payros A., Ortiz S., Dinarès-Turell J. & Flores J.A. 2018. The last Eocene hyperthermal (Chron C19r event, ~41.5 Ma): chronological and paleoenvironmental insights from a continental margin (Cape Oyambre, N Spain). Palaeogeogr. Palaeoclim. Palaeoecol., 505, 198-216.

ACKNOWLEDGEMENTS

Research funded by the Spanish Government (CGL2015-65404-R and PID2019-105670GB-I00, MINECO-FEDER, EU) and the Basque Government (IT-930-16). BI-Z and NM-B received pre-doctoral grants from the University of the Basque Country (UPV/EHU) and the Basque Government, respectively. NM-B received a post-doctoral Dokberri grant from the UPV/EHU.

Hydro-Environmental Processes Research Group (IT-1029/16): multidisciplinary work studying past and present landscapes, together with heading to the future

P. Bilbao-Lasa[1], J. A. Clemente[2], E. Izagirre[2], M. Ladrón de Guevara[3], J. L. Lechuga[2], M. Valiente[2] and the rest of the HGI team.

[1]Dept. of Mineralogy and Petrology, Faculty of Science and Technology; [2]Dept. of Geodynamics, Faculty of Science and Technology; [3]Dept. of Stratigraphy and Paleontology, Faculty of Science and Technology.

University of the Basque Country UPV/EHU, 48940 Leioa.

KEY WORDS: water, landforms, geotechnics, global change, Quaternary.

The Hydro-environmental Process Research Group (HGI) began its research in the 80s in the field of karst hydrogeology. In the 2000s, the Group expanded research on Geotechnics and contaminated soils. Eventually, it boosted its investigation lines seeking a transversal approach with Water and Environment domains, considering the Global Change and Climate Change contexts. Recently, the group extended research into Quaternary evolution records.

22 people currently compose the research group; six of them are predoctoral (precarious) researchers, fourteen of them have a degree in Geology, four in Geography (moreover, one of them also has a degree in Technical Engineering in Topography), two in Biology, one in Engineering and one in Chemistry.

Water is usually a forgotten geological element, although determines the main external environmental processes. The water (on its liquid and solid states) makes its path to the sea on the surface, subsurface and underground levels, transporting sediments (sometimes pollutants) and energy. It is also the basis of some ecosystems (soils, wetlands...), and it also leads to variable risks such as landslides, floods or glacier-related hazards. It transforms the landscape that can be observed nowadays, generating, affecting and changing rivers, lakes and/or glaciers, and carving and shaping aquifers or caves underground.

Analysing different signals of all these features, we are able to reconstruct and understand past and present processes, heading also to reveal future scenarios. The work of the consolidated research group can be divided in 6 main research areas, which have water as the main axis:

1. **Hydrologic-geoenvironmental processes.** Analysis of glaciers and cryosphere, surface and underground runoff, flux and transport modelling, fluvial dynamic of sediments, hillside processes and damn demolition effects.

2. **Characterization of sediments.** Physical-chemical-biological-petrological characterization, urban pollution inputs, toxicity-bioavailability and floods impact.

3. **Karst dynamics.** Karst aquifers analysis and enhancement of resources and landscapes associated to karst.

4. **Analysis of Quaternary records.** Karst fillings characterization from detritic and carbonate records, fluvial terraces, marine terraces and wave-cut platforms.

5. **Integrative approach in the study of Landscape-Heritage-Territory.** Recovery of degraded areas and multidisciplinary analysis (geotechnics, hydrogeology, petrology, cartographic techniques).

6. **Hydrological impacts of global change.** Hydrological retrospective and prospective of changes (on the cryosphere and hydrosphere) in climate and land uses, in addition to adaptation measures in the territory.

KLIMAREN AZTARNAK LURRALDEAN

Iragana eta oraina, gerora begira

GEOLOGOAK LANEAN HIDRO-INGURUMENEKO PROZESUEN IKERTALDEAN (IT-1029/16)

María Valiente[1], Peru Bilbao[2], Jon Ander Clemente[1], Eñaut Izagirre[1], Martin Ladrón de Guevara[3], Juan Luis Lechuga[1], Ane Zabaleta[1], Laura Damas Mollá[1], Martin Arriolabengoa[3], Arantxa Bodego[3], Maite Meaurio[4], Vicente Iribar[1], Jesus Ángel Uriarte[1], Arantza Aranburu[2], Tomás Morales[1], Iñaki Antigüedad[1]

[1]Geodinamika Saila. Zientzia eta Teknologia Fakultatea (Leioa); [2]Mineralogia eta petrologia Saila. Zientzia eta Teknologia Fakultatea (Leioa); [3]Estratigrafia eta paleontologia Saila. Zientzia eta Teknologia Fakultatea (Leioa); [4]Kimika Aplikatua Saila, Kimika Fakultatea (Donostia).

Euskal Herriko Unibertsitatea - Universidad del País Vasco (UPV/EHU)

GEOLOGIA, LURRA ETA URA

Lurraldea gure laborategia

KLIMAREN ERAGINA URETAN

Klima Aldaketa URAri lotuta dago halabeharrez. Klima aldatzean uraren zikloa aldatzen da, eta horrek urari lotutako prozesuetan ere aldaketak eragiten ditu:

- Uren **ibilbidean**, euri-elurretik hasi eta itsasoraino, azaleko zein lurpeko bideetan eragiten du eta bide hauetako energia zein materia fluxuetan (kutsagaiak barne) ere.
- Paisaian, arrisku geologikoetan eta ekosistematan: Urak **paisaia** modelatzen eta baldintzatzen du, kostaldean ere, batzuetan **arriskuak** (luiziak, uholdeak, glaziar-dinamikarekin lotutakoak...) sortzen lagunduz.. Bestalde, **ekosistemen** oinarria ere bada (lurzoruak, basoak, hezeguneak...).
- **Azaleko** ibai, aintzira, glaziar, erliebearen disoluzio-forma, labar, iturburu eta abarretan.
- **Lurpeko** kobazulo, estalaktita/estalagmita, eta ur-termaletan.
- **Gizarteak** garapen sozio-ekonomikorako baliatzen dituen (gatzagak, ur-paisaiak) lehengaietan.

Ura ingurumen-prozesuak baldintzatzen dituen **elementu geologiko** dinamikoa da eta uraren aztarnari jarraituz iraganetik orain arteko uraren eta klimaren historia irakurtzen dugu geologook, etorkizuneranzko bidean...

Transport and storing of substances of environmental interest and biomolecules in crystalline structures based on metal nodes

IMaCris/MaKrisI Research Team
Gotzone Barandika[1,4], Begoña Bazán[2,4], Arkaitz Fidalgo[3,4], M. Karmele Urtiaga[2]
[1]Inorganic Chemistry Department, [2]Mineralogy and Petrology Department, [3]Organic II Department;
Science and Technology Faculty. Universidad del País Vasco / Euskal Herriko Unibertsitatea;
[4]BCMaterials – Basque Center for Materials, Applications and nanostructures, Martina Casiano Bld.,
Sarriena s/n, 48940 Leioa, Bizkaia, Spain

KEY WORDS: MOFs, gas adsortion, emerging pollutants, growth factors, metalloporphyrins, nucleotides.

The IMaCris/MaKrisI research group focuses its work on the fields of Materials Science, Crystallography and Solid State Chemistry, having as target the applicability of the developed materials to support circular economy.

Crystallographic networks based on metal nodes can provide efficient solutions to the circular flow of consumer goods, energy and waste. Connecting metal nodes through ligands enables the creation, by a rational design, of complex crystallographic networks in which metals carry out functions beyond the strictly structural ones. This way, the investigation of the redox properties and molecular exchange processes of these networks can target their application to three of the thematic priorities of the challenge on safe, clean and efficient energy contained in the Spanish National Plan for Scientific and Technical Research and Innovation 2013-2016: waste treatment for energetic purpouses, capture and storage.

Specifically, the combination of metals of the first transition series with inorganic ligands (oxides and vanadates, among others) and organic (polycarboxylic, pyridinic and porphyrinic) opens up a range of networks gathered in six categories:

1. Heterogeneous catalysts for H_2 production and storage by reduction of water with Mn, Fe and Co and porphyrinic ligands,
2. Heterogeneous catalysts for the transformation of organic waste from refineries with environmentally friendly metals and pyridinic, carboxylic and porphyrinic ligands,
3. MOFs with nodes capable of adsorbing CO_2 and emerging pollutants and transform them into other products of interest,
4. Transport and storage of biomolecules,
5. Hybrid adsorbents MOF@IL (IL = ionic liquid) with high porosity and stability networks for adsorption of heavy metals and other pollutants from aqueous media.

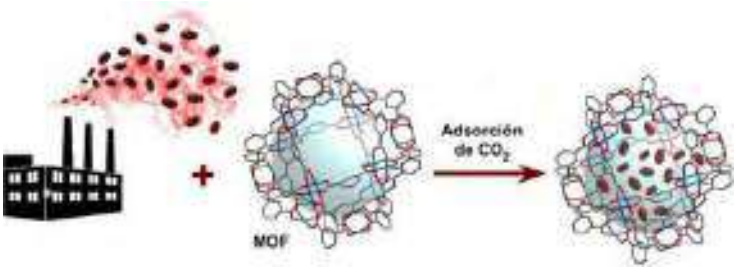

Fig. 1. CO_2 adsorption process into a MOF structure.

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European Commission: H2020-MSCA-RISE-2017-778412
MINECO: MAT2016-76739-R
Basque Government: IT-1290-19
University of the Basque Country (UPV/EHU): GIU18/197

Latest Publications/Patents of IMaCris/MaKrisI Research Team

J. Inorg. Biochem. 2020, *205*, 110977; *CrystEngComm*, 2020, DOI: 10.1039/C9CE01157A; *Molecules* 2019, *24*, 4059-4070; *IUCrJ* 2018, *5*, 569-573; *Daton Trans.* 2018, *47*, 958-970; *J. Solid State Chem.* 2017, *247*, 161-167; *CrystEngComm* 2017, *19*, 7244-7252; Patent: *"Alcohol and water sensor compounds, detection method and device"*, PCT/ES2012/070723.

IMaCris/MaKrisI Research Team

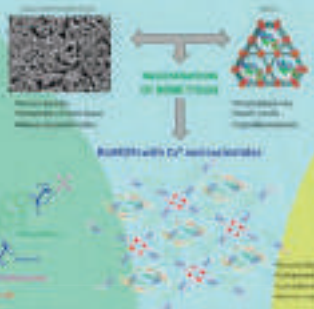
Transport and storing of substances of environmental interest and biomolecules in crystalline structures based on metal nodes

Gotzone Barandika[1,4], Begoña Bazán[2,4], Arkaitz Fidalgo-Marijuan[3,4], M. Karmele Urtiaga[2]

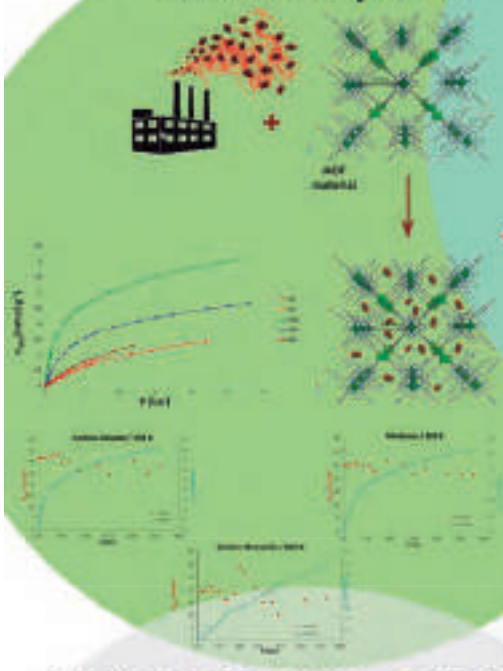
[1]Inorganic Chemistry Department, [2]Mineralogy and Petrology Department, [3]Organic II Chemistry Department; Science and Technology Faculty. Universidad del País Vasco / Euskal Herriko Unibertsitatea; [4]BCMaterials - Basque Center for Materials, Applications and Nanostructures, Martina Casiano Bld., Sarriena s/n, 48940 Leioa, Bizkaia, Spain

http://www.ehu.eus/imacris-makrisi

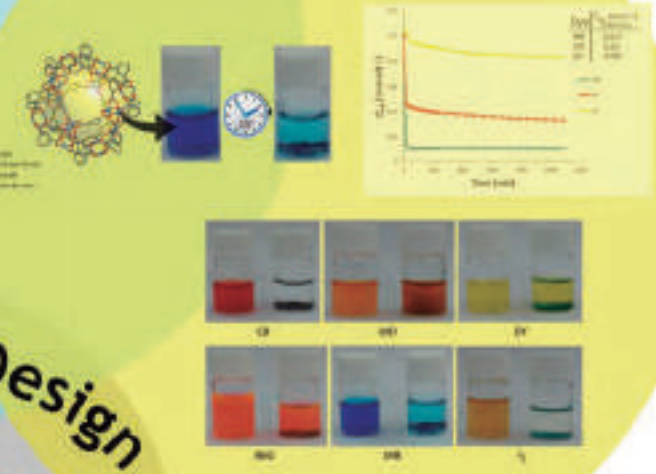
Transport and storage of biomolecules



Gas Adsorption

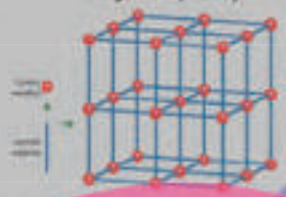


Water remediation



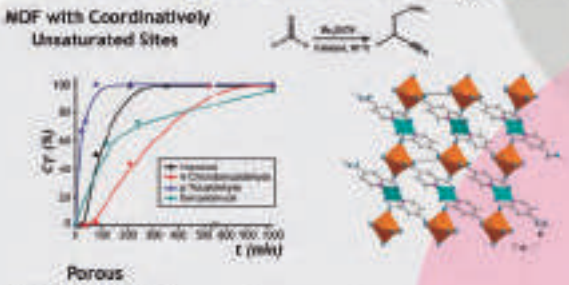
Materials Design

Coordination Polymers (MOFs)

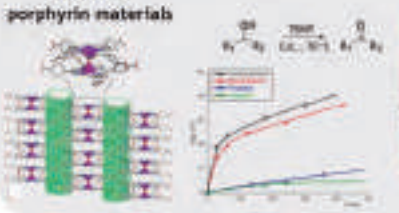


Heterogeneous catalysis

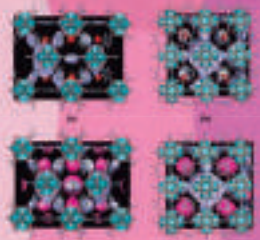
NDF with Coordinatively Unsaturated Sites



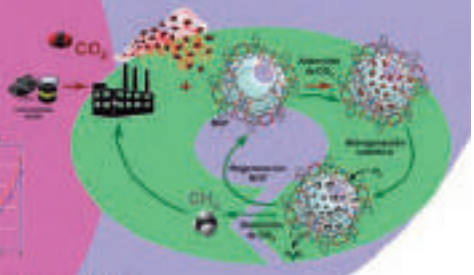
Porous porphyrin materials



Hybrid MOF@IL adsorbents



H_2 production and storage



Funding

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Latest Publications and Patents

- J. Inorg. Biochem. (2020), 201, 110977.
- CrystEngComm (2020), 22, 2904-2913.
- Molecules (2019), 24, 4059-4070.
- IUCrJ (2018), 5, 569-573.
- Dalton Trans. (2018) 47, 938-950.
- CrystEngComm (2017) 19, 7244-7252.
- Patent: "Alcohol and water sensor compounds, detection method and device". PCT/ES2013/070723

Collaborations

- Department of Chemical Engineering and Biotechnology, University of Cambridge.
- Laboratoire MADIREL, Aix Marseille Université.
- Conditions Extrêmes et Matériaux: Haute Température et Irradiation - CEMTHI-CNRS, Université d'Orléans.
- Instituto de Ciencia de Materiales, ICMM-CSIC, Universidad de Madrid.
- Sir Studient Research Fellow, Loire Valley Institute for Advanced Studies, Orléans & Tours, France.
- Instrumental analytic chemistry cathedra IQUIMEFA-CONICET. Faculty of Pharmacy and Biochemistry, Buenos Aires University.
- University of Chile. Advanced Mining Technology Center (AMTC).

Geology to characterize archaeological materials

Mª Cruz Zuluaga[1], Luis Ángel Ortega[1], Ainhoa Alonso-Olazabal[1], Iranzu Guede[1], Graciela Ponce-Antón[1] and Haizea Portillo[1]
[1] Dept. Mineralogy and Petrology

KEY WORDS: geological approach, lime mortars, heritage conservation, archaeological iron tools, technological development, pottery, trade.

A multi-disciplinary research group formed by mineralogists and petrologists in collaboration with archaeologists investigate socio-economics evolution of historic epoch from archaeological records. Research team formed by senior and junior members have been collaborating during the last ten years in various research lines related with archaeological material in the archaeometric field.
The characterization of **Archaeological materials** provides clues of human technological evolution, technological skills, and cultural and trade links. Besides **Human bones** remains allow to reconstruct social organization and changes in past society by means of palaeodiet and mobility patterns of ancient populations using isotope composition.

LIME MORTARS
Lime mortars studies allow assessing the durability of mortars over time and evaluating building deterioration and to formulate compatible repair mortars used in the historical buildings. Mineralogical, chemical and physical characterization and hydric behaviour studies allows to determine the durability of the historical mortars. Archaeometric features also can reveal repair works preformed during the lifespan of the historical building.
Some cases studied: (1) Ponce-Antón et al. (2020) Microchemical Journal. (2) Ponce-Antón et al. (2020) Materials.

ARCHAEOLOGICAL POTTERY
Pottery studies allow identifying raw materials sources areas and to characterise production technology and correlate to the function of pots. Ancient production workshops and production methods can be established by the petrologic study since different fabrics allows understanding the production systems. Besides mapping the spatial diffusion of pottery by tracking pieces with specific marks allows to understand the relationship between pottery production, interregional communications and practices of consumption. **Some cases studied: (1) Grassi et al. (2017) Antiquity.** (2) **Alonso-Olazabal et al. (2018). Antiquity.**

HISTORICAL IRON TOLLS
The slags are by-product of the iron production process. The composition of smelting slags depends on the furnace operation conditions (design, air supply mechanism), the raw material used (ore, charcoal, furnace lining) and the potential use of fluxes. To determine similarities or differences among slags of different epochs allows establishing the development of iron-making processes and technologies through time. **Some cases studied: (1) Portillo et al. (2018) Microchemical Journal. (2) Portillo et al. (2020) Minerals.**

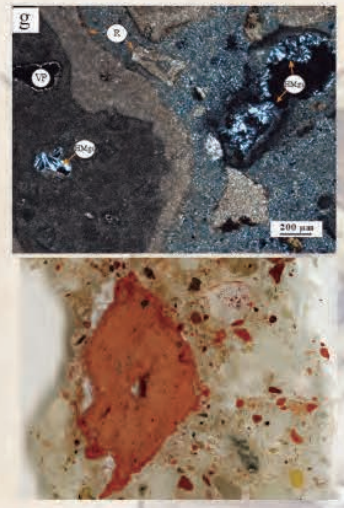
PALAEODIETARY AND MOBILITY PATTENS OF HUMAN POPULATIONS
The analysis isotope composition in human bone collagen constitutes an approach to reconstruct palaeodietary patterns and to identify migrants and to reconstruct movements of past populations. Some cases studied by our team correspond to: Guede et al. (2020) Journal of Archaeological Sciences: Reports.

GEOLOGY TO CHARACTERIZE ARCHAEOLOGICAL MATERIALS

Universidad del Pais Vasco | Euskal Herriko Unibertsitatea
ZIENTZIA ETA TEKNOLOGIA FAKULTATEA
FACULTAD DE CIENCIA Y TECNOLOGÍA

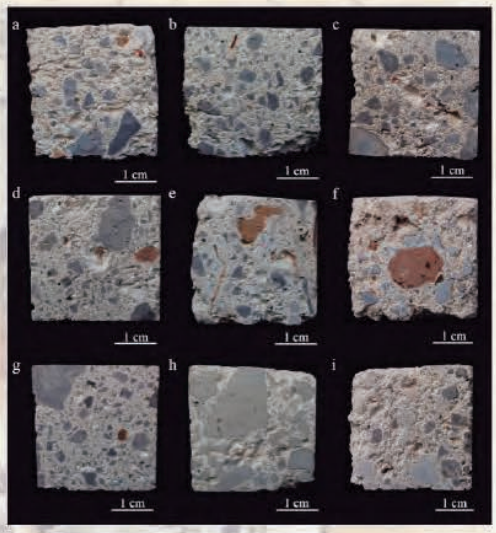
Mª Cruz Zuluaga; Luis Ángel Ortega; Ainhoa Alonso-Olazabal; Graciela Ponce; Iranzu Guede; Haizea Portillo
Dept. Mineralogy and Petrology

On Architectural Heritage Conservation: Historic lime mortars



Amaiur Castle (Navarre)

Top: Microscopic Images of historic lime mortars
Bottom: macroscopic image of mortar thin section



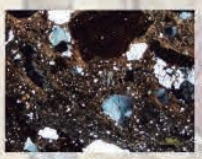
Macroscopic Images of historic lime mortars

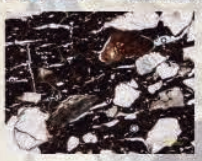
On raw material provenance and trade: ancient pottery

Archaeological pottery

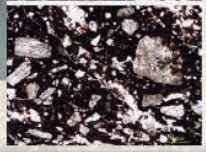
Pottery constitutes an important source of information regarding ancient civilizations, providing clues analysing craft production, exchange systems and consumption patterns as markers of social and political complexity.

Roman



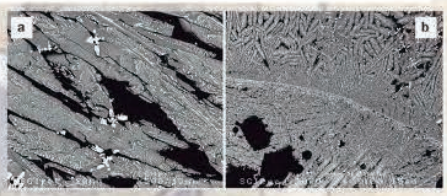


Medieval



On technological evolution: ancient iron slags and tolls

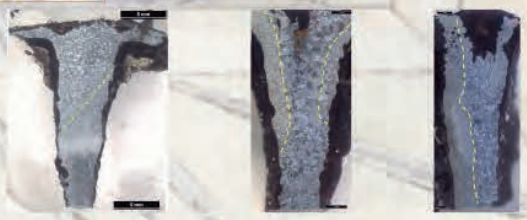
Iron slag



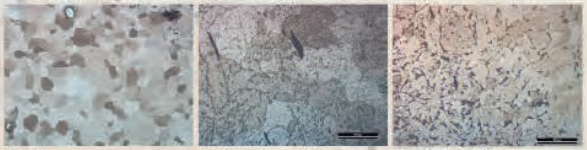
SEM Images

Olivine, Wuestite and Magnetite | Spinifex textures

Iron nails



Petrographic Images



Ferrite | Ferrite + Cementite | Ferrite + Pearlite

The textural and mineralogical features of ancient iron slags and tolls allow to observe a technological evolution in the iron production chain from ferriferous sponge to iron toll.

Acidic Pit Lakes: Environmental, geochemical, mineralogical and biotechnological implications of Metal-Microbe-Mineral-Rock interactions

Javier Sánchez-España[1], Iñaki Yusta[2], Andrey Ilin[2], William Burgos[3], Diana Ayala[3], Irene Sánchez-Andrea[4], Charlotte van der Graaf[4], Carmen Falagán[5], Jutta Meier[6], Bertram Boehrer[7].*

[1]Dept. of Geological Resources (IGME), [2]Dept. of Mineralogy and Petrology (UPV/EHU), [3]Dept. of Civil & Environmental Engineering (PSU), [4]Dept. of Food Sciences and Agrotechnology (WUR), [5]Camborne School of Mines (UoE), [6]Institute for Integrated Natural Sciences (UKL), [7]Dept. of Lake Research (UFZ).

KEY WORDS: Acid pit lakes, mineral neoformation, dissolved metals, biomineralization, bioaccumulation, acidophilic microorganisms, sulfate-reducting bacteria, toxicity.

Our research team includes geologists, microbiologists, environmental engineers and physicists from distinct centers of Spain (UPV/EHU, IGME), USA (PSU), Netherlands (WUR), UK (UoE) and Germany (UKL, UFZ). We develop a comprehensive research of Acidic Pit Lakes (APLs) with a highly multi-disciplinary perspective.

Currently, the group is focused on the interaction between anaerobic acidophilic microorganisms existing in anoxic zones of acidic systems (e.g., deep zones of APLs) and certain dissolved metals present at elevated concentrations in these systems (e.g., Al, Fe(II), Si, Mg, Zn, Cu, As). We study the mechanisms involved in the extra- and intra-cellular bioaccumulation of these metals leading to the formation of biominerals with yet undetermined crystallo-chemical properties. The result of this investigation will have implications on:

1. Geochemistry and Mineralogy: mobility and transport of Al, Fe, Si and trace metals like Zn, Cu, As, V, Se, Cr, Sb, or U in acidic anoxic environments, formation of amorphous and low crystalline solids (biominerals or bio-induced minerals) with usually unknown composition.
2. Environmental risks, remediation: acid pit lakes as a source of metal pollution, potentially hazardous deep-water CO_2 accumulation as a result of long-term interaction between acidic water and carbonates.
3. Geomicrobiology: detoxification mechanisms by different microorganisms with distinct metals, processes of bioaccumulation and/or biomineralization not described to date, and discovery of new bacterial or archaeal species adapted to these chemically extreme conditions.
4. Biotechnology: implications of toxic metal bioaccumulation via extra- and intra-cellular biomineralization on the kinetics and efficiency of biomining reactors, influence of the metabolism of microorganisms.

A wide range of scientific approaches and techniques are being used:

1. Mineralogy: Diffraction (XRD), electron microscopy (FESEM, TEM, STEM with EDX), laboratory incubation columns (neoformation and aging simulation), synchrotron-based techniques (SXRD).
2. Geochemistry: water and solid analyses (ICP-MS, ICP-AES, AAS, XRF) and synchrotron-based techniques (XAS), geochemical modelization (PHREEQC, Geochemist´s Workbench).
3. Molecular biology: anaerobic laboratory cultures, bioreactors, PCR amplification of 16S rRNA analyzes, pyrosequencing, flow cytometry, metagenomics, electron microscopy cryo-TEM, HRTEM, STEM.

RECENT PUBLICATIONS

Sánchez-España, J., Yusta, I., Ilin, A., van der Graaf, C., Sánchez-Andrea, I. (2020): Microbial Geochemistry of the Acidic Saline Pit Lake of Brunita Mine (La Unión, SE Spain). *Mine Water and the Environment*: 1-21.

Sánchez-España, J., Yusta, I., Boehrer, B. (2020): Degassing Pit Lakes: Technical Issues and Lessons Learnt from the HERCO2 Project in the Guadiana Open Pit (Herrerías Mine, SW Spain). *Mine Water Environ*.

Sánchez-España, J., Wang, K., Falagán, C., Yusta, I., Burgos, W.D. (2018): Microbially mediated aluminosilicate formation in acidic anaerobic environments: A cell- scale chemical perspective. *Geobiology* (16): 88-103.

Sánchez-España, J., Yusta, I., Burgos, W.D. (2016): Geochemistry of dissolved aluminum at low pH: Hydrobasaluminite formation and interaction with trace metals, silica and microbial cells under anoxic conditions. *Chemical Geology* (441): 124-137.

Sánchez España, J., Yusta, I., Gray, J., Burgos, W.D. (2016): Geochemistry of dissolved aluminum at low pH: Extent and significance of Al-Fe(III) coprecipitation below pH 4.0. *Geochimica Et Cosmochimica Acta* (175): 128-149.

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Acidic Pit Lakes: Environmental, geochemical, mineralogical and biotechnological implications of Metal-Microbe-Mineral-Rock interactions

Javier Sánchez-España[1], Iñaki Yusta[2], Andrey Ilin[2], William Burgos[3], Diana Ayala-Muñoz[3], Irene Sánchez-Andrea[4], Charlotte van der Graaf[4], Carmen Falagán[5], Jutta Meier[6], Bertram Boehrer[7].

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Abstract

Our research team includes geologists, microbiologists, environmental engineers and physicists from distinct centers of Spain (UPV/EHU, IGME), USA (PSU), Netherlands (WUR), UK (UoE) and Germany (UKL, UFZ). We aim to develop a comprehensive research framework to better understand **Acidic Pit Lakes (APLs)** from a highly multi-disciplinary perspective.

Our line of work includes detailed investigation of interaction between anaerobic acidophilic microorganisms existing in anoxic zones of acidic systems (e.g., deep zones of APLs) and certain dissolved metals present at elevated concentrations in these systems (e.g., Al, Fe, Cu, Zn, Cd, U, Si, Mg). We study the mechanisms involved in the extra- and intra-cellular biologically driven accumulation of these metals leading to the formation of biominerals with yet undetermined crystallo-chemical properties.

Furthermore, we investigate environmental issues related to high metal concentration, high water acidity and deep-water CO_2 accumulation are also considered.

Filón Norte, Huelva

Environmental Risks

Accumulation of large volumes (0.1-6 hm^3) of acidic waters (pH from 1.8 to 4.5) with high contents of dissolved sulfate and **metals (e.g., Al, Fe, Si, Mg, Zn, Cu, As, V, Se, Cr, Sb).**

Potential contamination of superficial water, aquifers and soils.

Limnic eruptions: accumulation of dissolved CO_2 at depth (up to ≈5.0 bar) as a result of long-term interaction between acidic water and carbonates, and permanent isolation from surface.

When approaching saturation values, external forces (for instance, pit walls failure, small earthquakes) may induce a "limnic eruption". After exsolution of CO_2-gas, an increase of volume ≈2.5 times displaces air, provoking deaths by suffocation.

Remediation strategy: upscaling plan of CO_2-degassing to the atmosphere (2014-2019).

CO_2-gas released in that period: ≈123,000 m^3.

Geochemistry and Mineralogy

Objectives

- Mobility and transport of Al, Fe, Si and trace metals (Zn, Cu, As, V, Se, Cr, Sb, or U) in acidic oxic and anoxic environments
- Identification of amorphous and low crystalline neoformed solids (biominerals or bio-induced minerals) with usually unknown composition.

A wide range of **techniques** are being used:

1. **Geochemistry:** water and solid analyses (ICP-MS, ICP-AES, AAS, XRF), synchrotron-based techniques (XAS), geochemical modeling (PHREEQC, Geochemist's Workbench).

Concentration of selected chemical constituents (in mg/L) in Brunita Lake (Murcia) related to other Spanish (IPB) and Australian Pit Lakes (AMMPL):

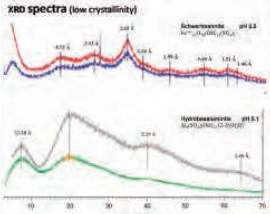
	Brunita	IPB pit lakes	IPB effluents	AMMPL
Major ions:				
SO_4^{2-}	26,000–38,500	2000–18,000	1000–20,000	31–25,000
Cl^-	750–1300	–	100–500	–
Mg^{2+}	5500	33–1250	0–1000	0–2463
Na^+	300–630	10–95	3–124	–
Metals				
Fe	10–7000	3–4620	1–5848	0–2463
Al	20–80	4–727	2–2580	0–1300
Mn^{2+}	500–2000	3–254	3–50	0–150
Zn^{2+}	200–440	6–550	0–300	0–46
Cu^{2+}	250	2–150	1–70	0–36

Other metals (maximum values in mg/L, except otherwise stated): 16.5 As, 0.5 Ni, 0.2 Co, 0.1 Pb, 0.15 Cd; 200 µg/L Se, 170 µg/L U

Cueva de la Mora Acidic Pit Lake

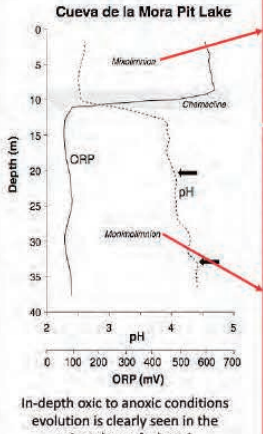
In-Lake facilities

XRD spectra (low crystallinity)



2. **Mineralogy**: filters from different APL depths and from laboratory Winogradsky-type incubation columns (neoformation and aging simulation) are examined under X-Ray Diffraction (XRD), electron microscopy (Scanning (SEM) and Transmission (FESEM, TEM, STEM with EDX) and synchrotron-based techniques (XAS and sXRD).

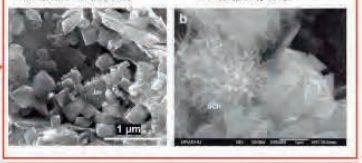
Cueva de la Mora Pit Lake

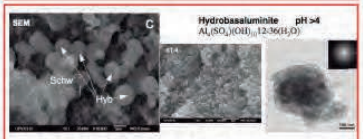


In-depth oxic to anoxic conditions evolution is clearly seen in the mineralogy of a layer!

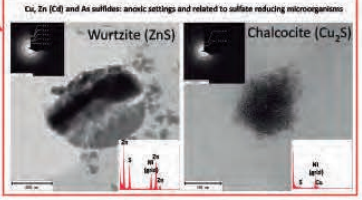
Jerosite pH 2-3.5 $(K, H_3O)Fe^{+++}_3(SO_4)_2(OH)_6$

Schwertmannite pH 3-3.5 $Fe^{+++}_{16}O_{16}(OH)_{12}(SO_4)_2$





Cu, Zn (Cd) and As sulfides: anoxic settings and related to sulfate reducing microorganisms



Geomicrobiology and Biotechnology

Scope

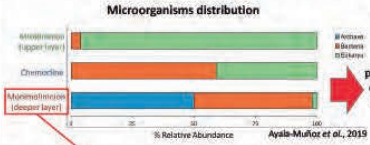
- Detoxification mechanisms by different microorganisms with distinct metals, processes of bioaccumulation and/or biomineralization not described to date.
- Discovery of new bacterial or archaeal species adapted to chemically extreme conditions.
- Implications for toxic metal accumulation via extra- and intra-cellular biomineralization on the kinetics and efficiency of biomining reactors, influence of the metabolism of microorganisms.

Methods

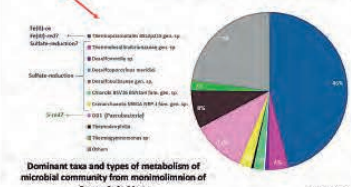
- ✓ 16S rRNA gene profiling – amplify 16S gene regions by PCR and sequence – allows to determine diversity, abundance and phylogenetic composition of the community.
- ✓ Shotgun metagenomics – sequence the whole community DNA, obtaining functional and taxonomic annotations.
- ✓ Metatranscriptomic – total rRNA and mRNA reads, permits whole gene expression profiling of microbial communities.

Results → Taxonomy and Functional Potential

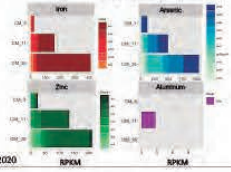
Microorganisms distribution



For instance in Cueva de la Mora, eukaryotes are dominant in the mixolimnion, bacteria are dominant in the chemocline and archaea are dominant in the monimolimnion. Among the prokaryotic population *Acidiphilium* sp. found to be dominant in the **mixolimnion.** *Desulfomonile* sp. is dominant in the **chemocline.** *Thermoplasmatales BSLdp215 gen.* sp. (shown in the pie chart) is dominant in the **monimolimnion.**



Functional potential for metal stress response



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KIMIKA

QUÍMICA

Klima-aldaketa
Cambio Climático

Natural products in food, beverages and plants

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KEY WORDS: Polyphenols, phenolic acids, anthocyanins, food science, red wine, fruits, vegetables, leaves, beverages, cider, honey, olive oil, agricultural food products, agricultural by-products, antioxidant, antiparasitic, antimicrobial, biotic agents

The chemical analysis of food and beverages has a huge interest in food science in order to develop deep knowledge of natural products, which can lead to an improvement of nutritional quality and manufacturing methods, as well as the detection of geographical origins, bad practices, adulterations and frauds.

Polyphenols are a relevant group of natural products which are widely found in the Plant Kingdom. Due to their antioxidant, antimicrobial and antiparasitic properties these compounds have attracted attention for their many benefits for human health (e.g. cardiovascular diseases, cancer...), and have also been associated with the development of biotic resistance in plants. In addition, they are a key element in explaining some food properties, such as flavour, bitterness, astringency, aroma and colour.

In this regard, and after successful studies in beverages such as ciders and wines, apples, fruit juices, edible oils, coffee, microalga, cyanobacteria and medicinal plants, our research group is currently working in the following projects:

- Anthocyanin and tannin analysis in red wines and in extracts of freeze-dried grape pomace in order to *(i)* evaluate and control vinification procedures; *(ii)* study the influence of microoxygenation and ionic exchange techniques on the vinification procedure; *(iii)* evaluate the influence of enological factors and climatology on different grape varieties and monovarietal wines; and *(iv)* be used as quality parameters related to local Protected Designation of Origin, such as wine colour, which is one of the most important parameters directly related to anthocyanins.
- Characterization of the phenolic profiles of agricultural food products determined by HPLC-DAD and UHPLC-DAD-QTOF/MS: Phenolic composition together with chemometrics (PCA, LDA, PLS-DA, PLS, neural networks) provides useful tools for quality control, authentication and detection of adulterations of agricultural food products (fruits, vegetables, leaves, fruit derived foods, cider, wine, honey, olive oil); to study the resistance of the tree towards biotic agents; detection of bad practices in food manufacturing (olive oil); optimization of production technologies to obtain foods (lettuce) with high phytochemical quality; and development of novel rapid methods to determine polyphenol composition of agricultural foods (*e.g.* wine) by vibrational spectroscopies and regression models.
- Untargeted metabolomic LC-MS fingerprinting of the phenolic profiles of apple cultivars for the identification of biomarkers related to resistance to apple tree diseases: Apple phenolic fingerprints and data on apple cultivar resistance to diseases are submitted to multivariate data analysis (PCA, HCA, PLS-DA, O-PLSDA) for this purpose.
- Multivariate data analysis of the phenolic profiles of apples, together with quantitative trait locus (QTLs) and molecular markers for the selection of genotypes with high fruit quality (apples) and interesting agro-technological properties such as resistance to biotic agents and regular productivity; with genome-wide association (GWAS) for the detection of important singles nucleotide polymorphism (SNPs) in the formation of phenolic compounds belonging to the leading phenolic families as a tool for the selection of new varieties with specific phenolic composition in the process of genomic selection in new generation of crossovers improvement; and for the technological characterization of apple varieties.
- Valorization of agricultural food by-products (apple pomace, grape pomace, olive pomace) generated during manufacturing processes by food industry to obtain high value-added bioactive molecules for the food, pharmaceutical and cosmetic industries, as well as for veterinary use, for instance in bee health to control, prevent and fight bee diseases such as American foulbrood or varroasis.
- Natural products in plants, microalgae and cyanobacteria in the search of high value-added bioactive compounds for the food, pharmaceutical and/or cosmetic industries.

PRODUCTOS NATURALES EN ALIMENTOS, BEBIDAS Y PLANTAS

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[1] Dpto. de Química Analítica, Facultad de Ciencia y Tecnología, UPV/EHU, Leioa.

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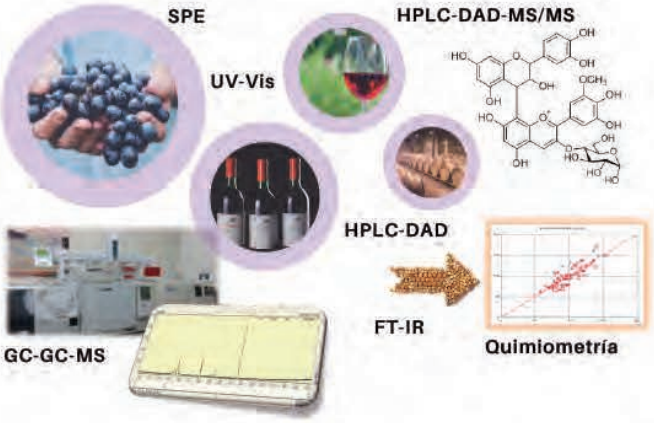
Los polifenoles son un grupo muy importante de productos naturales debido a su ubicuidad en el reino vegetal y su interés para explicar muchas de las propiedades de los alimentos, tales como el amargor, la astringencia, el aroma y el color, además de sus muchos efectos beneficiosos para la salud humana, debidos sobre todo a su gran potencial antioxidante.

VINOS

Efecto del empleo de técnicas de microoxigenación e intercambio iónico durante la vinificación en la calidad del vino.

Influencia de la climatología en la calidad (antocianos, taninos y componentes aromáticos) de variedades de uva tinta y de vinos monovarietales.

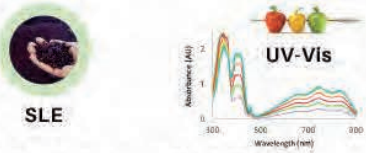


RESIDUOS AGROALIMENTARIOS

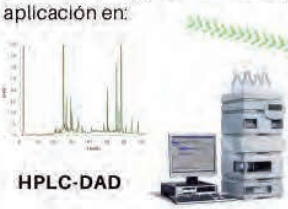
Valorización de subproductos alimentarios:

Evaluación del potencial antioxidante, bactericida y acaricida de extractos de orujos y raspones...

...en la prevención y control de enfermedades de las abejas (*loque americana* y *varroasis*).



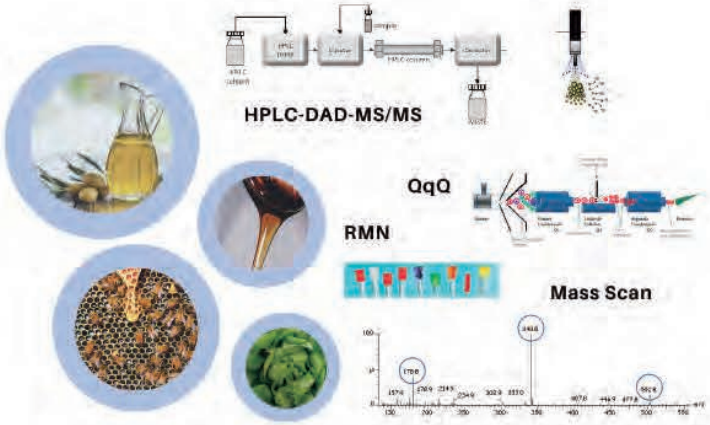
Caracterización de polifenoles presentes en frutas, vegetales y otros productos agroalimentarios por UHPLC-DAD-Q-ToF/MS para su aplicación en:



La relación entre el perfil polifenólico y el desarrollo de resistencia a enfermedades en hojas de manzano (oídio, fuego bacteriano).

AGROALIMENTOS

- Contribución a la selección de genotipos que combinen alta calidad de fruto (manzanas) y caracteres de elevado interés agronómico (resistencia a agentes bióticos y regularidad productiva).
- Optimización de tecnologías de producción para la obtención de productos (lechuga) con alta calidad fotoquímica.
- Tipificación de productos agroalimentarios (miel, aceite de oliva) para la detección de fraudes y la verificación de su calidad



QUIMIOMETRÍA-METABOLÓMICA

Uso de técnicas de reconocimiento de pautas aplicadas para:

- El establecimiento de relaciones entre el contenido de antocianos y taninos del vino y factores enológicos.
- La caracterización tecnológica de variedades de manzanas.
- La autenticación de agroalimentos (miel, aceite de oliva) según sus orígenes botánico y/o geográfico.

Selección de nuevos genotipos de manzanas amargas → Análisis multivariado de sus perfiles polifenólicos; QTLs; Marcadores moleculares.

Desarrollo de métodos rápidos de análisis para la determinación de polifenoles en agroalimentos (vino) mediante espectroscopías vibracionales y técnicas de regresión multivariante.

Metabolómica no dirigida por LC-MS de los compuestos fenólicos de las manzanas para la identificación de biomarcadores relacionados con la resistencia a enfermedades del manzano.

Integrative strategies to assess global issues in food safety and environmental analysis

I. Álvarez[1], D. Bilbao[1], L. Blanco-Zubiaguirre[1], J.A. Carrero[1], A. de Diego[1,2], N. Etxebarria[1,2], L.A. Fernández[1,2], A. Gredilla[1], B. González-Gaya[1,2], M. Irazola[1,2], L. Kortazar[1,2], N. Lopez-Herguedas[1], O. Liñero[1,2], J.M. Madariaga[1,2], L. Mijangos[1], M. Olivares[1,2], A. Prieto[1,2], M. San Nicolás[1], A. Usobiaga[1,2], A. Villate[1], I. Zabaleta[1], O. Zuloaga[1,2].

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KEY WORDS: environment, pollutants, emerging contaminants, xenobiotics, antibiotics, contamination, analytical chemistry, food safety, climate change, aquatic environment, metabolomics, bioactive compounds, bioaccumulation, toxicity, wastewater.

The use of a large number of compounds –some of them pollutants - in our daily life inevitably leads to their release into the environment, without really knowing which is their fate and behavior in the environment and overlooking their effects on the living organisms and on materials. These concerns require an integrative and multidisciplinar approach to understand the processes that take part in the hazardous effects or in the degradation processes. In IBeA (Ikerketa eta Berrikuntza Analitikoa) we lead several research topics in environmental analytical issues and we collaborate actively with many national and European research groups.

One of the research lines is focused on the occurrence of legacy and emergent contaminants, with the aim of studying the presence and fate of emerging contaminants in aquatic media. Conventional wastewater treatment plants are not capable of completely remover the millions of chemical compounds released to the aquatic systems. Suspect and non-target approaches using hyphenated mass spectrometry techniques allows identifying expected but also unknown contaminants that can be toxic to environment and human health. IBeA actively works developing new suspect and non-target screening methods to determine xenobiotics not only in aqueous media but also in biota or in food. Moreover, the combination of such methods with biological assays, the so-called effect directed analysis (EDA), is one effective approach to study the environmental exposome and the mechanisms of toxic action associated with exposure to emerging contaminants in the aquatic environment. Thus, we are focusing our efforts in the application of EDA, in-vitro cytotoxicity testing and metabolomics to diagnose the toxicity potential of urban and industrial water effluents. Among all the contaminants that can appear in the environment, antibiotics deserve special attention. In fact, now, development of target and suspect screening methods for their determination in environmental bodies, biota and fish is a new research line.

Together with the environmental bodies already mentioned, estuaries are also monitored when contamination is under study. Estuaries are affected by contamination inputs of different origin. Trace elements are important pollutants that threaten the equilibrium of estuaries due to their toxicity, long persistence and bioaccumulation. Most metal burden entering an estuary is finally stored in sediments. Chemical analysis of sediments have allowed us investigating temporal trends and geographical distribution of metal pollution in Basque estuaries and other estuaries of the world.

Additionally, IBeA participates in the REPLIM network aimed to monitor the dynamics of high mountain lakes and peatbogs and their responses to Climatic Change. REPLIM will reconstruct past changes, characterise present dynamics, and model future impacts, at both territorial and Pyrenean scales. REPLIM will also increase awareness among the stakeholders and the citizens about climate change in high mountains environments and, in definitive, will help to define a strategy of management integrated with the socioeconomic development of the Pyrenees.

Finally, food safety is also a new broad research line included among our priorities. In fact, we have studied the migration of contaminants from commercial packaging material to foodstuff or the speciation of mercury and selenium in tuna fish and importance of measuring carefully species of both metals to address the toxicity attributed to the accumulated fraction of mercury.

For most of these works the development of new and innovative analytical procedures based on cutting edge instrumentation is the key part of our research. In this sense, we can include the use of microfluidic devices or the development of non-target analytical methods.

2020
Irailak 28-29-30 de Septiembre

Integrative strategies to assess global issues in food safety and environmental analysis

I. Álvarez[1], D. Bilbao[1], L. Blanco-Zubiaguirre[1], J.A. Carrero[1], A. de Diego[1,2], B. Duval[1], N. Etxebarria[1,2], L.A. Fernández[1,2], M.Gallastegi[3], A. Gredilla[1], B. González-Gaya[1,2], M. Irazola[1,2], L. Kortazar[1,2], N. Lopez-Herguedas[1], O. Liñero[1,2], J.M.Madariaga[1,2], L. Mijangos[1], M. Olivares[1,2], A. Prieto[1,2], M. San Nicolás[1], A. Usobiaga[1,2], A. Villate[1], O. Zuloaga[1,2].

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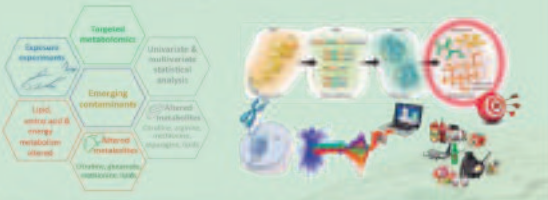
AQUASOME

Exposome assessment of emerging contaminants in the aquatic environment



The main aim of the project is to study the environmental exposome and the mechanisms of toxic action associated with exposure to emerging contaminants in the aquatic environment by integration of effect directed analysis (EDA), in-vitro cytotoxicity testing, metabolomics and wastewater based epidemiology (WBE) assays.

REPLIM

Towards the establishment of a Pyrenean network of global change in lakes and peatbogs

REPLIM is a network of scientists aimed to monitor the dynamics of high mountain lakes and peatbogs and their responses to Climatic Change. It will reconstruct past changes, characterise present dynamics and model future impacts. It will also increase awareness among the stakeholders and the citizens about climate change in high mountains environments and,

AKURA MÚGIL

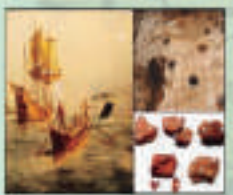
Development of an advanced and sustainable system for the Múgil breeding in captivity

AKURA_Múgil is an innovative project that aims to develop a sustainable culture of Chelon labrosus, commonly known as "mugil", developing for that purpose natural diets based on microalgae, improving water recirculating systems (RAS) and conferring to the whole process a sustainable character and a high market value to the final product.

Study of the acidification and monitoring inorganic pollution in estuaries

Due to the lack of information about the phenomenon of acidification in estuaries, there is a need to develop new strategies for the determination of the parameters related. IBeA studies and implements proper ways to deal with the data obtained in the potentiometric titrations carried out to determine accurately the total alkalinity (TA) of estuarine water samples in the wide range of salinities that can be found in these systems. Estuaries are also monitored when contamination is under study. Estuaries are affected by contamination inputs of different origin. Trace elements are important pollutants that threaten the equilibrium of estuaries due to their toxicity, long persistence and bioaccumulation. Most metal burden entering an estuary is finally stored in sediments. Chemical analysis of sediments have allowed us investigating temporal trends and geographical distribution of metal pollution in Basque estuaries and other estuaries of the world.

Searching for the origin of samples of geological, environmental and archaeological interest: organic biomarkers as key evidences



Organic biomarkers are specific molecules that provide valuable information about their source and about the materials in which they have been found. Despite their ubiquity, they are often found at trace levels and, thus, there is a call for the development of analytical methods that allow the determination of known and unknown organic biomarkers at trace levels.

ISOTOPO

Cross-border network for the protection of the authenticity of the Euroregion's quality marks

ISOTOPO

Use of analytical tools (Elemental & Isotopic) to check the authenticity and origin of foods, as a way to provide Eurorregional DPOs and IGPs with added value.

Market analysis of CBD oils and cannabis flowers in Europe

Given that in Europe there is a lack of regulation for cannabis derived products which are partly used for therapeutic purposes, there might be products in the market that are not in accordance with their label regarding cannabinoids content or that contain diverse contaminants, such as heavy metals, pesticides or pathogen microorganisms. In this sense, IBeA collaborates with Pot Sistemak company in order to assess the cannabinoids and terpenes profile as well as concentration levels of contaminants in cannabis flower and oil samples sold in the European market.

Studies in cultural heritage and landscape by means of Analytical Chemistry-IBeA research group

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KEY WORDS: Cultural Heritage, Landscape, material decaying, restoration, cleaning solutions, transdisciplinarity

The term cultural heritage encompasses several main categories of heritage but always responds to unique and invaluable spaces (anthropogenic or natural) and artefact deserving to be protected and safeguarded. However, generally this is not an easy goal because many conservation. Taking this into account, IBeA research group has made an important effort in the last years to understand the chemistry behind the decaying processes that affect the cultural heritage and to develop new solutions to revert them. Moreover, the IBeA research group strongly believes that the study of Cultural Heritage is a transdisciplinary commitment where several scientific disciplines converge to achieve the same purpose. In this sense, the main research lines and projects that are currently in progress are:

• **MADyLIN (Innovative diagnostic analytical methodologies and cleaning procedures for inorganic surfaces of the Built Heritage affected by anthropogenic impacts)**: studies degradations processes jeopardizing inorganic materials, and propose eco-friendly solutions (cleaning by natural products).
• **PHETRUM (Synthesis, characterization and validation of multi-functional nano-reinforced sustainable hybrid products for the recovery and protection of stone surfaces)**: develops new products based on hybrid epoxi-silicon "BPA-free" polymers to serve for the restoration and protection of stone materials.
• **Punta Begoña Galleries**: thanks to the interdisciplinary work and important citizen participation, this project aims to convert the galleries in a "living" resource.
• **APUV (Analytica Pompeiana Universitatis Vasconicae):** analyze the original materials used to build the Pompeian houses and try to provide innovative conservation solutions to the Archaeological Park of Pompeii.
• **Paestum:** analyze the original materials used to make sculptures and try to provide innovative conservation solutions to the Archaeological Park of Paestum.
• **Villa Belza:** evaluation of the marine atmosphere impact on the building materials used in Villa Belza building (Biarritz, France).
• **Conservation of paper:** development of new products based on green chemistry for the restoration of paper artefacts.
• **Study and enhancement of the Basque archaeological heritage:** in collaboration with the Archaeological Museum of Biscay analyzing metallic artefacts.
• **Spanish prehistoric paintings in open air-rock or archaeological excavation**: in collaboration with archaeologists to understand the decaying processes threatening their conservation.
• **Use of the spectroscopic techniques for planetary exploration:** study Martian meteorites, terrestrial analogues and their respective weathering with the help of the Raman and visible near-infrared spectroscopies since they will go on-board the rovers of the Martian missions carried out by NASA and ESA.
• **Chemical study of degradation processes in underwater metallic materials**: chemical analysis of the raw materials employed and on ascertaining which processes are generating the decaying of them. For this purpose, the non-destructive techniques are the most relevant analytical tools to achieve it while avoiding the damage of these important scenarios.
• **Salinas de Añana:** chemical analysis of the salts and springs from Valle Salado de Añana for the valuation of the production. The study is part of an ambitious project that tries to recover the landscape and cultural heritage of the valley in collaboration with GPAC (archaeologists from UPV/EHU) and HGI (hydrogeologists from UPV/EHU) research groups.

Studies in Cultural Heritage and Landscape by means of Analytical Chemistry – IBeA Research Group

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The sedimentary and volcanic layers in the Armintza outcrop (Bizkaia), the Geological Site of Interest (LIG24), a Terrestrial Martian analogue

Our research group develops innovative analytical strategies to evaluate the impact of chemical contaminants, micro-organisms and the environmental conditions on the Cultural Heritage and Landscape scenarios, like:

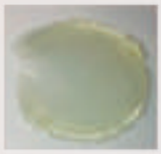
Wall paintings, Wallpapers, Sculptures, Historical Buildings (ornamental façades), Cave Paintings, Archaeological Sites, Terrestrial Analogs to Mars, Meteorites, Impact structures, etc.

Study of the impact of pollution in Pompeii

Our research group has been studying the impact of pollution in the archaeological city of Pompeii, analysing the colour changes in the wall paintings due to the acid gases (SO_x, NO_x, CO_2).

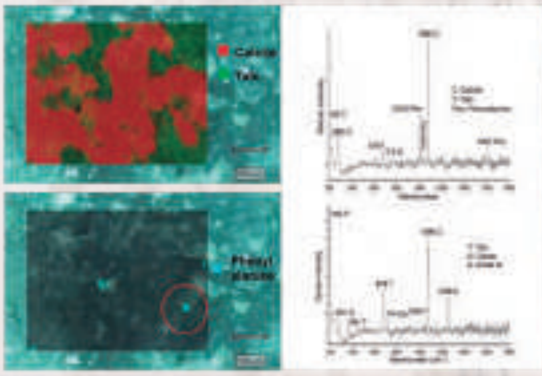
Cleaning and consolidation technologies

We have been working in the development of cleaning and consolidation technologies, essentially based on the use of ion exchange resins, nano-emulsions and hybrid epoxy-silica BPA free resins.

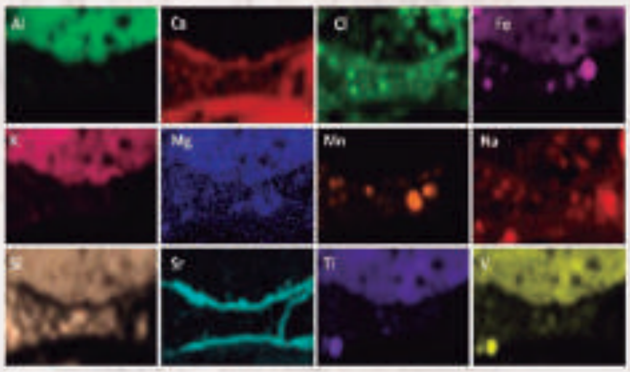


Analytica Pompeiana Universitatis Vasconicae

When the artwork cannot be moved to the laboratory, the equipments are moved to the objects. Raman, infrared (FTIR, DRIFT, Reflectance) and x-ray fluorescence (XRF) spectroscopies are of common use for this purpose. But when samples can be taken, high resolution spectroscopy can be performed with the same techniques



Micro-Raman image on a stromatolite



Micro-XRF image on a beachrock sample

Built Heritage

Archaeological heritage

Archaeological sites

The FARMARTEM research group trajectory

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[1]Analytical Chemistry Department, Faculty of Science and Technology, UPV/EHU
[2]Paint Department, Fine Arts Faculty, UPV/EHU

KEY WORDS: drugs analysis, metabolomics, microencapsulation, dielectric gases, food, documents, art conservation.

The trajectory of FARMARTEM research group is wide and along the years, it has been changed trying to give a response to the current challenges of our society. At the beginning of the group formation, drug analysis was its main topic, but nowadays the research developed plays an important role in very different applications fields:

CLINICAL AND PHARMACEUTICAL

- Drug dose in paediatric population. Metabolomics as a tool for biomarkers search of organ maturation involved in the drug metabolism.
- Antifungal drugs: echinocandins in cell culture.
- Controlled release formulations for ophthalmologic applications.
- Inorganic impurities in pharmaceutical formulations.
- Fumagillin, biomolecule found in the microbial organism Aspergillus fumigatus, in biological fluids.
- Buccal patches with natural products.

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ENVIRONMENTAL AND INDUSTRIAL

- Biocides microencapsulated with cyclodextrins. Introduction of new more environmentally friendly products to fight against domestic fly.
- Food baits applied to plague control of *Vespa Velutina* (Asian hornet).
- Dielectric gas mixture of medium voltage electrical distribution cells. Alternative to SF_6 use.
- Efflorescences in meat products. Quality control of food.

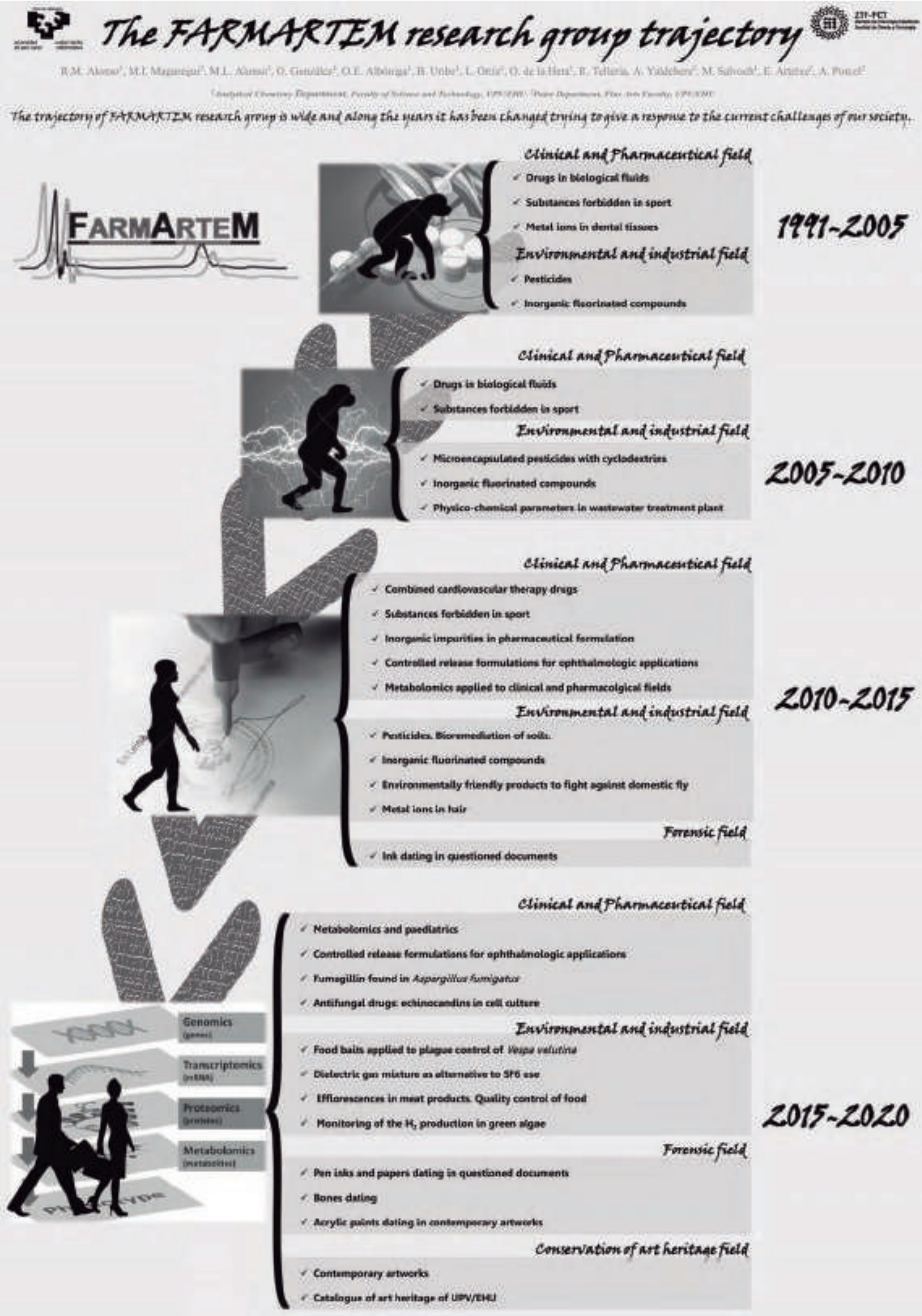
FORENSIC

- Pen inks and papers dating in questioned documents.
- Acrylic paints dating in contemporary artworks.

CONSERVATION OF ART HERITAGE

- Contemporary artworks.
- Catalogue of art heritage of the University of the Basque Country (UPV/EHU).

Several analytical techniques are used in order to tackle all these challenges. Mass spectrometry coupled to chromatographic techniques is the most employed together with sample treatment procedures such as solid phase microextraction or head-space procedures. Non-invasive analytical techniques (Visible microspectrophotometry, Raman spectroscopy and Infrared spectroscopy-Attenuated transmission reflectance) are also used especially in the forensic field. Chemometric tools have shown their great potentiality to extract useful information from different problems the group is faced with.


The FARMARTEM research group trajectory
The trajectory of FARMARTEM research group is wide and along the years it has been changed trying to give a response to the current challenges of our society.
FARMARTEM
Clinical and Pharmaceutical field
✓ Drugs in biological fluids
✓ Substances forbidden in sport
✓ Metal ions in dental tissues
Environmental and industrial field
✓ Pesticides
✓ Inorganic fluorinated compounds
1991-2005
Clinical and Pharmaceutical field
✓ Drugs in biological fluids
✓ Substances forbidden in sport
Environmental and industrial field
✓ Microencapsulated pesticides with cyclodextrins
✓ Inorganic fluorinated compounds
✓ Physico-chemical parameters in wastewater treatment plant
2005-2010
Clinical and Pharmaceutical field
✓ Combined cardiovascular therapy drugs
✓ Substances forbidden in sport
✓ Inorganic impurities in pharmaceutical formulation
✓ Controlled release formulations for ophthalmologic applications
✓ Metabolomics applied to clinical and pharmacolgical fields
Environmental and industrial field
✓ Pesticides. Bioremediation of soils.
✓ Inorganic fluorinated compounds
✓ Environmentally friendly products to fight against domestic fly
✓ Metal ions in hair
Forensic field
✓ Ink dating in questioned documents
2010-2015
Clinical and Pharmaceutical field
✓ Metabolomics and paediatrics
✓ Controlled release formulations for ophthalmologic applications
✓ Fumagillin found in Aspergillus fumigatus
✓ Antifungal drugs: echinocandins in cell culture
Environmental and industrial field
✓ Food baits applied to plague control of Vespa velutina
✓ Dielectric gas mixture as alternative to SF6 use
✓ Efflorescences in meat products. Quality control of food
✓ Monitoring of the H2 production in green algae
Forensic field
✓ Pen inks and papers dating in questioned documents
✓ Bones dating
✓ Acrylic paints dating in contemporary artworks
Conservation of art heritage field
✓ Contemporary artworks
✓ Catalogue of art heritage of UPV/EHU
Genomics
Transcriptomics
Proteomics
Metabolomics
2015-2020

Advanced spectroscopic and magnetic techniques in molecular and nanoscale research

Aran Insausti, Jon Gutiérrez, Otger Crehuet, Maider Parra, Lucía Martínez, Iker Lamas, Ander Camiruaga, Isaac Montoya, Camilla Calabrese, Elena R. Alonso, Imanol Usabiaga, José Andrés Fernández, Asier Longarte, Carolina Redondo, Rafael Morales, Emilio J. Cocinero, and Francisco J. Basterretxea
Department of Physical Chemistry, UPV/EHU.

KEY WORDS: laser spectroscopy, microwave spectroscopy, ultrafast processes, nanomagnetism, nanostructures, lipidomics, cancer, metabolites, vaccines, nanomedicine, biosensors.

The Spectroscopy Group works in research lines that comprise different subjects, all focusing on a molecular and nanometric scale. It designs and applies state of the art spectroscopic techniques to a variety of problems in chemistry that partly overlap with the fields of biology or physics. The group works in spectroscopic instrumentation to achieve high resolutions, both in time and energy, and high control of physical and chemical properties at the nanoscale. Thus, ultrafast lasers allow detection of phenomena in the timescale of femtoseconds, whereas microwave spectrometers can resolve molecular energy levels that differ only a few kHz. On the other hand, combining nanosecond laser pulses with mass spectrometric detection it is possible to discriminate among different molecular conformers of the same species. Finally, laser lithography techniques, together with magneto-optical spectroscopy, allow fabrication and characterization of singular patterned nanostructures.

The previous techniques are well suited to investigate numerous scientific problems at a molecular and nanometric level. A brief list of the ongoing research lines of the group is given below:

- The study of *ultrafast molecular phenomena* using femtosecond laser pulses, such as dissociative processes, energy transfer among excited electronic states, or between solute and solvent molecules. These phenomena are essential to understand intra- and intermolecular interactions.
- *Design of femtosecond laser pulses* of given time and energy to be used as a spectroscopic excitation source.
- *Microwave spectroscopy* techniques, combined with laser vaporization techniques, allow to obtain molecular structures and gas-phase dynamics of biomolecular building blocks, such as sugars, of which few experimental studies free from the interation with solvent molecules can be found. These studies are also the basis for the detection of prebiotic molecules in the interstellar space.
- *Laser electronic spectroscopy* with pulsed supersonic jets and mass resolution is a powerful tool to characterize electronic transitions of rather big molecules and can further discriminate among a usually numerous family of conformers. This techniques are adequate to study interactions between molecular moieties of interest in the biosciences, such as anesthesic-receptor, or bonding among the nitrogenated bases in DNA and RNA chains.
- More specific mass spectrometric techniques, such as *Matrix Assisted Laser Desorption Ionization* (MALDI), allow the obtention of bidimensional images of biological tissues; in this way the distributions of lipids or other substances can be monitored quickly. This technique has immediate medical applications.
- Nanofabrication and characterization of structures at the nanometer scale allow designing of *magnetic nanostructures* (discs, rods and other geometries) with distinctive properties, different from those of macroscopic elements. These patterned structures have a wide application in fields such as magnetic storage of information or biomedicine, for example, cancer diagnostics.

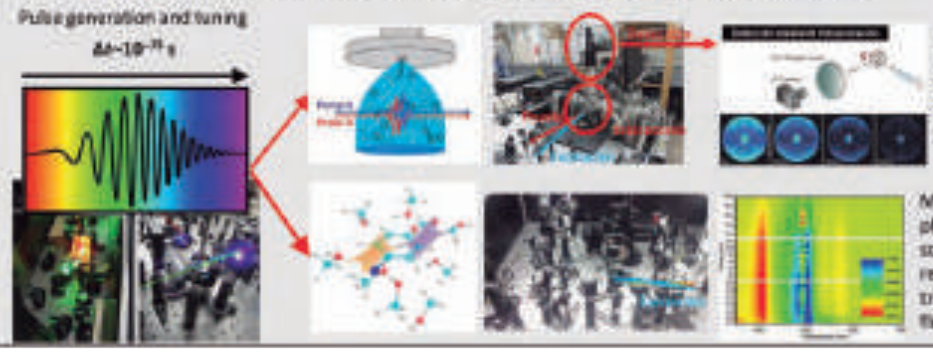
Advanced spectroscopic and magnetic techniques in molecular and nanoscale research

Aran Insausti, Jon Gutiérrez, Otger Crehuet, Maider Parra, Lucía Martínez, Iker Lamas, Ander Camiruaga, Isaac Montoya, Raquel Zurbano, Camilla Calabrese, Elena R. Alonso, Imanol Usabiaga, José Andrés Fernández, Asier Longarte, Carolina Redondo, Rafael Morales, Emilio J. Cocinero, and Francisco J. Basterretxea

Kimika Fisikoa Saila
Departamento de Química Física
Department of Physical Chemistry

The Spectroscopy Group designs and applies state of the art spectroscopic techniques to a variety of problems in chemistry that partly overlap with the fields of biology or physics. The group works in spectroscopic instrumentation to achieve high resolutions, both in time and energy, and high control of physical and chemical properties at the nanoscale.

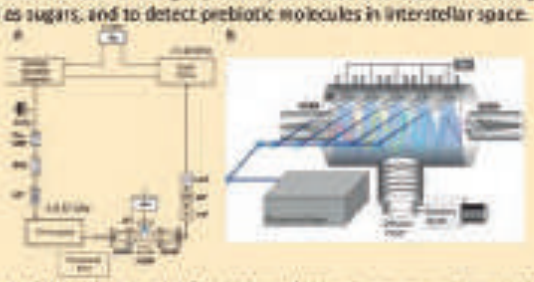
Ultrashort light pulses permit to induce and track ultrafast molecular phenomena



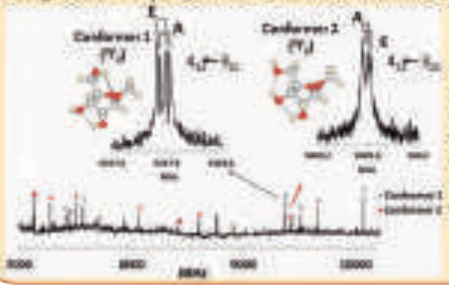
Relaxation of model molecular systems isolated in the gas phase. Detection by ionization (ions/electrons).

Molecular photochemical and photophysical processes in solution by time and frequency resolved methods. Femtosecond transient absorption and fluorescent emission.

Rotational spectroscopy with microwave techniques can be used to obtain molecular structures and gas-phase dynamics of biomolecular building blocks, such as sugars, and to detect prebiotic molecules in interstellar space.



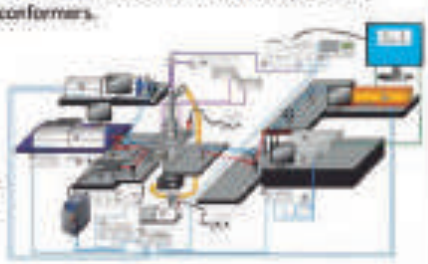
Design of the chirped pulse Fourier transform microwave spectrometer

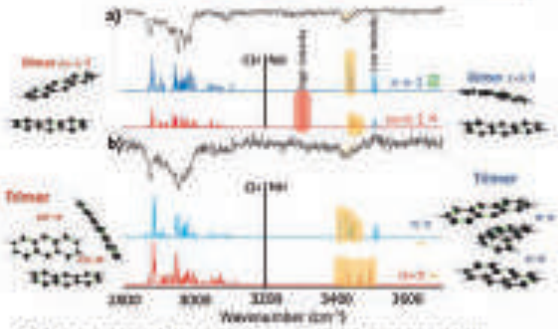


Spectrum of methyl β-D-ribofuranoside with two example rotational transitions split by internal rotation of the methyl group.

Laser electronic spectroscopy with pulsed supersonic jets and mass resolution is a powerful tool to characterize electronic transitions of rather big molecules and can further discriminate among a usually numerous family of conformers.

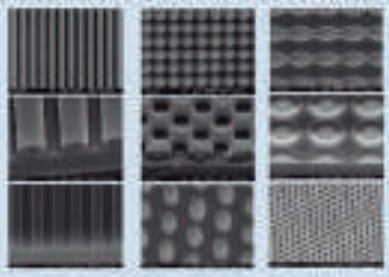
Layout of the experimental system:
- Laser devices
- Expansion chamber
- Mass spectrometer



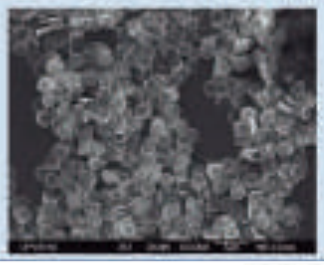


Folding process in a polymer based on anthracene units: structure assignment by comparing the Ion Dip Infrared Spectra (upper trace) with theoretical predictions (in color).

Nanofabrication and characterization of structures at the nanometer scale

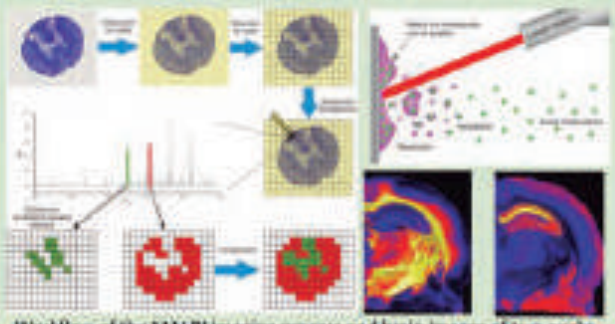


Nanofabrication and characterization of structures at the nanometer scale allow designing of magnetic nanostructures (discs, rods and other geometries) with distinctive properties, different from those of macroscopic elements.



These patterned structures have a wide application in fields such as magnetic storage of information or biomedicine, for example, cancer diagnostics.

Matrix Assisted Laser Desorption Ionization (MALDI) allows the obtention of bidimensional images of biological tissues; in this way the distributions of lipids or other substances can be monitored quickly. This technique has immediate medical applications.



Workflow of the MALDI imaging process and brain images of two peaks

Support

The chemistry of polymers

N. Álvarez[1], A. Martínez[1], I. Pinedo[2], G. Ventosa[1], R. Teijido[1,4], J. Andrade[1,3], S. Maiz[1,4], J. Sanchez[1], A. Valverde[1,4], C. Mendes[1,4], A. Reizabal[1,4], A. Burgoa[5], L. Etxebarria[5], A. Galdames[1], A. Veloso[1], J. M. Laza[1], L. Ruiz[1,4], L. Pérez[1,4], M. I. Moreno[2], J.L. Vilas[1,4]

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KEYWORDS: biocompatible implants, shape-memory polymers, hydrogels, nanogels, optical fibers, printable smart materials, bioremediation, active packaging materials, silkworm fibroine

Since polymers were discovered in 1920 by Herman Staudinger, polymer science has grown to become today one of the fundamental scientific areas. Nowadays, the discovery and development of new polymeric materials is essential to continue contributing to the advancement of humanity.

Our research deals with the synthesis and analysis of new materials based on polymers in order to improve fundamental aspects of life. Our efforts are focused on four areas: biomedical devices, environmental improvement, self-healing and shape memory materials, textile and additive manufacturing.

BIOMEDICINE

New materials that reduce the infections caused by the adhesion of bacteria in medical implants are needed to minimize the rejection. For that, we considered “click” reaction the most appropriate strategy for the conjugation of complex organic structures on the surface of many materials. Other branches of our laboratory are natural based injectable hydrogels that enhance cell adhesion and lead to the development of a new generation of electroactive hydrogels to be applied in tissue engineering. In addition, biodegradable nanogels are also studied as specific drug carriers for new cancer therapies. Implementation of hollow-core polymer microstructured optical fibres as sensing platforms to allow the enhancement of various sensing methods such as the Raman Spectroscopy.

SHAPE MEMORY AND SELF-HEALING MATERIALS FOR TEXTILE INDUSTRY

Shape memory polymers (SMPs) are capable of fixing temporary shape and recovering to the permanent shape in response to external stimuli. Hydrogels with the ability to repair themselves after damage are another hot pot in our laboratory. These materials present more than one triggering stimulus that can be used to induce the shape memory and self-healing effect. Beyond all these, hybrid organic-inorganic interactions represent a highly interesting possibility due to their properties and versatility, allowing the fabrication of multiresponsive systems. Over the past few decades, smart functional textiles have been developing rapidly in our laboratory, textiles with novel functions such as temperature regulated textiles and self-moving textiles have been studied.

ADDITIVE MANUFACTURING

Additive manufacturing has developed rapidly in the last 10 years and has demonstrated significant potential in cost reduction of performance-critical components. To follow this road, our group is researching the development of wireless, sustainable and interconnected autonomous smart systems. Despite the large maturity of 2D and 3D printed technologies, the number of materials with suitable properties to be printed is still small. For this deal, we promote the use of polymers as printable smart materials for the development of more environmental friendly technologies into devices of materials.

ENVIRONMENTAL IMPROVEMENT

Finally, in order to reduce human environmental impact, we are working in new bioremediation techniques and in the substitution of petrochemical compounds by new bio-based polymers in three different ways:

- Using different innovative methods for remediation, as treatments with zero-valent iron nanoparticles (nZVI) as a cost effective and environmentally friendly agent for environmental remediation.
- Working in the long range of morphologies adopted by silkworm fibroin for sensors and actuators
- Alginate printed hydrogels with TiO_2 NPs for the capture and subsequent degradation of dyes in water. Degradation under UV radiation catalyzed by NP is essential.

ZIENTZIA ETA TEKNOLOGIA FAKULTATEA
FACULTAD DE CIENCIA Y TECNOLOGÍA
UPV EHU

Eguneroko Polimeroak

Labquimac

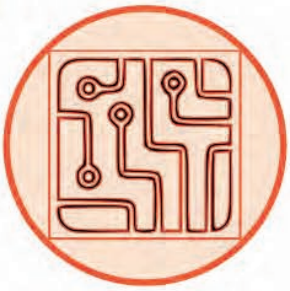
N. Álvarez[1], A. Martínez[1], I. Pinedo[2], G. Ventosa[1], R. Teijido[1,3], J. Andrade[1,4], S. Maiz[1,3], J. Sanchez[1], A. Valverde[1,3], C. Mendes[1,3], A. Reizabal[1,3], A. Burgoa[4], L. Etxeberria[4], A. Galdames[1], A. Veloso[1], J. M. Laza[1], L. Ruiz[1,3], L. Pérez[1,3], M. I. Moreno[2], J.L. Vilas[1,3]

[1]Kimika Makromolekularreko ikerketa-taldea(LABQUIMAC). Kimika Fisika Saila, ZTF, UPV/EHU; [2]Kimika Makromolekularreko ikerketa-taldea (LABQUIMAC). Kimika Organiko Saila I, ZTF. UPV/EHU; [3]BCMaterials. Basque Center for Materials, Applications and Nanostructures, UPV/EHU; [4]I+Med S.Coop, Arabako Parke Teknologikoa; [5]Leartiker. Markina-Xemein

Kimika Fisikoa sailaren barnean **Kimika Makromolekularreko ikerketa** taldea gara, **Jose Luis Vilas** irakaslearen zuzendaritzapean. Ikerketa ardatz nagusia material polimeriko berriak lortzea eta karakterizatzea da.

Sentsoreak

Sentsoreen fabrikaziorako material polimeriko berriak ikertzen dira, material polimerikoetan oinarrituriko tintak erabiliz material elektroniko malguen garapenerako, esaterako.

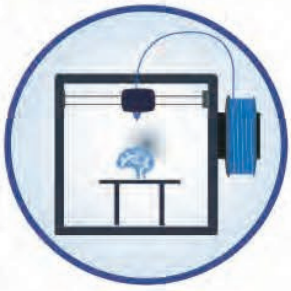


Aktuatzaileak

Kanpo estimulu baten aurrean birkonpontzeko ahalmena duten polimero ionikoak ekoizten dira, material aktiboak deiturikoak.

3D (Bio)inprimaketa

Egitura konplexuak aurkezten dituzten material polimerikoen 3D inprimaketa burutzen da biomedikuntza arloko aplikazioetarako, baita fabrikazio gehigarriarentzat mikroerreaktoreak edo dispositibo mikrofluidikoak eginez.

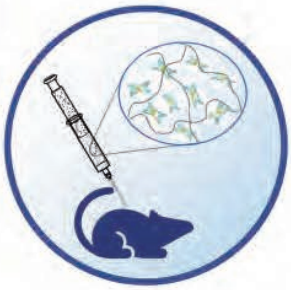


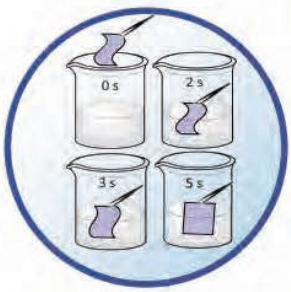
Inplante biofuntzionalak

Gainazal eraldaketak metodo eraginkorrak bilakatu egin dira inplante biofuntzionalak lortzeko. Horrela, material antibakterianoak, antifungikoak, antiinflamatoriak egin dira.

Hidrogel aktiboak

Hidrogelak aurkezten dituzten propietate oparotsuak direla eta, sintesi eta formulazio berriak dituzten material aurreratuak ekoiztu egin dira biomedikuntza aplikazioetarako.



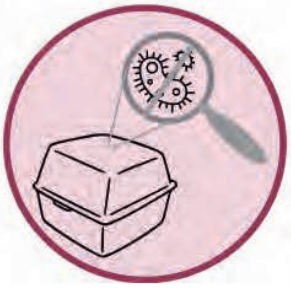


Itxura oroimena

Estimulu magnetiko edo termiko baten menpean aurre-itxura berreskuratzen duten polimero eta zuntzak garatzen dira, arropa eta dispositibo adimenduak sortzeko bidea zabalduz.

Paketatze aktiboa

Gainazalaren aldaketaren bidez propietate antibakterianoak eta hainbat propietate aurreratuak izan ahal dituzten paketatzeak ekoiztu egin dira.



Ingurumena

Polimeroz gaineztatutako metalezko nanopartikulak sintetizatzen dira lurzoruan aurkitzen diren hidrokarburo poli-ziklikoak degradatzeko, inguruneko kutsadura murriztuz.

@labquimac

Info gehiago

Computational and spectroscopic tools to design and study applied dyes and materials

Ruth Prieto, Edurne Avellanal, Ainhoa Oliden, Eduardo Duque, Leire Gartzia, Rebeca Sola, Jorge Bañuelos, Virginia Martinez, Teresa Arbeloa, Iñigo López Arbeloa.
Dpto. Química Física

KEY WORDS: dyes, fluorescence, nanomaterials, photoactive systems, laser, singlet oxygen, atomistic simulation, photodynamic therapy

The staff of the Molecular Spectroscopy Group features advanced skills in the synthesis and photophysical characterization of photoactive systems, as well as in the atomistic simulation of individual molecules and large-scale materials. To this aim, our laboratory is equipped with high-resolution and time-resolved spectroscopic, microscopic and laser-based techniques along the ultraviolet, visible and infrared spectral regions. Besides, we use computational clusters to run advanced excited state calculations and simulate complex molecular dynamics in the solid state. Such joined experimental and theoretical approaches allow us to tackle a wide assortment of dyes and nanostructure materials for different applications fields ranging for photonics to biomedicine and energy. Along the following lines, we briefly describe the three main topics of our research dealing with dye and materials chemistry, highlighting the pursued multifunctional applications.

1. **Organic applied dyes.** The computationally-assisted molecular design of versatile chromophores allows tailoring their photonic performance to develop lasers, fluorescent sensors and probes, photosensitizers and molecular antennae, which can be applied in photonics, chiroptics and biotechnology. The spectroscopic characterization of these dyes plays in key role, not only for a deep insight and understanding of the underlying photophysical mechanisms, but also to propose structural changes and improve their practical performance.

2. **Photoactive materials.** The rational design of photoactive hybrid systems based on the combination of organic dyes with different nanostructured hosts (mainly inorganic) ensures the achievement of new interesting photonic devices and materials for biomedicine. On the one hand, the tight confinement of dyes into zeolitic matrices (zeolites and aluminophosphates with different pore size), boots their luminescence properties and induces a preferential orientation of the dye, giving rise to materials featuring an optimal photonic performance for optical applications such as antenna systems, white-light emitters or frequency converters. On the other hand, the functionalization of silica-based nanoparticles and nanoMOFs with fluorescente dyes, singlet oxygen photosensitizersand other molecules of interest (such as polyethylene glycol and folic acid to enhance their stability in water and selectivity for tumor cells) renders new biocompatible agents for fluorescent bioimaging and photodynamic therapy applications to be potentially implemented in the detection and treatment of cancer diseases.

3. **Simulation of materials.** The use of computational methods, as molecular dynamics and more accurate DFT methods, provides valuable information for the interpretation of the experimental phenomena and for the design of new hybrid materials with tailored properties. These simulation tools can predict the diffusion, orientation and aggregation of dye molecules confined in inorganic host matrices and the mechanical performance by the study of strengthening mechanisms at atomic scale.

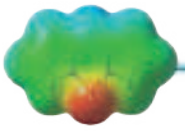
The successful achievement of our research scoped requires a multidisciplinary collaboration with research groups specialized in other fields, such as organic and inorganic synthesis, physics or biology. Such coordinated work enrich us and provide us the necessary feedback to improve and span the next generation of modern dyes and materials.

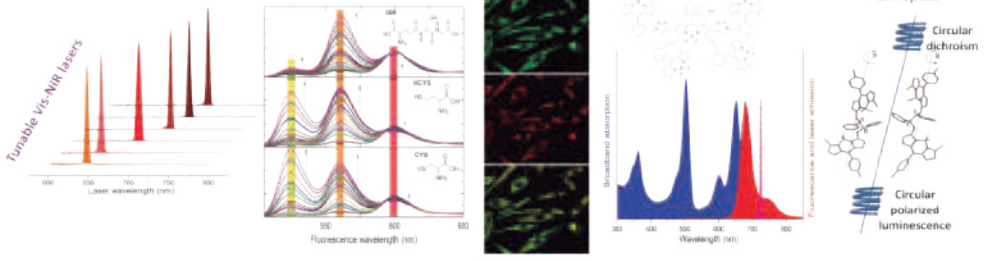
COMPUTATIONAL AND SPECTROSCOPIC TOOLS TO DESIGN AND STUDY APPLIED DYES AND MATERIALS

Dpto. Química Física

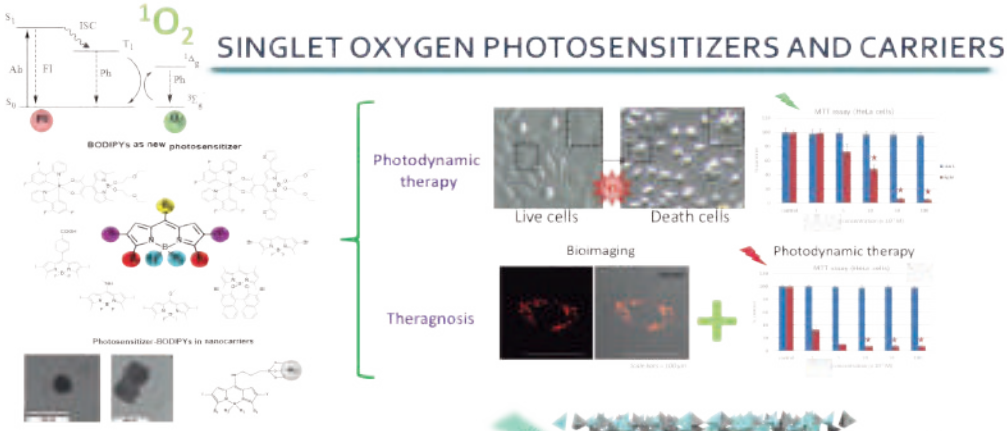
Iñigo López Arbeloa, Teresa Arbeloa López, Jorge Bañuelos Prieto, Virginia Martínez Martínez, Laire Cartzia Rivero, Rebeca Sola Llano, Eduardo Duque Redondo, Ruth Prieto Montero, Edurne Azcárate Zabalía, Aitziber Olaiz Sánchez, Carolina Díaz Norambuena

ORGANIC APPLIED DYES

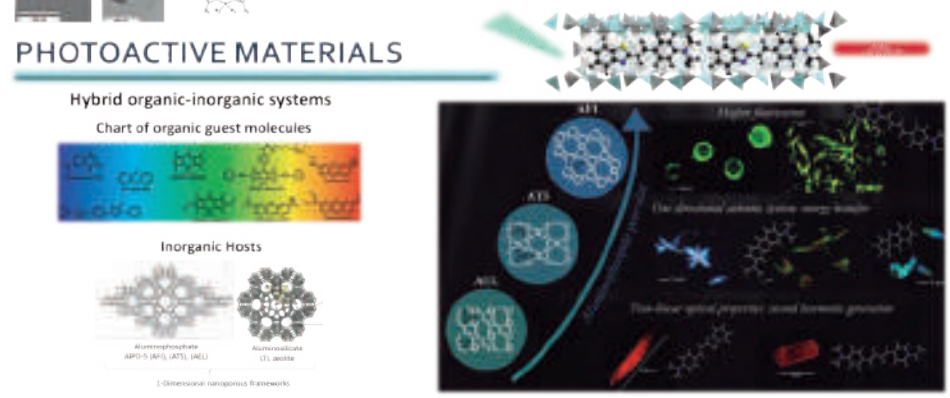




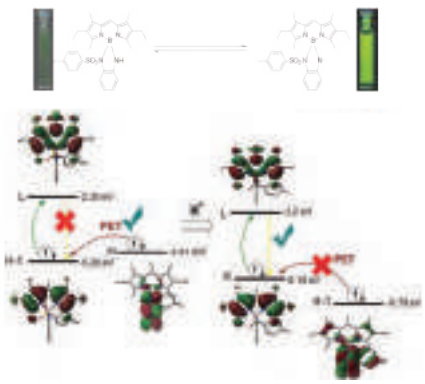
SINGLET OXYGEN PHOTOSENSITIZERS AND CARRIERS

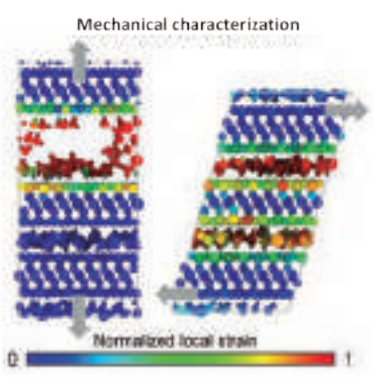


PHOTOACTIVE MATERIALS



THEORETICAL SIMULATIONS





MOLECULAR SPECTROSCOPY GROUP

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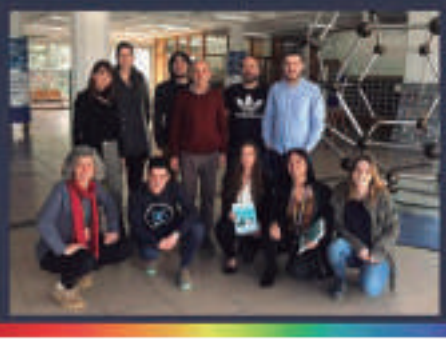
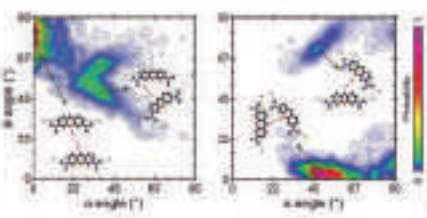


Prediction of dye aggregation



Quantum Computing and Quantum Technologies
QUTIS Center

Quantum Computing, Information, Sensing, and Optics. Microwave Quantum Technologies. Quantum Artificial Intelligence.

The International Center Quantum Computing and Quantum Technologies (QUTIS), led by Prof. Enrique Solano, develops cutting-edge theoretical research for the sake of fundamentals and applications in interdisciplinary fields related to quantum computing and quantum technologies. We relate concepts in quantum control and optics (Prof. Xi Chen), quantum sensing and information processing (Dr. Jorge Casanova), microwave quantum technologies and quantum architectures (Dr. Mikel Sanz), and quantum artificial intelligence (Prof. Enrique Solano). QUTIS Center is a dynamic, hard-working, and creative network of research groups led by world-class leaders with wide interests in arts, physics, science, technology, and entrepreneurship. We are strongly driven by intellectual curiosity, keeping as our main goal our aesthetic and scientific expression in an interdisciplinary and international environment. At the same time, we constantly search that our original cross-disciplinary ideas have a realistic approach towards experimental implementations and technological applications. QUTIS Center is committed to the team-oriented production of novel and influential ideas at the highest research level, where creative and innovative concepts merge with quantum technologies.

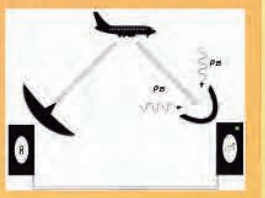
QUTIS CENTER

www.qutisgroup.com

The **International Center for Quantum Computing and Quantum Technologies (QUTIS)**, led by Prof. Enrique Solano, develops cutting-edge theoretical research for the sake of fundamentals and applications in interdisciplinary fields related to quantum computing and quantum technologies. We relate concepts in quantum optics (Prof. Xi Chen), quantum sensing and quantum information processing (Dr. Jorge Casanova), microwave quantum technologies and quantum architectures (Dr. Mikel Sanz), and quantum artificial intelligence (Prof. Enrique Solano). QUTIS Center is a dynamic, hard-working, and creative network of research groups led by world-class leaders with wide interests in arts, physics, science, technology, and entrepreneurship. We are strongly driven by intellectual curiosity, keeping as our main goal our aesthetic and scientific expression in an interdisciplinary and international environment. At the same time, we constantly search that our original cross-disciplinary ideas have a realistic approach towards experimental implementations and technological applications. QUTIS Center is committed to the team-oriented production of novel and influential ideas at the highest research level, where creative and innovative concepts merge with quantum technologies.

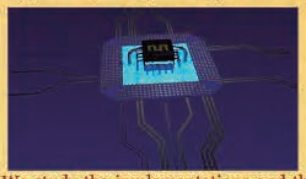
Microwave Quantum Technologies & Architectures (Mikel Sanz's group)

The main research line revolves around using **propagating quantum microwaves** in quantum sensing and quantum communications. In the former, we make use of techniques derived from **quantum metrology** to push ahead the limits of quantum illumination and Quantum Radars. On the latter, the problem of **distributed quantum computing** between several quantum processors (quantum LAN) attracts our interest.



The second fundamental research line is **quantum computing** in noisy intermediate-scale quantum (NISQ) devices. We look for quantum algorithms for real world applications, especially finance, chemistry, logistics and fluid dynamics, and study their implementation in current cloud quantum computers.

Based on the experience in this area, we are also exploring alternative quantum computing paradigms which can outperform digital quantum computation in these NISQ devices. In particular, we are exploring **hybrid classical-quantum algorithms**, especially variational quantum algorithms, and hybrid **digital-analog quantum computing**



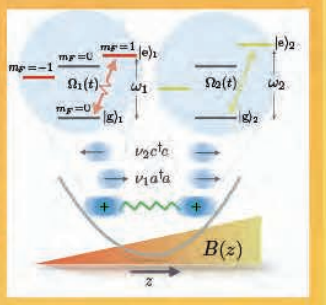
The third fundamental research area of the MQTA group comprises the theoretical and experimental applications derived from the **quantum memristor**, fundamentally in the technology of superconducting circuits.

We study the implementations and the properties of these devices not only with a purely fundamental interest, but also with a practical view focused on possible applications in **quantum neural networks**, simulation of non-Markovian dynamics, neuromorphic quantum computing, new non-linear optical devices in microwaves, such as photodetectors, among others.

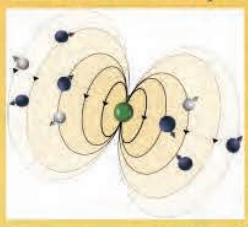
In general, we also feel attracted by the possibilities and applications superconducting circuit technology, such as the stronger novel **light-matter interaction**, which allows us to observe the quantum Rabi model, the implementations of the Dynamical Casimir effect, and their use in quantum simulations and quantum computing, among others.

Quantum Information Processing and Quantum Sensing (Jorge Casanova's Group)

We study how quantum information can be manipulated with trapped-ion quantum processors. Ion-trap quantum technology consists in the control and manipulation of single or multiple cold atomic ions that are trapped by means of electromagnetic fields. Lasers or microwave fields can be used to control two electronic levels of the ion that serve as a qubit. The motion of the ion is cooled down until it reaches the quantum regime. Currently, trapped-ion technology offers one of the highest degrees of controllability among quantum technologies, making it a good candidate for quantum simulation and quantum computation protocols.



We develop proposals for quantum simulations with trapped ions that include relativistic quantum mechanics and interacting fermion lattice models. This quantum platform also seems specially suitable for implementing digital-analog quantum simulations, a new approach that employs the complexity present in the system together with digital steps to enhance the simulator capability.



In our group we also study the **nitrogen-vacancy color center** (NV) as a platform for different future technologies. NV centers are diamond point defects that present a spin-1 ground state structure that can be initialized, measured and controlled using lasers and microwaves. NV centers show long coherence times even at room temperature.

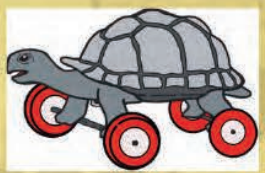
In our group we treat two different areas regarding the study of the NV center. On the one hand, we design radiation patterns that exert robust and coherent control over the NV for its two more promising applications: **Quantum sensing and hyperpolarization**, which are expected to have a big impact in different areas such as chemistry, biology and medicine.

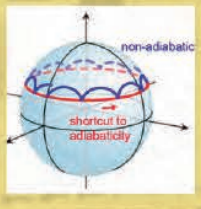
On the other hand, we develop tools based on machine learning and bayesian inference that are able to fit the measured signal coming from the NV into our mathematical models. This allows us to reconstruct the useful information collected by the NV in noisy and complex environments, which is key for its implementation in real applications.

Quantum Optics (Xi Chen's Group)

The quantum optics group performs research on **quantum optics**, as well as applied quantum technologies. We are interested, among others, in quantum optics, **cold atoms**, **photonic crystals**, **metamaterials**, **spintronics**, and **shortcuts to adiabaticity**.

We develop the technique of "shortcuts to adiabaticity" that provides an alternative to adiabatic protocols to control and guide the dynamics of classical and quantum systems without the requirement of slow driving. Particularly, the atom cooling and transport have been proposed by using shortcuts to adiabaticity, supplemented by variational approximation method, **optimal control theory**, and **deep machine learning**. These have the wide applications in quantum interferometry, quantum information and quantum thermodynamics.





Precise quantum controls in cold atom and solid-state physics platforms are investigated by hybridizing different methods. For instance, optimal STIRAP in atomic three-level systems is proposed by combing inverse engineering, optimal control, and composite pulse approaches. Similarly, the performance of quantum sensing in NV center spin can be further improved by incorporating shortcuts to adiabaticity into dynamical decoupling.

Our research also covers other aspects in physics, such as **spin-orbit coupled BEC**, **charge/spin states in quantum dots**, coupled optical waveguides, and **soliton dynamics in nonlinear optics**.

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Organic functionalization: the key factor to obtainsustainable polyoxometalate-based materials

Juan M. Gutiérrez-Zorrilla, Santiago Reinoso, Leire San Felices, Beñat Artetxe, Pablo Vitoria, Estibaliz Ruiz-Bilbao, Leticia Fernández-Navarro, Ángela Barros, Celia Elicegui, Luis Menéndez
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KEYWORDS: Polyoxometalates, Organic functionalization, Multifunctional behaviour.

Polyoxometalates (POMs) are a well-known class of metal–oxo anionic nanoclusters with a large compositional, structural and electronical versatility, which makes them suitable for a wide range of applications in fields such as catalysis, magnetism, biomedicine and material science, among others. Owing to their inherent features (high solution and thermal stability, high acidity, versatile redox properties), POMs are ideal candidates to be used as active molecular entities in the formation of advanced functional materials. More specifically, their combination with organic moieties constitutes a key factor to obtain active materials able to display novel properties derived from the synergy of both components. As much as four different research lines focused on the obtention of POM-based hybrid systems have been developed in our research group, which could be briefly described as follows:

1.- REPLACEMENT OF SHELL OXYGEN ATOMS: SMART POM/POLYMER COMPOSITES
This procedure is based on the substitution of surface oxygen atoms of the POM clusters with those belonging to either O– or N–donor ligands. Most typical examples following this approach include the covalent attachment of trisalkoxo ligands to Anderson–Evans type polyoxomolybdates, Lindqvist–type hexavanadates or trivanadium–capped Well–Dawson phosphotungstate derivatives. Covalent anchoring of those hybrids to classical organic polymers constitutes an optimal strategy to afford long-lived smart materials with self-healing and shape-memory behavior. Analogously, this approach can be used to covalently anchor bioactive POM species to polysaccharide nanoparticles, which are being tested for breast cancer treatments.

2.- ORGANIC DERIVATIZATION OF 4F-METAL SUBSTITUTED POMs WITH MAGNETO-LUMINESCENT PROPERTIES
The incorporation of 4f-metals into the vacancies of *lacunary* POMs, able to act as inorganic O-donor ligands, has resulted in one of the most extensively studied topics in synthetic POM chemistry. These 4f/POM systems can be combined with compartmental organic ligands which allow them to i) exhibit slow magnetization relaxation and magnetic hysteresis, being able to act as single-molecule magnets (SMM) and, more interestingly, as single-ion magnets (SIM); and ii) act as *antenna groups* to intensify the efficiency of the luminescent emission of lanthanides which is forbidden by Laporte rule.

3.- GRAFTING OF 3d-COMPLEXES AT POM SURFACE: GAS SORPTION, ENERGY STORAGE AND SCSC TRANSITIONS
The grafting of first-row transition metal complexes of macrocyclic ligands to POM surfaces results in three-dimensional crystalline frameworks with permanent porosity able to exhibit interesting functionalities for selective gas absorption (such as CO_2) and heterogeneous catalyst. This family of compounds have also shown the ability to display single-crystal-to-single-crystal (SCSC) structural transformations promoted by external stimuli, among which thermal dehydration processes stand out. Recently we have also extended our studies to sustainable energy storage systems, in which some hybrid networks have preliminarily demonstrated to display potential applications as cathodic and anodic materials of electrolytic cells.

4.- IMMOBILIZATION OF POMS IN METAL-ORGANIC SYSTEMS: BIFUNCTIONAL CATALYSTS
The catalytic activity of POMs in heterogeneous phase is limited because they usually display very low specific surfaces that make it difficult for the substrates to access to catalytically active centers. Thus, immobilization of POMs in porous solids such as metal-organic frameworks (POM@MOF) and gels (POM@MOG) overcomes these difficulties and facilitates the regeneration and recycling of the catalyst. Environmentally friendly solvent free synthetic methods have recently allowed the incorporation of the desired and controlled amount of POM species into both matrixes. The resulting hybrid materials could display synergistic effects and exhibit higher catalytic activity than that shown by both constituents separately.

COLLABORATORS: Dr. Óscar Castillo (UPV/EHU), Dr. J.L. Vilas, Laboratorio de Química Macromolecular (UPV/EHU), Dra. Eider Goikolea (UPV/EHU), Dr. J.A. García (UPV/EHU), Dr. J. Alcañiz-Monge (Universidad de Alicante), Dra. M.M. Vivanco (CICBiogune), Dr. U. Kortz (Jacobs University, Bremen), Dr. T. Liu (University of Akron, USA), Dra. E. Aranzabe (IK4-Tekniker).
FUNDING: MCIU (MAT2017-899553-P), EJ/GV (Grupos consolidados IT1291-19; PIBA 2018-59), ELKARTEK (KK2018/00054) and Predoctoral Grants to ERB (EJ/GV PRE_2018_1_0143) and LFN (EJ/GV PRE_2019_1_106).

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2020 Klima-aldaketa / Cambio Climático

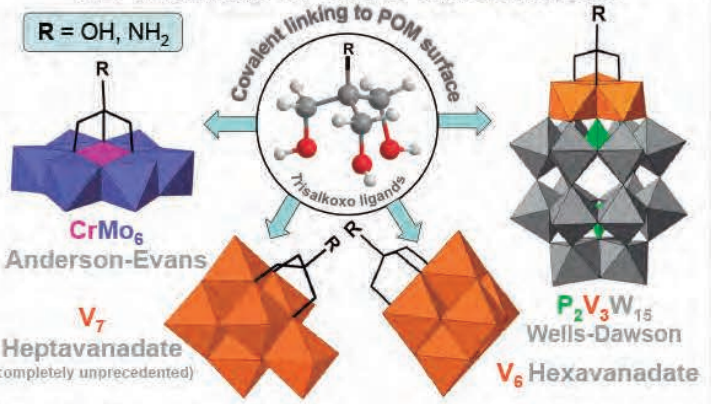
POM Research group

ORGANIC FUNCTIONALIZATION: THE KEY FACTOR TO OBTAIN SUSTAINABLE POLYOXOMETALATE-BASED MATERIALS

Juan M. Gutiérrez-Zorrilla, Santiago Reinoso, Leire San Felices, Beñat Artetxe, Pablo Vitoria, Estibaliz Ruiz-Bilbao, Leticia Fernández-Navarro, Ángela Barros, Celia Elicegui, Luis Menéndez

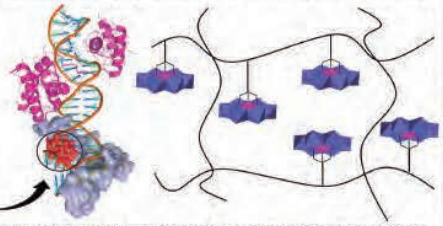
Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, P. O. Box 644, 48080 Bilbao, Spain

REPLACEMENT OF SHELL OXYGEN ATOMS



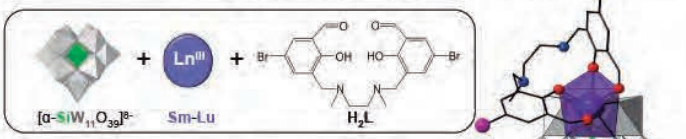
Covalent anchoring of these hybrids to organic polymers affords long-lived smart materials with **self-healing** and **shape-memory** behavior. Analogously, the grafting of bioactive POM species to polysaccharide NPs can be suitable for **biomedical applications**.

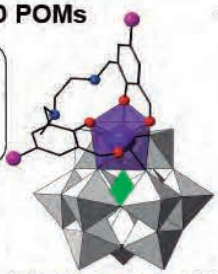
Bioactive Wells-Dawson-based POM@Chitosan pH-responsible nanohybrids are suitable for breast cancer therapy against the transcription activity of Sox2.



Pérez-Álvarez, L., Ruiz-Rubio, L., Artetxe, B., Vivanco, M. dM., Gutiérrez-Zorrilla, J. M., Vilas-Vilela, J. L. *Carbohydrate Polymers* **2019**, *213*, 159-167.

4f-METAL SUBSTITUTED POMs

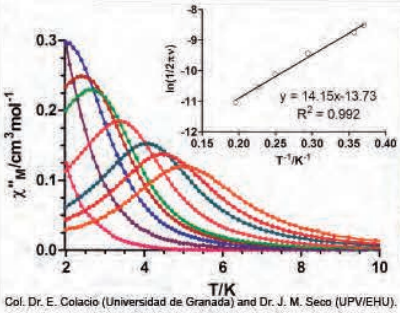


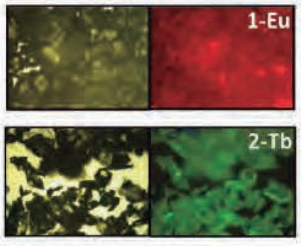


The self-assembly of 4f-based POMs with compartmental organic ligands (H_2L) allows these systems to: i) act as single-molecule magnets (**SMM**) and ii) **luminescent** materials

$K_5[Ln^{III}(\alpha\text{-}SiW_{11}O_{39})(L)]$

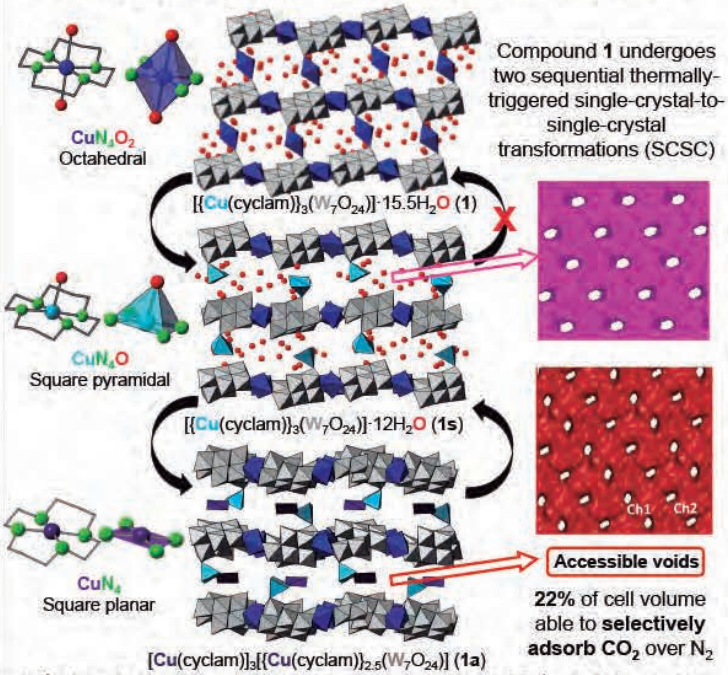
	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SMM	x	x	✓	x	x	x	x	x	✓	x
PL	✓	✓	x	✓	x	x	x	✓ IR	✓ IR	x





Col. Dr. E. Colacio (Universidad de Granada) and Dr. J. M. Seco (UPV/EHU).

GRAFTING OF 3d-COMPLEXES AT POM SURFACE



Compound **1** undergoes two sequential thermally-triggered single-crystal-to-single-crystal transformations (SCSC)

Accessible voids

22% of cell volume able to **selectively adsorb CO_2** over N_2

J. Martín-Caballero, B. Artetxe, S. Reinoso, L. San Felices, O. Castillo, G. Beobide, J. L. Vilas, J. M. Gutiérrez-Zorrilla, *Chem. Eur. J.* **2017**, *23*, 1-14.

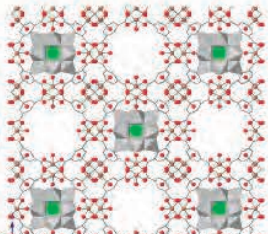
POMs IN METAL-ORGANIC SYSTEMS

POM@MOF

$Cu(Ac)_2{\cdot}H_2O$ 3 mmol + $C_9H_3O_6$ (H_3Btc) 2.1 mmol

$H_4SiW_{12}O_{40}$ 0.05-0.15-0.25 mmol

Manual milling



Green chemistry — Solvent-free reaction

C. Y. Sun *et al. J. Am. Chem. Soc.* **2009**, *131*, 1883-1888.

$[Cu_2(Btc)_3]{\cdot}x(H_4SiW_{12}O_{40}){\cdot}nH_2O$ (x = 0.03, x = 0.11, x = 0.25)

Incorporation of the desired and controlled amount of POM species

Bifunctional Heterogeneous catalysis
- Synergist effect of catalytic properties
- Catalytic centers increase
- Surface area decreases

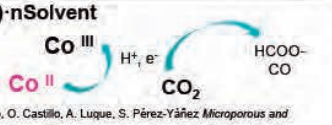
POM@MOG

$ZrCl_4$ 1.66 mmol + $C_9H_3O_6$ (H_3Btc) 1.35 mmol

POM: $K_4(CoSiW_{11}O_{39})$ / $H_4SiW_{12}O_{40}$

$[Zr_6O_4(OH)_4(Btc)_{2.13}(HBtc)_{2.81}]{\cdot}x(POM){\cdot}nSolvent$

Photocatalysis
Photo/electro-reduction of CO_2



J. Santos-Lorenzo, R. San José-Velado, J. Albo, G. Beobide, P. Castaño, O. Castillo, A. Luque, S. Pérez-Yáñez *Microporous and Mesoporous Materials* **2019**, *284*, 128-132.

Collaborators: Dr. J. L. Vilas, (Laboratorio de Química Macromolecular, UPV/EHU), Dr. J. A. García (Dpto. De Física Aplicada II, UPV/EHU), Dr. J. Alcañiz-Monge (Universidad de Alicante), Dra. M. M. Vivanco (CICBiogune), Dr. U. Kortz (Jacobs University, Bremen), Dr T. Liu (University of Akron, USA), Dra E. Aranzabe (IK4-Tekniker).

Financial support: MCIU (MAT2017-899553-P), EJ/GV (Grupos consolidados IT1291-19; PIBA 2018-59), ELKARTEK (KK2018/00054) and Predoctoral Grants to ERB (EJ/GV PRE_2018_1_0143) and LFN (EJ/GV PRE_2019_1_106).

Materials and Solid State Chemistry Group: Unravelling Materials for a Better World

T. Rojo L. Lezama, A. Goñi, M. Insausti, I. Gil de Muro, A. Peña, I. Ruiz de Larramendi, J. Lago, J.M. Rojo, V. Palomares, E. Goikolea, I. Castellanos-Rubio, O.K. Arriortua, I. Galarreta, V. Vadillo, N. Nieto, D. Iglesias, J. Rodríguez, A. Barón
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KEY WORDS: spinel, nanoparticles, superparamagnetism, electron magnetic resonance, magnetic hyperthermia, lithium/sodium-ion batteries, lithium/sodium-ion hybrid capacitors and lithium/sodium-O_2 batteries, electrochemistry.

The Materials and Solid-State Chemistry group is specialized in the design, synthesis and characterization of materials of technological and biomedical interest. Currently, the materials we develop seek to respond to the society's challenges, focusing in particular on (i) health and (ii) climate, energy and mobility.

DESIGN OF NOVEL THERANOSTIC PLATFORMS BASED ON MAGNETIC NANOPARTICLES

Magnetic nanoparticles (MNP) are revolutionizing the field of biomedicine for their capacity to generate localized heating so as to accomplish cellular stimulation or to attain tumour selective hyperthermia, among others. Moreover, their dual function, as magnetic hyperthermia agents and as contrast enhancement agents, has made them grow into a paradigm in the theranostics field. The magnetic properties and the heating capacity of the MNPs are strongly dependent on the size, shape, crystallinity, homogeneity and collective behaviours. Our goal is to design novel multifunctional platforms with large magnetothermal actuation and minimal agglomeration among NPs to contribute to the improvement of magnetic hyperthermia therapies. Thus, our research line is focus on three main tasks:

- Optimization of the chemical routes to obtain high quality ferrite-based nanoparticles of different sizes, composition and shapes.
- Surface modification of MNPs to achieve bio-functionalized polymeric coatings.
- Fabrication of multilayered microdisks loaded with MNPs, biomolecules and fluorophores.

Optimal formulations have been successfully used for hyperthermia treatment in-vitro using colon cancer-derived cell line, and have caused complete cell death at 48 h post-hyperthermia. In addition, these platforms have shown high resistance to endocytosis and unprecedented reproducibility of the heating power within cell environment. These results open up promising opportunities in the development of next-generation medical technologies.

MATERIALS FOR THE NEXT GENERATION OF ELECTROCHEMICAL ENERGY STORAGE TECHNOLOGIES

The research on new energy storage technologies, both for portable and stationary applications, has become an urgent need for the transition from the existing energy model to a more sustainable one based on renewable energies. Three emerging technologies, lithium/sodium-ion batteries, lithium/sodium-ion hybrid capacitors and lithium/sodium-O_2 batteries, have the ability to meet this demand and revolutionize the energy storage industry. Our work focuses on the development of new materials with potential applications in the three mentioned technologies. Based on the experience accumulated in our group in the synthesis and characterization of advanced materials, we develop new series of families of materials that allow improving the efficiency of these electrochemical devices. Specifically, the systems explored are:

- Cathodes: polyanionic compounds and transition metal layered oxides.
- Anodes: carbon derivatives from biomass residues.
- Electrolytes: new formulations in glyme-type solvents, ceramic materials and inorganic/polymeric type composite materials.

Characterization of the different materials comprises powder X-ray diffraction, thermogravimetric analysis, Dynamic Light Scattering (DLS), Scanning and Transmission Electron Microscopy (SEM/TEM), magnetic and hyperthermia measurements and Electron Magnetic Resonance Spectroscopy. The electrochemical measurements are conducted using coin-cell and Swagelok-type cells. In addition, post mortem studies of the cycled electrodes are performed by EPR and XPS techniques in order to further analyze the evolution of the materials.

Universidad del País Vasco · Euskal Herriko Unibertsitatea

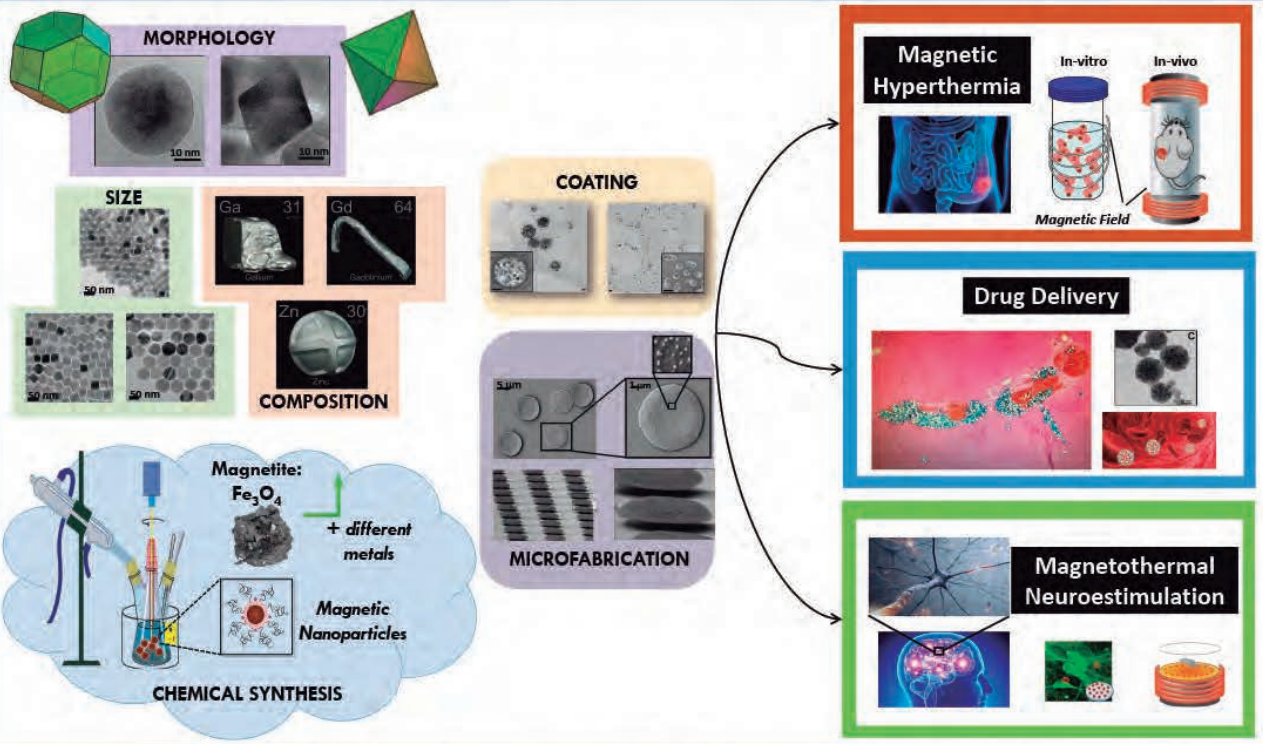
FACULTY OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF THE BASQUE COUNTRY

Materials and Solid State Chemistry Group: Unravelling Materials for a Better World

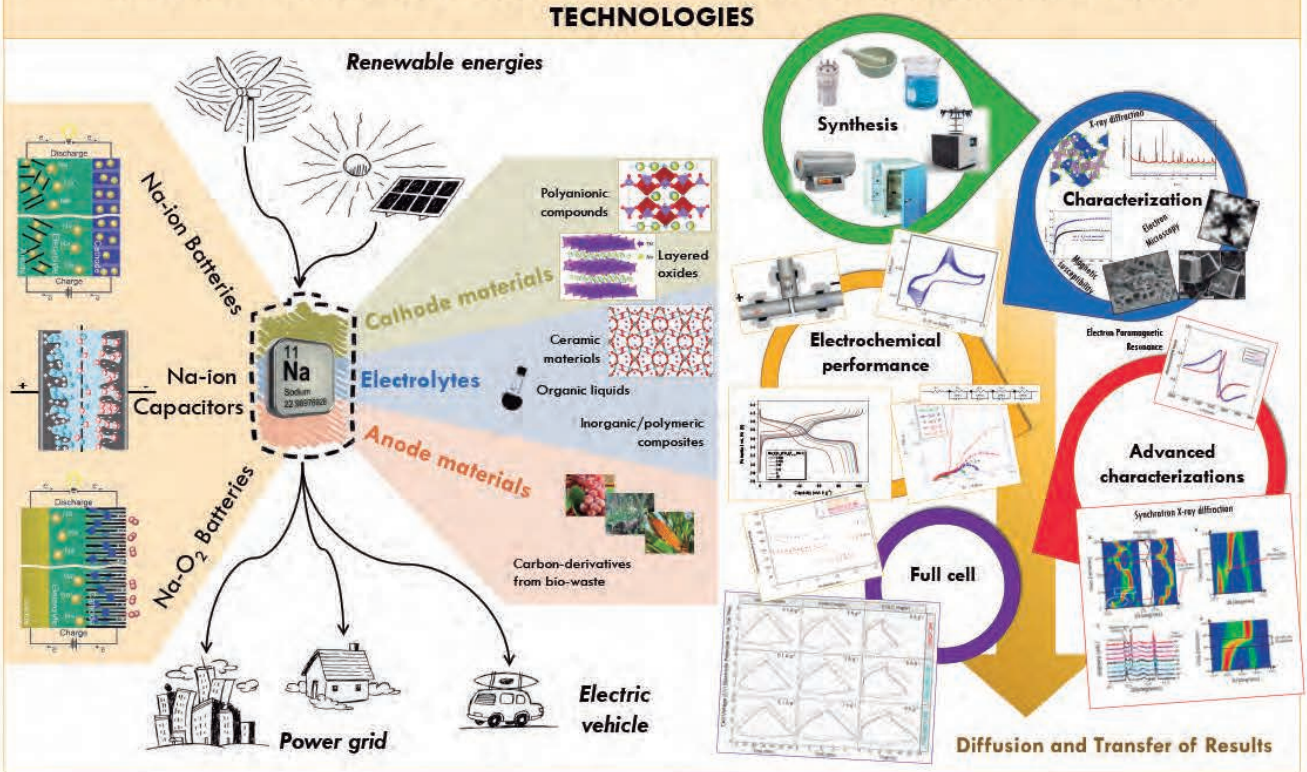
T. Rojo L. Lezama, A. Goñi, M. Insausti, I. Gil de Muro, A. Peña, I. Ruiz de Larramendi, J. Lago, J.M. Rojo, V. Palomares, E. Goikolea, I. Castellanos-Rubio, O.K. Arriortua, I. Galarreta, V. Vadillo, N. Nieto, D. Iglesias, J. Rodríguez, A. Barón

Departamento de Química Inorgánica

DESIGN OF NOVEL THERANOSTIC PLATFORMS BASED ON MAGNETIC NANOPARTICLES



MATERIALS FOR THE NEXT GENERATION OF ELECTROCHEMICAL ENERGY STORAGE TECHNOLOGIES



Financial support from the University of the Basque Country (UPV/EHU), the Eusko Jaurlaritza/Gobierno Vasco and the Ministerio de Economía y Competitividad of Spain is acknowledged.

Porous metal-organic materials

O. Castillo, G. Beobide, A. Luque, M. Lanchas, J. Pascual, R. Pérez-Aguirre, S. Pérez-Yañez, M. Perfecto, and P. Román
Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apartado 644, E-48080 Bilbao, Spain.
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KEY WORDS: Metal-organic frameworks, metallogels, aerogels, porosity.

This contribution aims to provide an insight into the main lines of our research group. They comprise a great variety of materials that share two common features: their metal-organic and porous nature. Below you can find a more detailed description of each family of materials

Metal−organic frameworks (MOFs). Metal–organic frameworks (MOFs) are a class of hybrid materials comprising metal ion-based vertices and organic ligands (linkers) that serve to connect the vertices into two or three-dimensional periodic structures. The structures and properties of MOFs can be carefully tailored by judicious selection of metal ion and organic linker building blocks. They encompass an area of chemistry that has experienced impressive growth during the last decades because of their various potential applications in catalysis, gas storage, chemical separations, sensing, ion exchange, drug delivery, and optics. Regarding the adsorption field, it is worth mentioning that their large surface areas, adjustable pore sizes, and controllable functionalities are key factors that make MOFs promising candidates for adsorptive separations and purification purposes.

Supramolecular Metal-Organic Frameworks (SMOFs). Taking into account the great potential of MOFs, we decided to explore a related type of material, in which the coordination bonds are replaced with hydrogen bonds as connectors, which are also directional and predictable interactions, to sustain the three-dimensional (3D) crystal building containing potentially accessible voids. Although such kinds of alternative materials can arise a similar fascination to that of MOFs, the crystal engineering principles and the synthetic approach are not yet settled, and examples of this kind of material are rather scarce.

Metal-organic gels (MOGs) and Metal-organic aerogels (MOAs). In the last few years, metal-organic gels (MOGs), also called metallogels, have emerged as an alternative material to MOFs. Ideally, during the gel formation, the coordination polymer grows as nanoscopic primary particles that crosslink stochastically into the reaction media, creating a 3D solid network that entraps all synthesis solvent within. Gel drying by evaporation of the solvent induces a severe shrinkage of the microstructure and leads to a material called xerogel (MOX, metal-organic xerogel) with reduced porosity. Contrarily, supercritical drying of MOGs removes the solvent without collapsing their microstructure, and it leads to metal-organic aerogels (MOAs) that are hundred of times lighter than MOFs. Therefore, porosity in MOGs and MOAs has a microstructural origin and not a strictly crystallographic one like in MOFs. Thus, the gelation approach enables the preparation of porous materials from metal-organic systems that do not necessarily render an open framework. Keeping in mind that the examples of MOGs and MOAs are still relatively rare, there is an exciting chance to prepare metal-organic porous materials from coordination polymers that lack crystalline origin porosity but gather striking electrical, magnetic, and optical properties.

Finally, another objective of the research groupr is to incorporate into these materials a broad scope of biomolecules with the aim of taking advantage of their molecular recognition capabilities for sensing, catalysis, capture and separation purposes.

METAL-ORGANIC POROUS MATERIALS

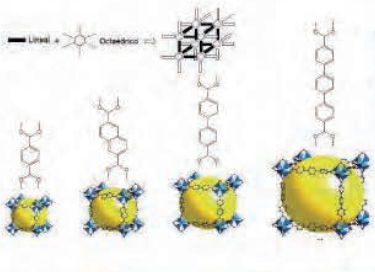
Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are microporous crystalline materials, which have become a very substantial field of research over the last years. Structures of MOFs consist essentially of inorganic nodes, isolated metal atoms or metal clusters, which are linked by organic molecules. Fascinated by the properties of MOFs, we are immersed in the following issues:

- **MOFs (Metal-Organic Frameworks) based on group 4 metals**
- **SMOFs (Supramolecular Metal-Organic Frameworks) based on metal-nucleobase systems**
- **MOGs (Metal-Organic Gels) and MOAs (Metal-Organic Aerogels)**
- **Solvent-free synthesis**

GREEN CHEMISTRY

Production of MOFs by novel, ecological and efficient synthetic routes. These procedures are industrially scalable, reduce production costs and have a greater convergence with the criteria of green chemistry.

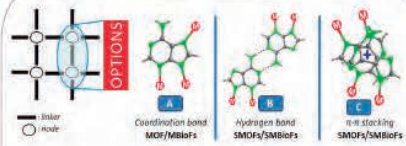
Metal source + Nucleobase + Carboxylic acid

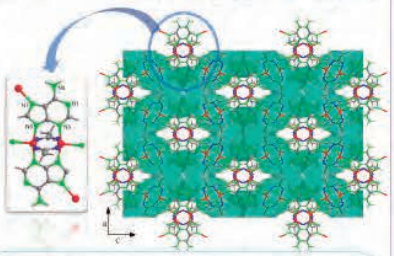


Metal-Organic Framewoks (MOFs) consist of metal ions or clusters coordinated to mostly rigid organic molecules to form porous 3D-structures. They constitute an emerging class of materials useful in gas storage, purification and separation applications as well as in heterogeneous catalysis. They not only offer higher surface areas than currently used materials like zeolites or activated carbon, but also provide shape/size selectivity which is important for both separations and catalysis.

SEM image of a Metal-Organic Porous Material

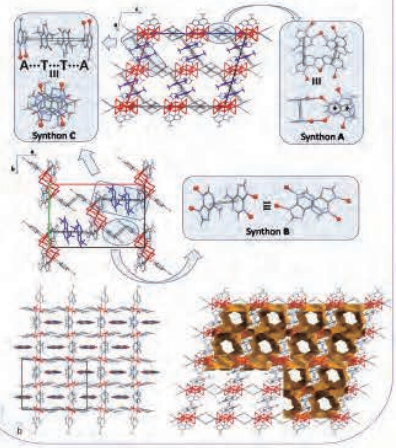
SMOFs / MBioFs





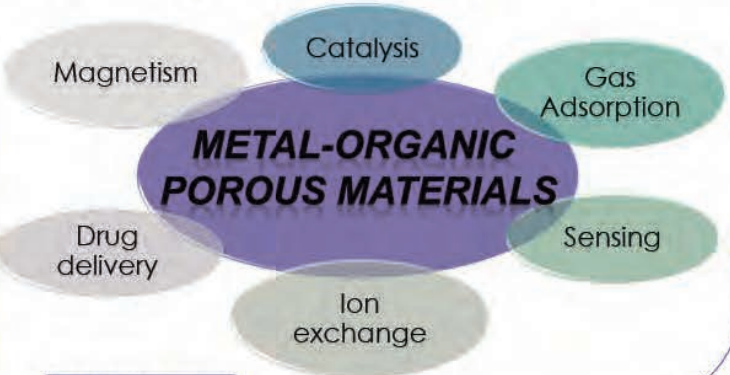
Recently, biomolecules have emerged as building blocks for constructing **Metal-Biomolecule Frameworks (MBioFs)**. MBioFs are defined as MOFs constructed from at least one biomolecule which serves as an organic linker.

When the interactions present among these biomolecules are supramolecular, as in the double helix of the DNA, (hydrogen bonds and / or π-π interactions), we have the so-called **SupraMBioFs.**



MOGs / MOAs

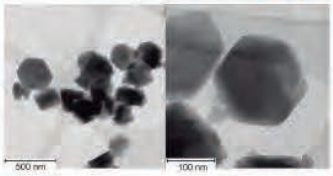
Aerogel is a synthetic porous ultralight material derived from a gel, in which the liquid component of the gel has been replaced by a gas. The result is a solid with extremely low density (< 0,05 g/cm³), low thermal conductivity and high inner unoccupied space (95%),

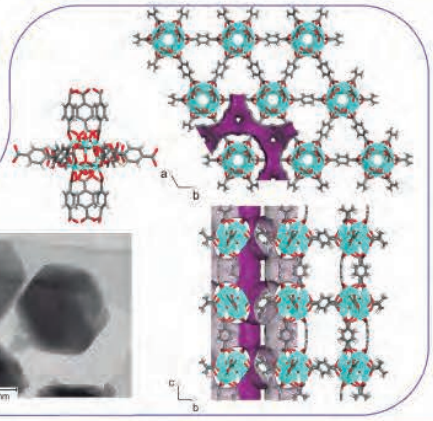


M^{IV}-MOFs

Metal-organic frameworks based on group 4 metals (Ti, Zr, Hf): MOFs based on tetravalent metals (4+) establish strong bonds that allow the formation of highly stable porous structures with a wide range of applications.

Zr-EHU-30



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VII JORNADAS DE INVESTIGACIÓN DE LA FACULTAD DE CIENCIA Y TECNOLOGÍA

16-18 de marzo de 2020

Organometallics in synthesis

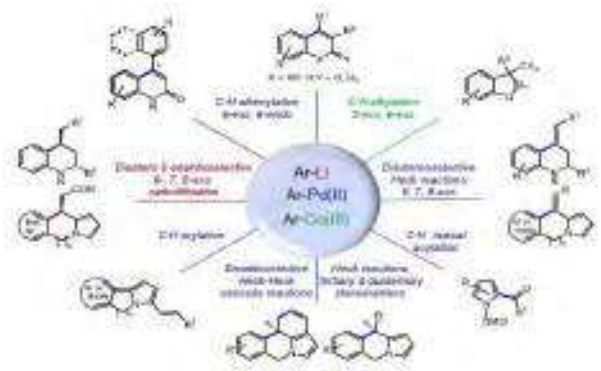
I. Barbolla,[1] A. Carral,[1] C. Santiago,[1] M. Martínez,[1] E. Vasquez [1] K. Dieguez,[1] R. Santana,[1] A. S. Beltrán,[1] B. C. Fundora,[1] X. J. Aberasturi,[1] Y.A. Velasquez,[1] S. He,[1] S. Arrasate [1] H. González-Díaz,[1,2] N. Sotomayor,[1] E. Lete[1]
[1]Departamento de Química Orgánica II, Facultad de Ciencia y Tecnología, UPV/EHU. [2]IKERBASQUE

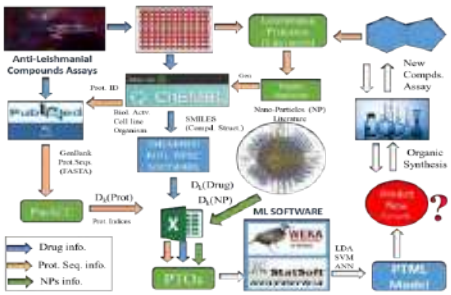
KEY WORDS: synthesis, catalysis, chemoinformatics.

The group has a solid background in Organic Synthesis, which allows us to face the preparation and structural determination of any kind of organic molecules. Our projects are focused on the development of effective and selective methods of C-C bond formation via transition metal-catalyzed C-H functionalization reactions to provide access to biologically relevant molecules. Here asymmetric catalysis becomes the vehicle to address the issue of enantioselectivity in an atom-economic fashion. Perturbation-Theory Machine Learning Predictive Algorithms are also developed to help in the reaction optimization and the drug-discovery process.

Synthesis. Metal-catalyzed reactions in the synthesis and functionalization of heterocycles. The application of palladium-catalyzed C-C bond forming reactions is studied for the synthesis of heterocyclic systems. We have shown that Heck-type reactions, direct C-H arylation and both inter and intramolecular C-H alkenylation reactions are versatile and effective tools for the synthesis of polyfunctionalized medium-size rings. Asymmetric variants and cascade reactions have also been developed. Palladium-catalyzed dehydrogenative heck reaction for the generation of axial quirality, as well as C-H radical acylation has also been studied. Now we are involved in C-H activation reactions catalyzed by a cheap and earth-abundant Cp*Co(III) catalyst.

Computational chemistry. Machine learning approaches for prediction of chemical reactivity/biological activity. We are also developing new computational multi-target QSRR methods capable of predicting reactivity or enantioselectivity of a given reaction when structural modifications (on substrates, ligands or catalysts) or experimental conditions are carried out. On the other hand, multi-target QSAR (quantitative structure-activity relationship) or QSTR (structure-toxicity relationship) models are also being carried out models that may be useful tools for the prediction of more effective and safer drugs.





For a recent review on our work, see: *Targ. Heterocycl. Syst.* **2019**, *23*, 340.

For some selected publications: *J. Org. Chem.* **2020**, *85*, 4, 2486-2503; *J. Chem. Inf. Model.* **2018**, *58*, 1384; *J. Org. Chem.* **2019**, *84*, 2048; *J. Chem. Inf. Model.* **2019**, *59*, 31109; *Curr. Top. Med. Chem.* **2019**, ahead of print; *ACS Chem. Neurosci.* **2019**, *10*, 4476-4491; *J. Org. Chem.* **2019**, *84*, 10183; *Eur. J. Org. Chem.* **2017**, 2462 (*SYNFACTS* **2017**, *13*, 0693), *ACS Omega,* **2017**, *2*, 2706; *Mar. Drugs* **2017**, *15, 276; RSC Adv.* **2016**, *6*, 38602; *Adv. Synth. Catal.* **2015**, *357,* 3206; *Adv. Synth. Catal.* **2015**, *357*, 463; *Adv. Synth. Catal.* **2014**, *356*, 1853.

More detailed information can be found in our web page: www.ehu.eus/es/web/oms/home

Organometallics in Synthesis

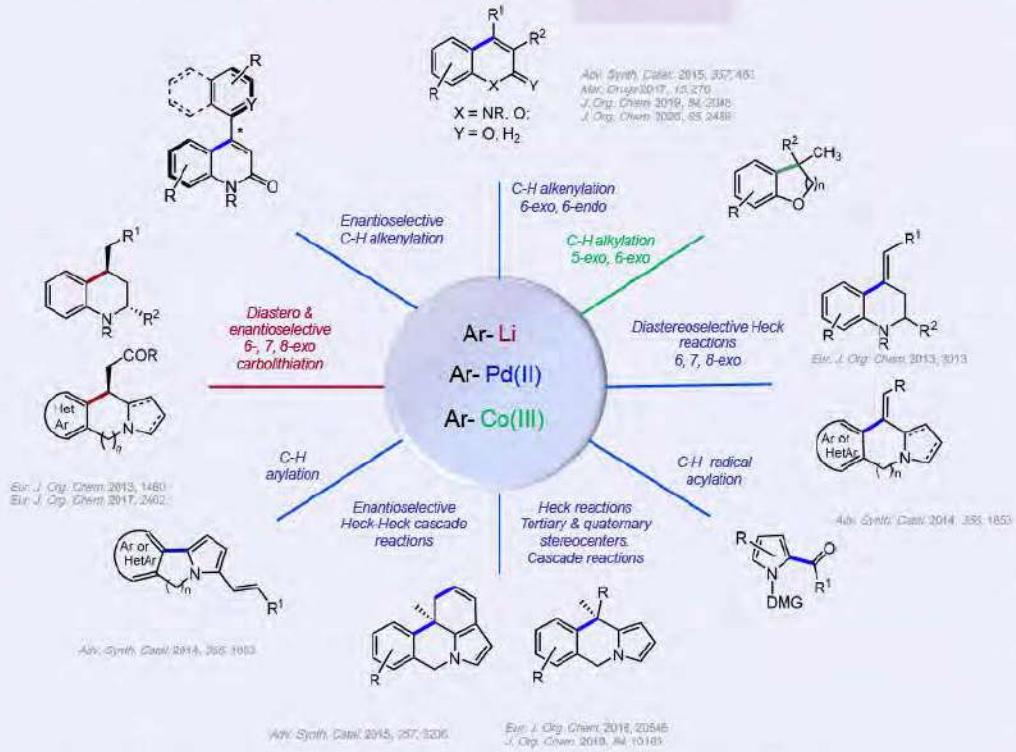
I. Barbolla,[1] A. Carral-Menoyo,[1] C. Santiago,[1] M. Martínez-Nunes,[1] E. Vasquez,[1] K. Diéguez,[1] A. Beltrán,[1] B. Fundora,[1] X. Jiménez de Aberasturi,[1] Y. Velasquez,[1] S. He,[1] S. Arrasate,[1] H. González-Díaz,[1,2] N. Sotomayor,[1] E. Lete[1]

[1]Departamento Química Orgánica II, Facultad de Ciencia y Tecnología, Universidad del País Vasco/Euskal Herriko Unibertsitatea
[2] IKERBASQUE
www.ehu.es/oms

Collaborations and visiting students: R. Santana *(Universidad de Deusto),* H. Bediaga *(Dpto. Química Física, UPV/EHU),* L. Hernandez; C. Lanza *(F. Medicina, UPV/EHU),* G. Yong Macías *(Universidad Autónoma del Estado de México).*

Our group works on Organic Synthesis. Our projects are focused on the development of synthetic methodology based on organometallic chemistry and asymmetric catalysis, and applied to the synthesis of heterocyclic systems, potentially active compounds, natural products or drugs. We also carry out interdisciplinary projects that involve computational chemistry and machine learning tools for reactivity prediction, and for the design of biologically active molecules.The group has a solid background in Organic Synthesis, which allows us to face the preparation and structural determination of organic molecules. Our research interests are summarized in the following topics

Metal-catalyzed reactions in the synthesis and functionalization of heterocycles



The synthetic utility of the carbolithiation reactions has been shown by application to the synthesis of a variety of structures with relevant biological activities.

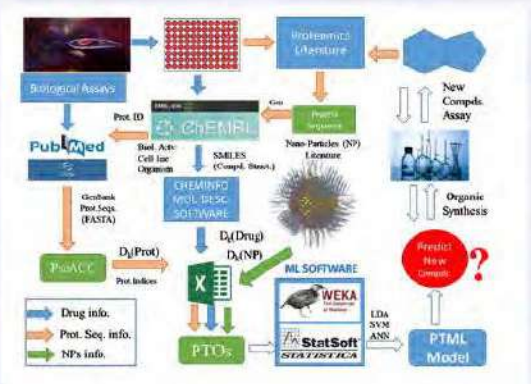
Methodologies based on Pd(0) and Pd(II) catalysis are also developed. We have shown that Heck-type reactions, direct C-H arylation and both inter- and intramolecular C-H alkenylation reactions are versatile and effective tools for the synthesis of polyfunctionalized medium-size rings. Asymmetric variants, including generation of axial chirality, and cascade reactions have also been developed. Pd(II) catalyzed oxidative C-H acylation reactions are also being developed for the synthesis of drug-like compounds.

The use of more abundant and less toxic first raw metals, such as Co(III) for these types of reactions is also being studied.

Computational models for the prediction of chemical reactivity, biological activity and toxicity

We are developing new computational multi-target QSRR (quantitative structure-reactivity relationship) methods capable of predicting reactivity or enantioselectivity levels of a given reaction when structural modifications (on substrates, ligands or catalysts) or experimental conditions are carried out.

On the other hand, we are also developing PTML multi-target QSAR (quantitative structure-activity relationship) or QSTR (structure-toxicity relationship) models that may be useful tools for the prediction of more effective and safer drugs (anti-microbial, anti-cancer, neuroprotective drugs, etc.).



PTML models for biological activity

J. Chem. Inf. Model. 2019, 59, 1109
ACS Chem. Neurosci. 2019, 10, 4475
ACS Comb. Sci. 2018, 20, 621
J. Proteome Res. 2017, 16, 4093
Curr. Top. Med. Chem. 2017, 17, 2991

PTML models for chemical reactivity

J. Chem. Inf. Model. 2018, 58, 1364
RSC Advances. 2016, 36602
ChemistryOpen 2016, 540

Vistit our web page

Seeking more sustainable alternatives for chemical synthesis

Esther Domínguez, Raul SanMartin, María Teresa Herrero, Imanol Tellitu, Garazi Urgoitia, Galder Llorente, Maria Obieta, Miriam Feijoo and Eduardo Gil

[1] Department of Organic Chemistry II, Faculty of Science and Technology, University of the Basque Country (UPV/EHU). Sarriena auzoa z/g, 48940 Leioa.

KEY WORDS: sustainable chemistry, new catalysts, renewable sources

Our research group (NEWSYNMETH) works actively on the synthesis of compounds of industrial interest using new catalyst systems in sustainable media. New applications for metal complexes featuring improved catalytic profiles are constantly sought so that the access to chemical entities (biologically active compounds, natural products, new materials) is simplified, the presence of metal traces in final products minimized and sustainable reaction media are used. Cascade and multicomponent reactions are explored in order to shorten synthetic sequences and to improve the atom-economy of the whole process. As part of the so-called chemical recycling and circular economy, catalytic degradation of industrial waste materials is also under research in our laboratories.

SEEKING MORE SUSTAINABLE ALTERNATIVES FOR CHEMICAL SYNTHESIS

Department of Organic Chemistry II

NEWSYNMETH Group Staff

Esther Domínguez
M. Teresa Herrero
Raul SanMartin
Imanol Tellitu
Garazi Urgoitia

PostDoc, PhD & MS students

Miriam Feijoo
Eduardo Gil
Galder Llorente
Maria Obieta

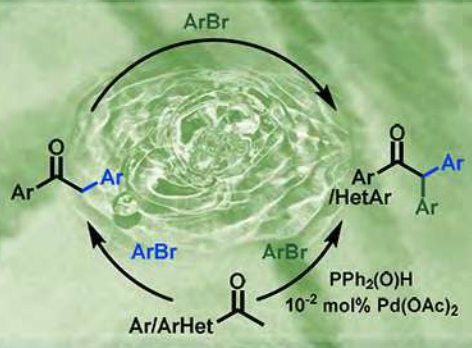
Our research group works actively on the synthesis of compounds of industrial interest using new catalyst systems in sustainable media

- New applications for metal complexes featuring improved catalytic profiles are constantly sought so that the access to chemical entities is simplified, the metal traces in final products minimized and sustainable reaction media used

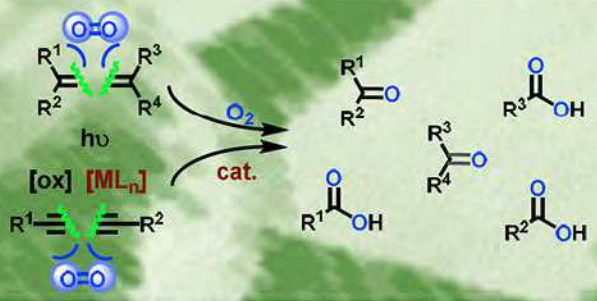
- Cascade and multicomponent reactions are explored in order to shorten synthetic sequences and to improve the atom-economy of the whole process

- Catalytic degradation of industrial waste materials is also under research in our laboratories as part of the so-called chemical recycling and circular economy

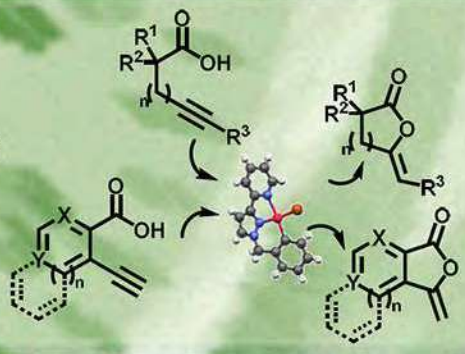
REACTIONS IN AQUEOUS OR SUSTAINABLE MEDIA



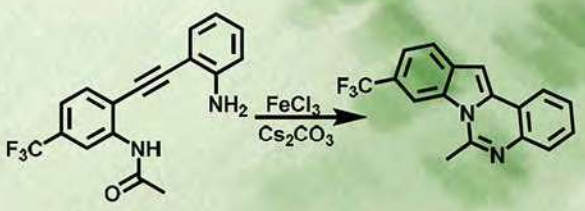
ENVIRONMENTALLY BENIGN REAGENTS



DEVELOPMENT OF METAL CATALYST SYSTEMS ACTIVE IN INFINITESIMAL AMOUNTS



REPLACEMENT OF MULTI-STEP SYNTHETIC PATHWAYS BY CASCADE REACTIONS



SOME RESEARCH PAPERS

Group of Asymmetric Synthesis, Sustainable Chemistry and Biomimetic Processes ORGANOCatalysis and Climate Change

Jose L. Vicario, Luisa Carrillo, Efraím Reyes, Uxue Uria, Liher Prieto, Javier Luis, Sandra Rodriguez, Lorena Garcia, Estefanía Capel, Jana Sendra, Aketza Romaniega, Nerea Betanzos, Chiara Portolani*
Department of Organic Chemistry II, Faculty of Science and Technology, UPV/EHU.

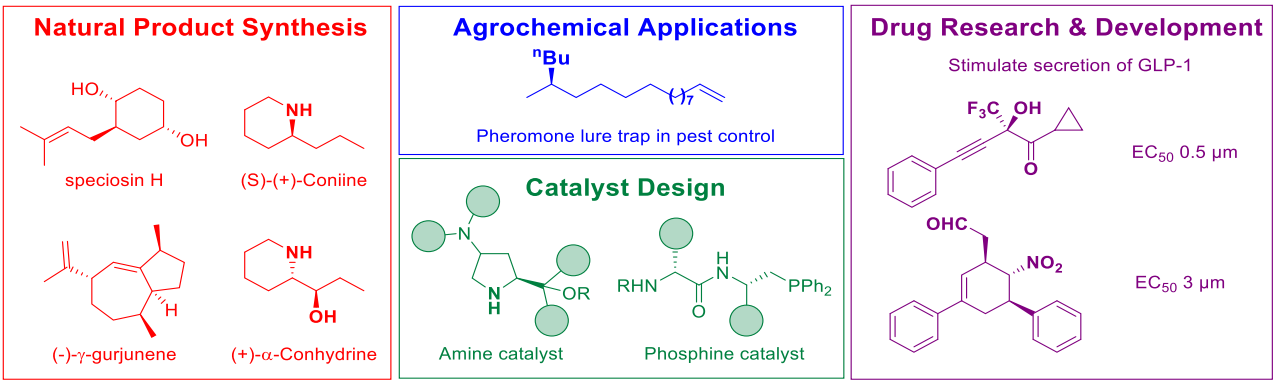
KEY WORDS: Organocatalysis, Sustainable Chemistry, Green Chemistry, Climate Change, Biomimetic Processes.

In recent years, society is demanding concrete actions to mitigate the environmental consequences that human beings have caused in last centuries. Specifically, climate change is one of the most devastating result due to the accumulation of so-called greenhouse gases in the atmosphere. Among the most ambitious solutions to diminish global warming and the generation of waste products from the chemical industry, catalysis has already proven to be a crucial alternative in the production of cleaner fuels with minimal environmental effect. With regard to the generation of chemical products necessary for the advancement of society, catalysis is at the forefront: it can generate the necessary chemicals with high efficiencies, minimum cost of energy and reducing the amount of by-products. Different types of catalysis exist being the so-called ORGANOcatalysis the one reducing the use of low abundant but expensive metals. In conclusion, catalysis is meant to play an important role in the search for mitigation of global warming and climate change.

Our research in this field has prompted us to study several organocatalytic methodologies in different research lines with the aim to design new catalysts, which has allowed us to carry out reactions in water. These findings, together with the well-known advantages of organocatalysis are in accordance with the principles of Green Chemistry.

In the field of asymmetric synthesis, not only should the catalyst accelerate the reaction but it should also be very stereoselective and flexible, in order to allow its use for the synthesis of different target molecules such us natural products or agrochemicals. Additionally, organocatalysts are stable in air, water-compatible, most of them commercially available, thus showing a great advantage when employed by pharma, especially in drug research, because the presence of traces of contaminating transition metals is absolutely forbidden by legal regulations.

Scope and Applications of ORGANOcatalysis



Our experience in Asymmetric Synthesis is well known and internationally recognized. Our research group provides laboratory facilities for students in the last year of degree, Master students, PhD. students or post-doctoral researchers. More information can be found in the group web page (http://www.ehu.es/gsa).

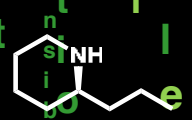
ORGANOCatalysis and Climate Change

J. L. Vicario,* L. Carrillo, E. Reyes, U. Uria, L. Prieto, J. Luis, S. Rodríguez, L. García, E. Capel, J. Sendra, A. Romaniega, N. Betanzos, C. Portolani

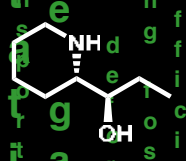
Responsible Agrochemicals

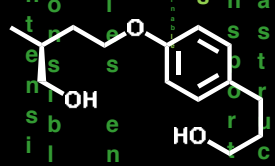
(S)-(+)-14-Metiloctadec-1-ene
Pheromone lure trap in pest control

Natural Medicines



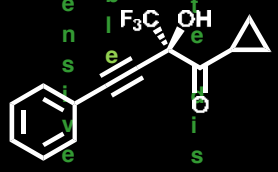
(S)-(+)-Coniine and (+)-Conhydrine
Sedative and Antispasmodic
Antidote

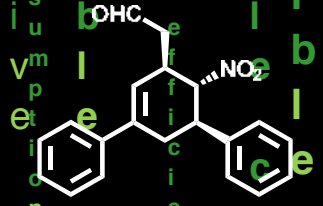




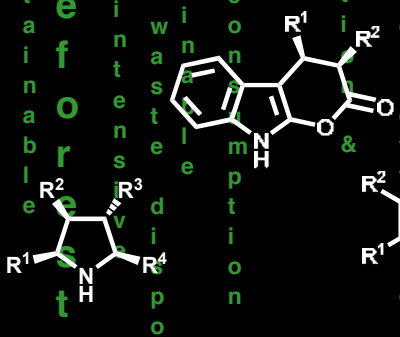
(+)-Dihydrocuspidiol
Antifungal activity

Sustainable Drug Research & Development



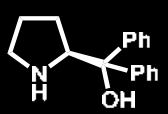


Stimulate secretion of glucagon-like peptide one (GLP-1)
EC_{50} 0.5 μm EC_{50} 3 μm

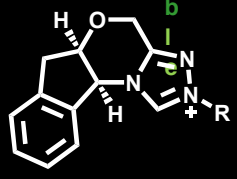


New heterocyclic compounds
Library of Pharmaceutically Interesting Compounds

Efficient Metal-free Catalysts

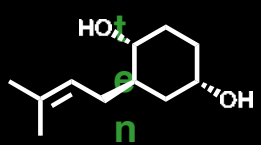


An aminoacid derivative

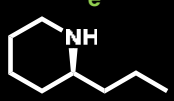


A carbene catalyst

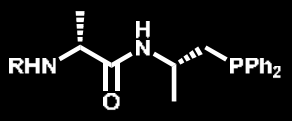
Productive Natural Product Synthesis



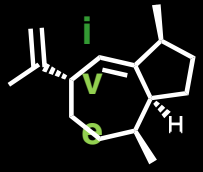
speciosin H



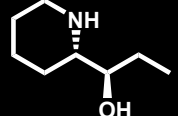
(S)-(+)-coniine



Phosphine catalyst



(-)-γ-gurjunene



(+)-α-Conhydrine

INGENIERITZA KIMIKOA

INGENIERÍA QUÍMICA

Klima-aldaketa
Cambio Climático

Replacing oil and valorizing CO_2

A.T. Aguayo, J. Alvarez, S. Alvarez, A. Ateka, M.J. Azkoiti, P.L. Benito, J. Bilbao, T. Cordero-Lanzac, G. Elordi, E. Epelde, J. Ereña, N. García-Gómez, A.G. Gayubo, L. Landa, A. Portillo, A. Remiro, M.J. San José, S. Izaddoust, I. Sierra, Z. Tabernilla, J. Valecillos, B. Valle, H. Vicente

Department of Chemical Engineering, University of the Basque Country (UPV/EHU), P.O. Box 644, 48040, Bilbao, Spain

KEY WORDS: Biorefinery, Waste-refinery, Fuels, Raw materials

Climate change is a priority issue for the Catalytic Processes and Waste Valorization research group. It is an opportunity to develop new thermochemical and catalytic processes aimed at the sustainable production of fuels and raw materials from non-fossil sources (biomass and its derivatives) and CO_2, by decreasing gradually the dependence on oil and other fossil sources (coal, natural gas). We are in a new industrial era in which Chemical Engineering faces changes and technological solutions over the current energy model.

The valorization routes studied by the group are: i) the pyrolysis and subsequent valorization of the liquid product (bio-oil) to obtain fuels, raw materials, and H_2: ii) the in-line pyrolysis-catalytic reforming for the production of H_2, and iii) the gasification and valorization of the product (syngas), for the synthesis of fuels and raw materials.

The group has developed technologies for the fast pyrolysis of lignocellulosic biomass, attaining a bio-oil (liquid product) yield above 65 wt%. Within the current energy transition scenario, the capacity of the existing refinery units is considered a key factor for the large-scale valorization of bio-oil. In particular, that of the fluidized catalytic cracking (FCC) and hydroprocessing (hydrotreatment and hydrocracking) units. The ideal strategy is the delocalized pyrolysis in small equipments, which is technologically viable and leads to reduced emissions. The resulting bio-oil would be transported and co-feed into a refinery. The benefits are: i) creation of a new eco-industry; ii) rational valorization of forest and agricultural exploitation wastes; iii) reduction of fire hazard; iv) reduction of the net CO_2 emissions; v) decrease in oil consumption. The products (gasoline and diesel) would be commercialized using the current distribution systems. The group's research has demonstrated the short-term viability of co-feeding bio-oil (up to 20 wt%) in the FCC unit, and improvements in the production. The FCC units are amortized and have great versatility and capacity (50 thousand barrels day^{-1}). The hydroprocessing of bio-oil leads to encouraging experimental results, although its industrial implementation is conditioned by the low availability and low technological development of these units.

The production of H_2 from biomass is studied by two routes. The direct route consists of two stages in line; fast pyrolysis and volatile catalytic reforming. The combination of a conical spouted bed reactor for the pyrolysis and a fluidized-bed reactor for the reforming is technologically suitable, and gives way to a H_2 yield similar to the stoichiometric one. In the indirect route, the reforming of raw bio-oi is carried out by means of an original system that separates the pyrolytic lignin.

The syngas (H_2+CO) obtained by biomass gasification has a low tar content when primary and secondary catalysts are used. The activity of the group is remarkable in the reactions involving: i) direct dimethyl ether (DME) synthesis from syngas, co-feeding CO_2 and; ii) direct synthesis (in a single reaction stage) of gasoline and raw materials (aromatics, olefins) from syngas + CO_2 mixtures. The main innovations consist in the proposal of core-shell catalysts and membrane reactors to enhance the yield and energy efficiency of the processes. DME is interesting as fuel and is studied in the group as a raw material for the synthesis of other raw materials. The DTO process (DME to olefins) is proposed as a reasonable route for the large-scale CO_2 valorization and as an alternative to the MTO process (methanol to olefins), due to its greater energy efficiency. In addition, the oligomerization of light olefins to gasoline and diesel is also studied in other processes. All these fuels and raw materials are free of S, N, metals and contaminants common in the derivatives of fossil sources.

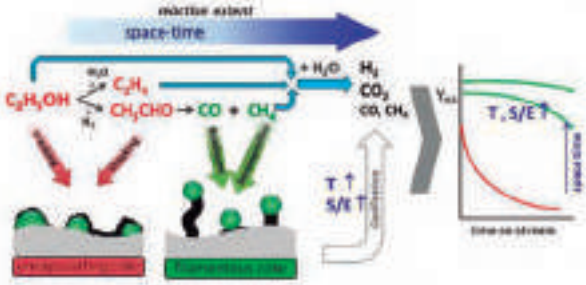
The study of these catalytic processes is part of the Biorefinery R&D platform, and they address different features as are: catalyst design and furthering the reaction mechanism, kinetic modeling, proposals and design of new reactors, and simulation and scaling up of industrial processes. In all these aspects, the university group character leads to the incorporation of methodological improvements in different aspects of the research. The collaboration with other universities is also noteworthy, as reflected in the publications (Málaga, UAM, UPV, Calabria, Messina (Italy) King Abdullah (Saudi Arabia), California, Los Andes (Colombia), Western Ontario (Canada), Sao Paulo, Sao Carlos (Brazil)).

REPLACING OIL AND VALORIZING CO_2

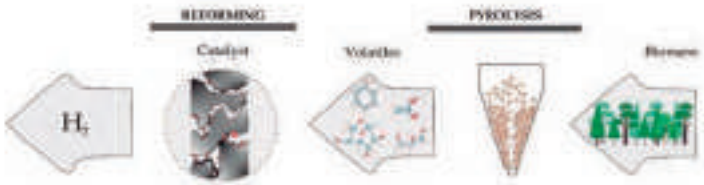
A.T. Aguayo, J. Alvarez, S. Alvarez, A. Ateka, M.J. Azkoiti, P.L. Benito, J. Bilbao, T. Cordero-Lanzac, G. Elordi, E. Epelde, J. Ereña, N. García-Gómez, A.G. Gayubo, L. Landa, A. Portillo, A. Remiro, M.J. San José, S. Izaddoust, I. Sierra, Z. Tabernilla, J. Valecillos, B. Valle, H. Vicente

Green hydrogen production

Hydrogen from bio-ethanol

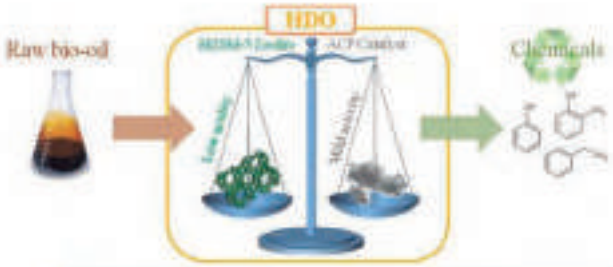


Hydrogen from biomass

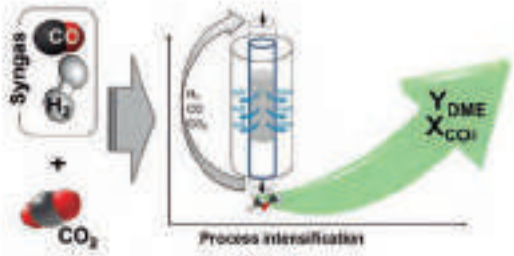


Bio-chemicals and bio-fuels

Chemicals from bio-oil

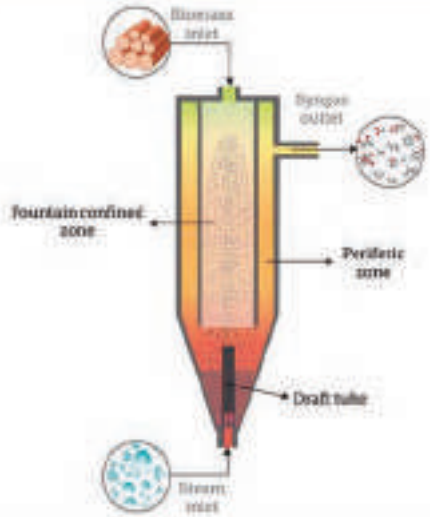


Dimethyl ether from CO and CO_2

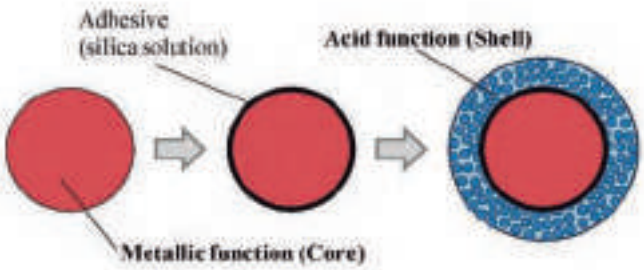


Technological innovations

New reactors



New catalysts



CPWV ehu group
Catalytic Processes & Waste Valorization
Department of Chemical Engineering
University of the Basque Country UPV/EHU
Universidad del País Vasco · Euskal Herriko Unibertsitatea
FACULTY OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF THE BASQUE COUNTRY

Waste valorization (plastics and tires)

A. Atxutegi, R. Aguado. H. Altzibar, M. Amutio, M. Arabiourrutia, J.M. Arandes, A. Arregi, M. Artetxe, M. Cortazar, I. Estiati, E. Fernández, I. García, A. Gutiérrez, J. Izquierdo, G. Lopez, M. Olazar, S. Orozco, A. Pablos, R. Palos, L. Santamaría, X. Sukunza, M. Tellabide, D. Trueba, F.J. Vela

Department of Chemical Engineering, University of the Basque Country (UPV/EHU), P.O. Box 644, 48040,

Bilbao, Spain
KEY WORDS: Waste-refinery, Plastics, Tires, Fuels, Raw materials

The Catalytic Processes and Waste Valorization research group offers the society different technological solutions for the rational valorization of used plastics and tires (Waste refinery). These solutions (subject to UPV/EHU patents) overcome the outstanding deficiencies in the recycling of these wastes of the consumer society, and the arising environmental problems.

The group addresses plastics valorization with three strategies: i) the recovery of monomers by means of fast pyrolysis; ii) the incorporation of plastics or pyrolysis waxes into a refinery unit (fluidized catalytic cracking (FCC) or hydroprocessing); iii) the production of H_2 through in line fast pyrolysis and steam catalytic reforming; iv) gasification of the wastes of syngas production, which is the raw material for the production of fuels and other raw materials.

All plastics (low density polyethylene (LDPE), high density (HDPE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET)) are suitable for the recovery of their monomers and raw materials. High performance is achieved with the fast pyrolysis technology in conical spouted bed. The use of acid catalysts in situ allows lowering temperature and selectively directing the production towards gasoline and diesel fuels. The same strategies are studied for the valorization of tires. In this case, a liquid product (tire pyrolysis oil, TPO) is obtained in the pyrolysis, with limitations for its direct use as fuel, but may be a source of raw materials (limonene, aromatics). The capacity of the proposed pyrolysis technology for the joint valorization of different plastics and their mixtures with other waste (biomass or sewage sludge) is remarkable.

In the short term, the solution of the dramatic problem of valorizing such a large number of plastics and tires suggests involving the industries generating these materials (the oil industry) to their recycling. The refineries have the means to convert them into fuels and raw materials, and the capacity to commercialize the products complying the usual quality requirements. The capacity of a refinery FCC unit is sufficient to co-feed all the polyolefins collected (2/3 of the plastics in urban solid waste) in Spain. Accordingly, 5 wt% of polyolefins should be fed along with the usual feedstock. The results of the group, obtained in laboratory scale units similar to industrial reactors, have shown that this co-feeding increases the production of gasoline and light olefins. In addition, the gasoline has lower sulphur content than the standard one, and is less aromatic and more olefinic, which is an advantage to comply with fuel market requirements. Likewise, the co-feeding of the TPO to the FCC units is technologically feasible. The sulphur content in the obtained gasoline is similar to the standard one, whereas the aromatic content is higher, but it may be corrected with a hydrocracking treatment. This function of the refineries (Waste-refinery) would be a relevant contribution to society.

TPO hydroprocessing treatment requires two successive stages (hydrogenation and hydrocracking, with transition metal and noble metal catalysts, respectively) to achieve the properties of the fuels required by the market. The group's studies, on a laboratory scale, guarantee the viability of this treatment, both for pure TPO, and for the TPO co-fed with other aromatic streams of the refinery, such as light cycle oil (LCO).

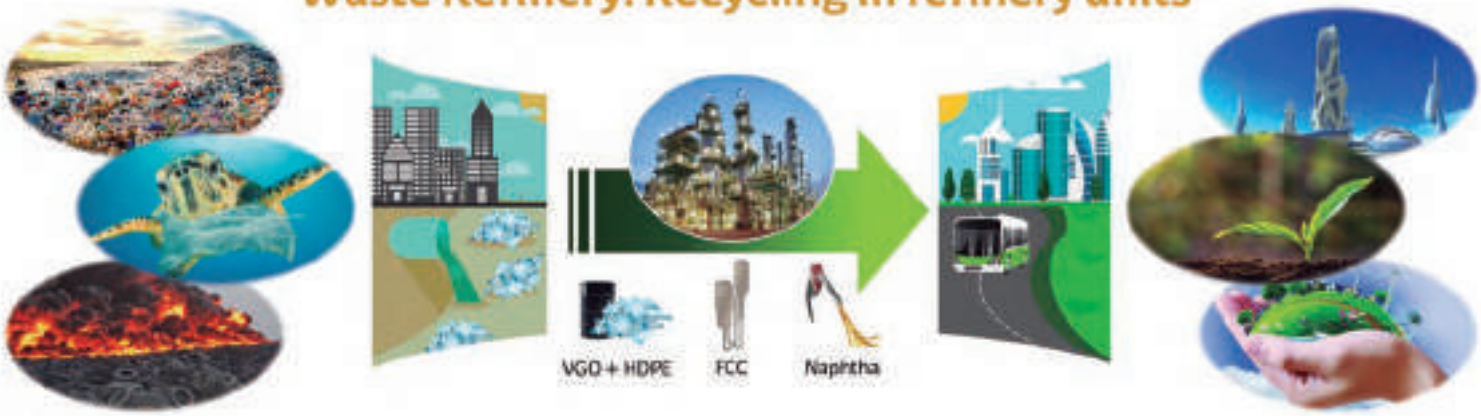
The production of H_2 from plastics and tires is studied in pilot plant units with an original technology consisting of two reactors in line (conical spouted bed-fluidized bed). H_2 yield and energy efficiency are superior to those of other technologies. The study of the units is subject to continuous innovations in catalysts and reactors. Advanced studies on the fluid dynamics are carried out in order to develop design models suitable for scaling up.

The scaling up of the original processes proposed devotes a great deal of attention to the group, and is conducted collaborating with spin offs (such as NOVATTIA). Likewise, the current interest for recycling, explains the collaboration with companies (such as Petronor), technology centers (Gaiker, Ikerlan) and other universities (Ilam, Tehran, Islafan Islamic Azad, Yazd (Iran) Clakson (USA), Stellenbosch, KwaZulu-Natal (South Africa) and so on).

VALORIZING WASTES (PLASTICS AND TIRES)

A. Atxutegi, R. Aguado, H. Altzibar, M. Amutio, M. Arabiourrutia, J.M. Arandes, A. Arregi, M. Artetxe, M. Cortazar, I. Estiati, E. Fernández, I. García, A. Gutiérrez, J. Izquierdo, G. Lopez, M. Olazar, S. Orozco, A. Pablos, R. Palos, L. Santamaría, M. Tellabide, D. Trueba, F.J. Vela

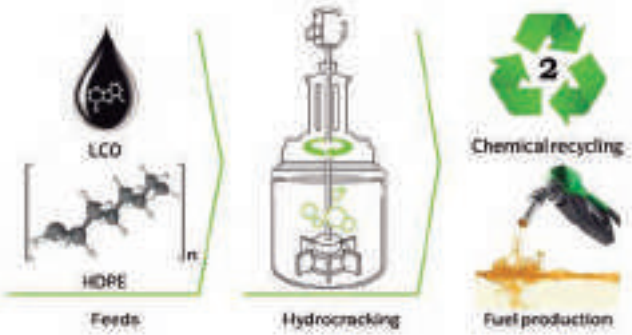
Waste Refinery: Recycling in refinery units



Reactions under industrial conditions

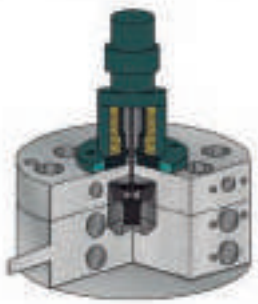
Cracking of discarded tires

Hydrocracking of plastic wastes

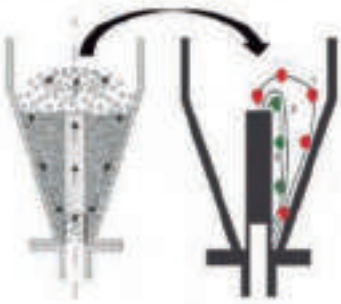


New reactors and equipment

Laboratory-scale reactors

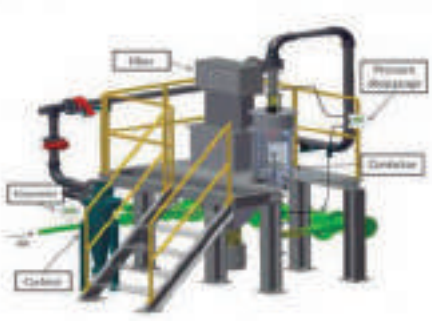


FCC riser simulator reactor



Conical spouted bed reactor

Pilot plant units



Fluid dynamics plant

Minihydrocyclones plant

For more information visit: http://www.ehu.es/cpwv

CPWV ehugroup
Catalytic Processes & Waste Valorization
Department of Chemical Engineering
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Universidad del País Vasco
Euskal Herriko Unibertsitatea

Environmental sustainability: pollutants abatement and CO_2 to hydrocarbons over heterogeneous catalysts

A. Aranzabal, J.L. Ayastuy, A. Bermejo, Z. Boukha, A. Choya, U. De La Torre, B. De Rivas, A. Gil, J.A. González-Marcos, M.P. González-Marcos, J.R. González-Velasco, M.A. Gutiérrez-Ortiz, J.I. Gutiérrez-Ortiz, U. Iriarte, R. López-Fonseca, J.A. Martín, A. Morales-Marín, J.A. Onrubia, G. Penche, B. Pereda-Ayo, A. Quindimil, A.J. Reynoso, A. Sanz and N. Vera-Hincapié
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KEY WORDS: environmental catalysis, NSR, SCR, NOx removal, CO_2 methanation, CO_2 to hydrocarbons

CATALYTIC TECHNOLOGIES FOR POLLUTANTS ABATEMENT FROM STATIONARY AND MOBILE SOURCES

Mobile sources. TQSA does focuses on two technologies for NOx removal from diesel engine exhaust gases: NOx storage and reduction (NSR) and selective catalytic reduction (SCR). The NSR technology requires a catalyst combining NOx adsorption sites and metallic sites to enhance oxidation and reduction reactions, what is achieved on a Pt-Ba/Al_2O_3 formulation washcoated over cordierite monolith. On the other hand, the SCR technology feeds continuously a reducing agent (NH_3 or hydrocarbon) which is adsorbed on Cu-zeolite catalyst and subsequently reacts with NOx to selectively form N_2. More recently, we have combined both technologies in two consecutive bed reactors achieving potential zero emission levels of pollutants (CO, HC and NO_x).

Stationary sources. Among the variety of pollutants coming from industrial effluents, we are interested in reduction of methane emissions (energy power plants and natural gas engines), halogenated volatile organic compounds (HVOC in PVC chemical plants, and textile, electronic and metallurgical industries) and dioxins/furanes with NOx (solid wastes incineration plants). Under this frame, TQSA develops:

1. Catalysts for individual pollutant removal, such as chlorinated volatile organic compounds from industrial off-gases, or methane from exhaust gases of natural gas-powered vehicles.
2. Catalysts for simultaneous elimination of dioxins (PCCD)/furanes(F) together with NOx from municipal waste incineration plants.

ADVANCES IN CO_2 HYDROGENATION TO HYDROCARBONS OVER HETEROGENEOUS CATALYSTS

The concept power-to-gas or abbreviated as P2G, is based on the process which is able to produce hydrogen from exceeding electric energy, which is directly introduced into the transport and distribution gas network to be used, when demand exists or well is utilized for production of methane, used as synthetic natural gas (SNG), which is also injected into the mentioned network. Wind, solar or any other renewable energy can be used in the P2G process.

Catalytic hydrogenation of CO_2 using H_2 produced with renewable energy is considered as a potential path forward for the sustainable production of lower olefins, higher hydrocarbons, formic acid, methanol, and higher alcohols (Fig. 1).

In the group TQSA, we are challenging:

1. To adjust the catalyst surface H/C ratio to facilitate C-C coupling and generate high-value-added products.
2. To improve the support basicity and oxygen vacancies and increase the CO2 adsorption and activation.
3. To explore more novel catalytic materials and improve the catalyst stability.
4. To explore more active catalysts for low-temperature and energy-saving CO_2 hydrogenation.

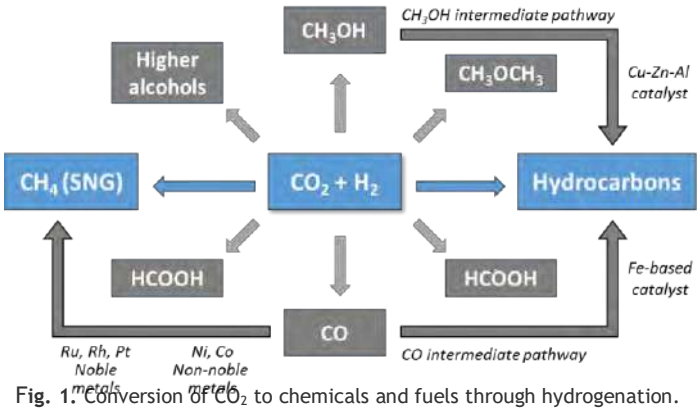

Fig. 1. Conversion of CO_2 to chemicals and fuels through hydrogenation.

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INGURUMENAREN IRAUNKORTASUNERAKO TEKNOLOGIA KIMIKOAK • TECNOLOGÍAS QUÍMICAS PARA LA SOSTENIBILIDAD AMBIENTAL
INGENIARITZA KIMIKOA SAILA • DEPARTAMENTO DE INGENIERÍA QUÍMICA

Environmental sustainability: Pollutants abatements and CO_2 to hydrocarbons over heterogeneous catalysts

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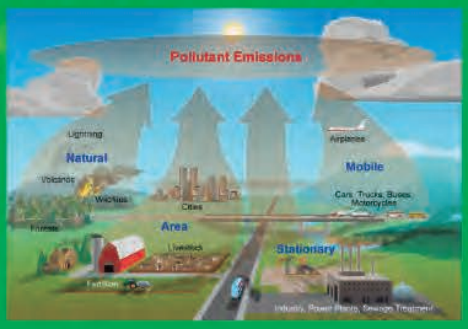
CATALYTIC TECHNOLOGIES FOR POLLUTANTS ABATEMENT FROM STATIONARY AND MOBILE SOURCES



Mobile: Cars, Trucks, Buses, Motorcycles

We investigate different catalytic technologies for CO, HC, NOx and PM removal from mobile engine exhaust gases: three-way catalysts (TWC), particulate filters (PMT), NOx storage and reduction (NSR), and NOx selective catalytic reduction (SCR), and their combination in size-reduced, robust and efficient hybrid systems.

Actually, new materials as modified perovskites are being synthesized in our laboratories allowing to reduce or even eliminate noble metals from the catalysts, which turns in more economical and size-reduced efficient DeNOx aftertreatment systems, especially for light-duty vehicles.

Stationary: Industry, Power Plants, Waste Incinerators, Sewage Treatment

Among the variety of pollutants from industrial processes, we mainly focus our research interest on methane (NG engines and power plants), halogenated volatile organic compounds (HCOV, in PVC production plants, textil, electronic and methalurgy industries)), and dioxines and furanes in combination with NOx (municipal solid waste treatment plants, MSWTP).

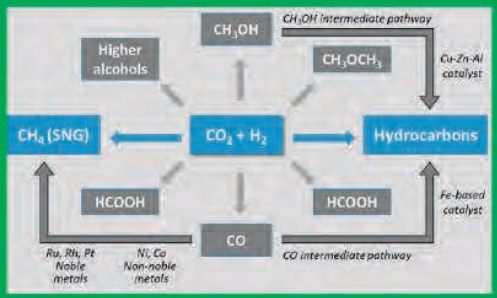
At present, we are developing: (i) Catalysts for elimination of pollutants emited from specific applications (chlorinated COV and methane; and (ii) Catalysts for simoultaneous elimination of dioxines and furanes (PCDD/F) when produced together with NOx as in MSWTP including incineration.

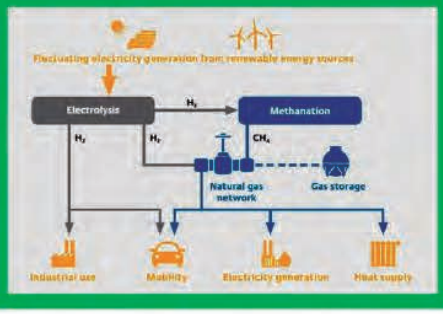
ADVANCES IN CO_2 HYDROGENATION OVER HETEROGENEOUS CATALYSTS

Environmental issues have boosted the necessity to reduce CO_2 emissions caused by the use of fossil fuels. Heterogeneous thermocatalysis is a promising direction for application in CO_2 conversión. Catalytic hydrogenation of CO_2 using H_2 produced with renewable energy is considered as a potential path towards the sustainable production of lower olefins, higher hydrocarbons, formic acid, methanol, and higher alcohols.

CO_2 can be also identified as an energy carrier for the transformation of renewable energy. The production of synyhetic natural gas (SNG) or liquid fuels is the most feasible and convenient way to store large amounts of intermitent energy produced fron renewable sources for long periods. Among them, we are investigating the so-called "power-to-gas (PtG) concept.

At present, we are investigating the catalyst performance, which can be affected by many factors, such as metal-support interaction,metal particle size and promoters. Ni-based catalysts are mainly used. In addition, Co, Ru, Ir and Rh are also applied. Fe is an active metal for CO_2 methanation to C_2, hydrocarbons through modified FST route or metanol.





Challenges in clean and safe energy: technologies for sustainable hydrogen production

A. Aranzabal, J.L. Ayastuy, A. Bermejo, Z. Boukha, A. Choya, U. De La Torre, B. De Rivas, A. Gil, J.A. González-Marcos, M.P. González-Marcos, J.R. González-Velasco, M.A. Gutiérrez-Ortiz, J.I. Gutiérrez-Ortiz, U. Iriarte, R. López-Fonseca, J.A. Martín, A. Morales-Marín, J.A. Onrubia, G. Penche, B. Pereda-Ayo, A. Quindimil, A. Reynoso, A. Sanz and N. Vera-Hincapié
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KEY WORDS: Hydrogen production, gas-phase reforming, APR, biomass, glycerol, HDO, spinel catalysts.

The increasing economic development in the world has brought an increase in energy consumption, so it is necessary to develop a new energy map where renewable energies would occupy a prominent place to meet the demand and assure the energy supply, protecting the environment. In addition to reducing air pollution and emissions of greenhouse gases, the use of hydrogen as an "energy vector" would reduce the current dependence on fossil fuels, thus promoting the development of fuel cell technology (particularly in the transport sector).

Hydrogen, as a new energy vector, will be the main energy supply by means of the fuel cells in the near future. TQSA research group has focused its efforts on the development of catalysts for producing H_2 —rich streams by different strategies (POX (Partial Oxidation), DR (Dry Reforming), SR (Steam Reforming), OSR (Oxidative Steam Reforming))— from hydrocarbons with varying chemical nature —natural gas (CH_4), gasoline (i-C_8H_{18}), diesel (n-$C_{14}H_{30}$)—. Among the catalysts developed for this purpose, $NiAl_2O_4$(Al_2O_3), obtained from the nickel aluminate spinel, offers several advantages in reforming processes, such as high catalytic stability and high metal dispersion after reduction at high temperature. These catalysts have been tested in their traditional powder form, but the objective now is to incorporate them in structured metallic wire mesh and foam catalysts, which would allow working at higher space velocity with a minimal pressure drop.

Interestingly, in recent decades, several catalytic processes have been developed and improved for upgrading biomass into valuable fuels and chemicals. Among these processes, Aqueous Phase Reforming (APR) produces hydrogen and other value-added chemicals from biomass derived feedstock under significantly mild reaction conditions. APR can be carried out in a single-step chemical reactor, though various chemical reactions like Water-Gas Shift (WGS) reaction, dehydration and carbon bond cleavage could also compete. With proper catalysts, APR generates H_2 without the necessity of evaporate large amount of water, representing major energy savings. Furthermore, APR minimizes undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures. Likewise, it is one of the most technically feasible approaches to produce H_2 streams with trace amounts of CO. In general, oxygenated hydrocarbons such as sugars (glucose, fructose) and alcohols (sorbitol, xylitol, glycerol, ethylene glycol, ethanol, and methanol) can be valorised into hydrogen and carbon dioxide among other gaseous and liquid products. Another interesting process is the aqueous phase Hydrodeoxygenation (HDO) using in-situ generated or co-feeding hydrogen to produce high value-added fuels and useful chemical building blocks.

Considering the importance of H_2 in a society inclined to the use of clean and renewable energy, our research has focused, firstly, in the development of active catalysts for obtaining H_2-rich streams from the APR of biomass-derived glycerol; and in parallel, in the production of high value-added chemical products via HDO using in-situ generated hydrogen. The interest of the project is oriented to the non-conventional design (preparation, composition and activation protocol) of new transition metal cost-effective catalysts (Co, Ni) whose catalytic behaviour can be comparable to that of the benchmark noble metal catalysts.

ZTF-FCTko VII. IKERKUNTZA JARDUNALDIAK

VII JORNADAS DE INVESTIGACIÓN DE LA ZTF-FCT

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INGURUMENAREN IRAUNKORTASUNERAKO TEKNOLOGIA KIMIKOAK
INGENIARITZA KIMIKOA SAILA

TECNOLOGÍAS QUÍMICAS PARA LA SOSTENIBILIDAD AMBIENTAL
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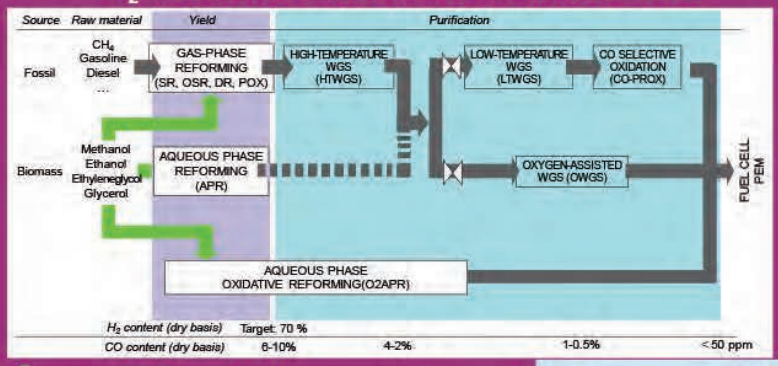
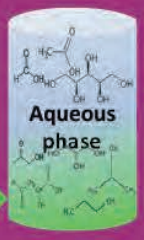
H_2 YIELD AND PRODUCTION FOR FUEL CELLS

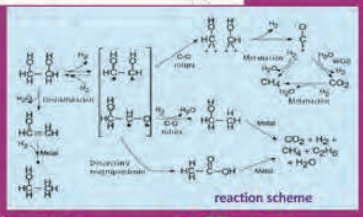


APR: H_2 yield

Bio-oil

Thermal processes





Aqueous phase reforming

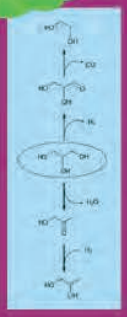
200-350 °C (20-60 atm)

H_2 CO_2 CO Light HC

$C_3H_8O_3 \rightarrow 3CO + 4H_2$ reforming

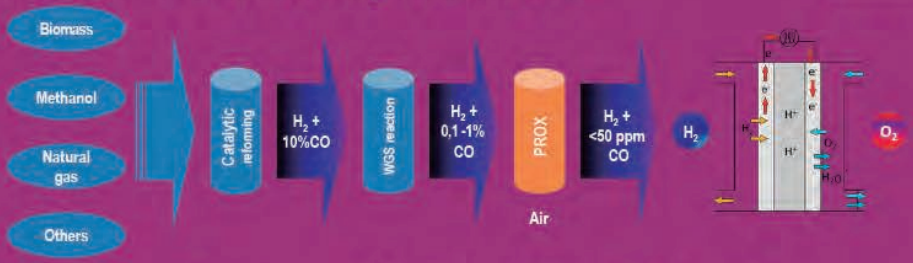
$3CO + 3H_2O \leftrightarrows 3CO_2 + 3H_2$ WGS

$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$ overall reaction

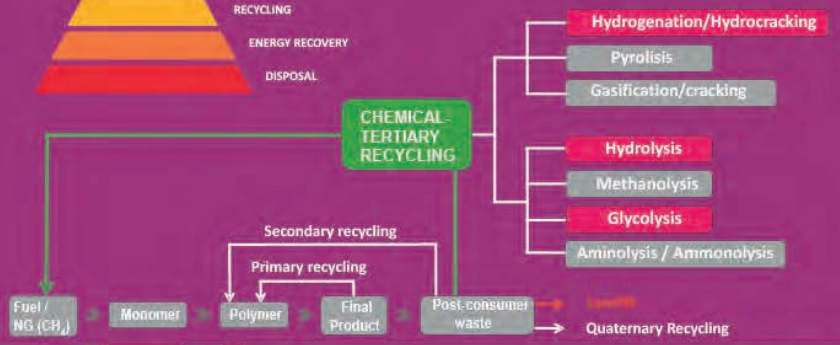


Objective:
Development of catalytic technologies to increase the use of hydrogen as energy carrier

PROX: CO REMOVAL FROM H_2-RICH STREAMS



PLASTIC WASTE VALORISATION



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BESTE IKERGUNE BATZUK

OTROS CENTROS DE INVESTIGACIÓN

Klima-aldaketa
Cambio Climático

SGIKER

Klima-aldaketa
Cambio Climático

Advanced research facilities of the UPV/EHU SGIker

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KEY WORDS: Advanced, research, facility.

Advanced Research Facilities, SGIker, created by the University of the Basque Country / Euskal Herriko Unibertsitatea, UPV/EHU, were born in 2002 with the vocation to respond and provide support for research, being available to the university itself, other Public Institutions and Business.

SGIker have front-line technical and human resources, and aims to offer research support at the highest level, with modern equipment and high technology equipment. This infrastructure allows SGIker to respond to a variety of problems in the field of research and technological development.

SGIker units are present in the three Campus of the UPV/EHU and are distributed in the following scientific areas:

- Materials and Surfaces
- Biotechnology and Biomedicine
- Environment
- Common Services
- Geographical-Historical Sciences
- Social Sciences
- Technological support

As a result of this proposal of the university, the scientific indicators of the UPV/EHU have increased, mainly the publications indexed in JCR in the fist quartile or decile.

This actions have been possible thanks of the efforts of the SGIker staff, other university's departments, the Basque Government and the corresponding Spanish Ministry.

Universidad del País Vasco · Euskal Herriko Unibertsitatea

sgiker
Servicios Generales de Investigación

The SGIker Platforms aligned with the strategic lines of the Horizon 2020 Program

AUTHORS

Advanced Research Facilities of University of the Basque Country (UPV/EHU) (SGIker)

KEY WORDS

SGIker, Horizon 2020 Program, PCTI Euskadi 2020.

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ABSTRACT

The Platforms of the Advanced Research Facilities, SGIker, have been developing an essential support for research since 2004 in the areas of Advanced Manufacturing, Energy and Sustainability, Biosciences and Health, all of which are considered strategic lines in the European Horizon 2020 Programme, in Science, Technology and Innovation, Plan Euskadi 2020, and world research, both inside and outside the UPV/EHU.
A highly qualified staff and infrastructure, present in the three campuses of the UPV / EHU, accompany the research staff in all phases of knowledge generation. As a result of this team work, an analysis of the publications generated by the users of the SGIker Platforms reveals the multidisciplinary relationship of the areas, as well as the pre-eminence of those topics that most concern society.

In a graphic view, the existence of multiple intangible research networks is shown in which the different knowledge and techniques necessary to face the challenges of current Science meet.

ACTIVITIES CO-FINANCED BY

SGIker PLATFORMS

- **Advanced manufacturing**
  - Microscopy: Polymer Characterization
  - Macrobehaviour - Mesostructure - Nanotechnology
  - X-Ray Photoelectron Spectroscopy (XPS)
  - X-Rays
  - Electronic Microscopy and Material Microanalysis
  - Magnetic Measurements
  - Nuclear Magnetic Resonance (NMR)
  - Coupled Multispectroscopy Singular Laboratory (Raman-LASPEA)
- **Energy**
  - Laser Facility
  - Geochronology and Isotopic Geochemistry
  - Cartography Service and Geographic Information Systems
  - X-Rays
  - Electronic Microscopy and Material Microanalysis
  - Magnetic Measurements
- **Biosciences / Health**
  - Animal Unit
  - DNA Bank
  - Gene Expression
  - Sequencing and Genotyping
  - Biological Containment Laboratory Level 3 (NCB3)
  - Forensic Entomology
  - Analytical and High-Resolution Microscopy in Biomedicine
  - Proteomics
  - Radioisotopes
  - Phytotron and Greenhouse
- **Areas of opportunity**
  - IT applied to Research (Scientific Computing Service)
  - Central Analysis Service
  - Quality and Innovation Unit
  - Scientometrics Unit
  - Agri-food industry more linked to sustainability and the human environment
  - Territorial planning and urban regeneration
  - Certain niches related to leisure, entertainment and culture
  - Specific activities in relation to ecosystems

BC³
Basque Centre For Climate Change

Klima-aldaketa
Cambio Climático

BC3 - Basque Centre for Climate Change
klima aldaketa ikergai

Basque Centre for Climate Change (BC3)

KEY WORDS: climate change, climate emergency, transdisciplinary research, multidisciplinary team

BC3 – Basque Centre for Climate Change is a research centre on the causes and consequences of climate change. Led by one of the most recognized scientists in the Climate Change field -Prof. Maria José Sanz, we produce multidisciplinary knowledge to support decision making towards sustainable development at the international level.

BC3, Basque Centre for Climate Change has become, ten years after its creation, a benchmark for climate change research at international level. BC3 created in 2008 by Ikerbasque, IHOBE and the UPV/EHU was promoted by the Basque Government through its BERC program and today has a team of 67 people. BC3 was accredited by the State Research Agency in 2018 as a María de Maeztu unit, in recognition of the quality and level of excellence of the research it develops,

With a multidisciplinary team, connected to the main scientific institutions, networks and socio-economic agents, for a decade, our contribution to research of climate change and to the science-policy interface puts us in a unique position to offer knowledge, tools, new methodologies and cross-cutting proposals, that we lead towards action in a collaborative framework with stakeholders, to design and help implement policies aimed at sustainable development.

The 6 strategic objectives of BC3 cover a 360º vision of the challenges and opportunities of climate change, in line with the Sustainable Development Goals; 1) Understand the past and future of climate change, 2) be useful for making decisions that allow the transition to a low carbon society, 3) understand and support sustainable management of terrestrial systems, 4) facilitate the adequate decision-making for adaptation to climate change and its impacts, 5) provide integrated models of human-natural systems, 6) ultimately promoting integrated knowledge in a multi and transdisciplinary way.

The contribution to these objectives is made from the 5 main lines of research of our team, which structure the scientific activity of the centre: Fundamentals of Climate, Low Carbon Society, Terrestrial Ecosystems, Adaptation Laboratory and Integrated Models of natural human systems. There are also two transversal lines to these objectives such as Governance and Climate Policy.

bc3

BASQUE CENTRE
FOR CLIMATE CHANGE
Klima Aldaketa Ikergai

Sustainability, that's it!

We are what we do.

1 About us

We are a centre of excellence in researching the causes and consequences of climate change. We produce multi-disciplinary knowledge to facilitate and drive decision-making toward sustainable international development.

We are an interdisciplinary team led by the renowned climate change expert, Prof. María José Sanz, and connected with the main institutions, scientific networks and socioeconomic players. For the past decade, our contribution to the international community in climate-change research places us in a unique position to offer knowledge, tools, new methodologies and cross-cutting proposals orientated to the design and support of sustainable development policies.

MISSION

BC3 aims to strategically foster co-production of knowledge relevant to decision making by integrating environmental, socioeconomic, and ethical dimensions of climate change.

OUR VISION

We want to contribute with our skills to sustainable development. Steering climate change science towards co-production of new knowledge and co-design of policies in collaboration with other interested stakeholders, with a solid transdisciplinary focus.

We embrace the challenge of going down a solid path, from research that deepens on the knowledge, and compares hypothesis and results from different models, to the development and implementation of integrated solutions, which are complex in their consideration of climate change's multiple facets.

2 What moves us STRATEGIC OBJECTIVES

Our strategic objectives encompass a 360º view of climate change's challenges and opportunities, in harmony with the Sustainable Development Goals: understanding climate change causes and consequences, offering knowledge and tools to progress as a sustainable society, contribute to research, regulatory and policy related aspects, as well as to overall society, through our contribution and integrated work.

WE WANT TO UNDERSTAND THE PAST AND FUTURE CLIMATE CHANGES

Because, based on the analysis and interpretation of existing data, we need to understand the physical processes that drive climate change, especially in more sensitive areas affected by phenomena with important repercussions, such as dramatic changes in the cryosphere.

WE WANT TO BE USEFUL FOR DECISION-MAKING IN THE TRANSITION TO A LOW-CARBON SOCIETY

To be able to design, communicate, implement and assess actions towards a low carbon society and energy secure, we need to better understand challenges and opportunities, within a context of risks and uncertainties, with an interdisciplinary focus.

WE WANT TO UNDERSTAND AND MANAGE TERRESTRIAL SYSTEMS FOR SUSTAINABILITY

And to do so, we need thorough understand of the relationship between environmental effects and the social and economic factors associated with sustainable use of the land. It is necessary to analyse both vulnerability and the effects of climate change on fields such as agriculture, biodiversity, food safety, as well as on terrestrial systems in general.

WE WANT TO FACILITATE DECISIONS FOR SUCCESSFUL AND EFFECTIVE ADAPTATION TO CLIMATE CHANGE AND ITS IMPACTS

Based on scientific proof, we assess and constantly monitor the risks of climate change and the capacity of our systems to be resilient against extreme events, such as flooding, heatwaves, etc. We accompany policy makers and socioeconomic agents on their decision making process to facilitate regulatory and programmatic action.

WE WANT TO PROVIDE INTEGRATED MODELLING OF COUPLED HUMAN-NATURAL SYSTEMS

Using interdisciplinary scientific evidence and data in an integrated way to understand the evolution of interdependencies between human beings and nature, and designing solutions that bear the complexity of biophysical and social planes in mind.

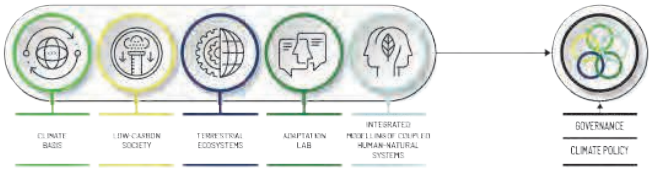
WE WANT TO PROMOTE INTEGRATED INTERDISCIPLINARY AND TRANSDISCIPLINARY RESEARCH

Because only with an interdisciplinary approach is it possible to generate knowledge that addresses the climate challenges that we are facing. Excellent, cross-cutting knowledge, based on and with the cooperation of all kinds of stakeholders, to even further support the shared vision defined in the Paris Agreements, as the foundation for a coordinated transdisciplinary action.

BC3's RESEARCH LINES

Five research lines are contributing to our strategic objectives, providing structure to the centre's research activity.

As cross-cutting themes to all the objectives above, we also work with Governance and Climate Policy. That are addressing local, national and international issues.



3 Who we cooperate with

I. THE ACADEMY

We provide knowledge and scientific criteria as an interdisciplinary and international research group, connected to point-of-reference research and scientific centres all over the world, such as the IPCC intergovernmental panel on climate change.

We are a centre that creates and shares knowledge, contributing to excellent training for future researcher generations.

We contribute to the development and visibility of the Basque science, technology and innovation system, providing top-rate specialist resources and access to point-of-reference international environments in terms of climate change.

II. GOVERNMENTS AND MULTILATERAL GOVERNANCE AGENTS

We offer world-scale research proof, objectivity and knowledge to support informed decisions. Our interdisciplinary vision, connected with good practises all over the world, could accompany and become a solid basis to implement complex actions to address climate change.

III. SOCIOECONOMIC AGENTS

We facilitate the transfer and application of essential scientific knowledge. We offer knowledge on good practises in different fields, to design and implement well-informed actions.

IV. SOCIETY

We contribute to activate society to face climate change and sustainable development challenges. We offer greater and better knowledge regarding climate change's causes and consequences, and we connect scientific knowledge and participation, training and greater awareness for society.

4 We are what we do CONTRIBUTIONS 2007–2018

Some of our contributions up until 2018

TRANSFER OF KNOWLEDGE

- Over 525 articles published in indexed journals.
- Over 85% of 01 articles published over the past 5 years.
- Over 170 books, book chapters and monographs published.
- 95 technical reports for public and private decision-making agents.
- 50 policy briefings published.
- More than 150 seminars organized.
- More than 20 scientific and training events organised.
- Over 7,500 high school students provided with knowledge on Climate Change.

TRAINING

- 30 doctorate students supervised.
- 30 master students supervised.
- More than 65 training activities organised.

EXCELENCIA MARÍA DE MAEZTU
Jul. 2018 - Jun. 2022

EUSKO JAURLARITZA GOBIERNO VASCO

ABSTRACTS

AHOZKO KOMUNIKAZIOAK

COMUNICACIONES ORALES

Klima-aldaketa
Cambio Climático

BIOZIENTZIAK

BIOCIENCIAS

Klima-aldaketa
Cambio Climático

Specific interaction of Adenylate Cyclase Toxin with membrane cholesterol through CRAC-like motifs

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KEY WORDS: *Bordetella pertussis*, whooping cough, Adenylate Cyclase Toxin

Infectious respiratory diseases are among the main death causes in humans worldwide. The bacterial pathogen Bordetella pertussis causes whooping cough, a highly contagious respiratory disease that remains an important cause of childhood morbidity and mortality. Among the different virulence factors secreted by this bacterium, adenylate cyclase toxin-haemolysin (ACT) is one of the most important ones. It has a crucial role in the early steps of colonization of the respiratory tract by the bacterium. However, after decades of research, the molecular mechanisms used by ACT to intoxicate the host cells are still poorly understood.

In the present study, we explored the effect of membrane cholesterol or free cholesterol in the toxin interaction with lipid membranes. Additionally, we examined whether ACT-cholesterol interaction may be specific and whether Cholesterol Recognition/interaction Aminoacid Consensus (CRAC) motifs may be involved.

Based on our results we conclude that ACT directly interacts with cholesterol and we discover that such interaction relies on a CRAC-like sequence located at the AC-to-Hly linking segment of the ACT sequence.

Characterization of six novel *ApoE* pathogenic variants causing familial hypercholesterolemia

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KEY WORDS: Familial Hypercholesterolemia, ApoE, Pathogenic

Cardiovascular diseases are the most common death reason worldwide, and they are often related to high cholesterol levels in blood. Although that increase can be related to unbalanced diet or sedentary life, in some cases genetic reasons underlie familial hypercholesterolemia (FH), one of the most common genetic autosomal diseases. In 80%-60% of FH cases, the disease is caused by mutations in *LDLR*, *ApoB* or *PCSK9* genes. However, in up to 20-40% of FH cases, the mutated gene has very low frequency. Among the latter, we can find *ApoE* gene that is involved in cholesterol cycle through VLDL (very-low density lipoprotein). VLDL is synthetized in the liver and its function is to provide cholesterol and triacylglycerols to peripheral tissues, so any mutation in *ApoE* that alters this cycle could result in a disorder.

Therefore, in this study we have assessed the pathogenicity of six novel *ApoE* variants found in hypercholesterolemic patients. In order to gain insight on protein activity, we purified VLDL from plasma obtained from patients carrying these mutations. Then, we characterized the activity by measuring VLDL affinity of the particles carrying the *ApoE* variants to LDLR by ELISA and by determining VLDL uptake by HepG2 cells.

The obtained results show that the six *ApoE* variants are pathogenic, being a decrease of the binding affinity the cause in four of the *ApoE* variants. In contrast, an induced downregulation of LDLR is the cause of pathogenicity in the other two variants, which is produced by a higher affinity of the VLDL to LDLR.

Integration of Ecosystem Services into urban and peri-urban planning for local biodiversity conservation and human health

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and UNESCO Chair on Sustainable Development and Environmental Education - UPV/EHU

KEY WORDS: Urban Green Infrastructure, urban ecosystems, connectivity, *Nature based Solutions*.

In urban environments, green and blue spaces create an Urban Green Infrastructure (UGI) and provide ecosystem services (ES) beyond their aesthetic and recreational functions (1), effectively integrating different elements of the urban landscape: such as parks, walls or green roofs (2). Knowing which ES these spaces are providing can facilitate decision-making in their design and management (3). Thus, integrating UGI through Nature-based Solutions (NbS) into policy implementation makes it possible to achieve, in whole or in part, the objectives of territorial policies (4).

Therefore, the main objective of this research is to include ES in urban planning to improve the protection of local biodiversity and thus the ES that urban ecosystems (UE) provide to the society (5).

A methodology will be developed to achieve this objective through the development of effective UGI. Within this main objective, a series of specific objectives have been defined:

- To quantify the ES provided by UE and those demanded by the population: supply and demand of ES, such as air purification, runoff retention, reduction of the heat island effect (cooling), carbon storage, noise damping or recreation, among others. These will be addressed analysing the spatial distribution of ES delivery and demand through different neighbourhoods of the city of Bilbao.
- To design a quantitatively and qualitatively an effective UGI for the conservation of local biodiversity and the improvement of UE services.
- To develop new connectivity analysis techniques that include NbS to facilitate the connection between urban and peri-urban green infrastructure.

Thus, the integration of ES in urban planning will improve our health and help to maintain local biodiversity.

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Ecosystem services of bats and their role as pest suppressors in vineyards: from ecology to management

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KEY WORDS: bats, pests, ecosystem services.

Grape is the fruit crop with the largest acreage (7.5 M ha) and the highest economic importance globally, but it is annually attacked by arthropod pests leading to significant yield losses.
Current pest control methods are still largely based on unspecific chemical pesticide use, but both the need to enhance integrated pest management programmes and the increasing global concern for less invasive, more sustainable and environmentally friendly methods have encouraged farmers to focus on biological control strategies. In this context, there is growing evidence that insectivorous bats play a vital role in the fight against agricultural pests as their voracious suppressors but still, there are multiple knowledge gaps. In this thesis I aim to 1) examine the pest suppression capacity and potentiality of bats foraging in vineyard systems; 2) inspect whether bats track grapevine pests by analysing the functional and aggregational responses of these predators to pest populations throughout the grape-growing season; 3) develop molecular protocols for the rapid and direct identification of aimed pests in bat faeces by using qPCR techniques and 4) outline the key factors to be considered in order to establish a base for future research on this topic, enhancing more precise study design and pest management recommendations.

Catadromous *Chelon labrosus* population dynamics in connection to xenoestrogenicity and intersex condition in estuaries

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Keywords: Catadromous, estuaries, intersex condition, microsatellites, molecular biomarkers, panmixia, pollution, population dynamics, *Chelon labrosus*, xenoestrogens.

Endocrine disrupting chemicals (EDC) found in many common day products have been found to mimic oestrogens and cause oestrogen-like responses in organisms exposed through contaminated food sources and water. Such xenoestrogenic effects have been reported in aquatic organisms resulting in the feminization of juveniles and male fish. This has led to intersex gonads where you can find oocyte formation within testicular tissues. Over the last 10 years, intersex condition has been detected in the thicklip grey mullets (*Chelon labrosus*) along the Basque Coast, from Bilbao, Pasaia and Ondarroa harbours, and in estuaries in Deba and in the Biosphere Reserve of Urdaibai in Gernika. This occurs in scenarios associated to waste water treatment plant effluents and industrial activities in harbour areas. Intersex mullets have been found all along the reproductive annual cycle, with percentages ranging from 3% to 80% of analysed males depending on the site, month and year of capture, with Pasaia and Gernika having been defined as “hotspots”.

The study aims to evaluate the effects of pollution on male and female mullets in terms of sperm quality and oocyte atresia respectively and, describe mullet populations affected by high prevalence of intersex conditions. It intends to make use of Computer Assisted Sperm Analysis (CASA) to evaluate sperm quality in normal vs. intersex male individuals, in addition to evaluating the prevalence of atretic oocytes in gonads. The study further seeks to understand the sources and implications of gonad alterations in mullet populations with respect to time of exposure to chemicals (mullet distribution) and population dynamics and, define the homogeneity and/or relation between mullets from different estuaries.

To achieve this, one of the tasks involves the genotyping of mullet populations from the Basque Coast. Considering that inshore schooling adults are catadromous inhabiting estuaries but migrating to spawn in the ocean, information on whether they return to their original estuary is unknown. It is still unclear whether the populations being studied in different estuaries are from the same population or, the estuaries have geographically subdivided the populations into sub-populations. Such a series of migration behaviours can generate different patterns of population genetic structuring, from total panmixia (random mating/open population) to a moderate structuring due to distance isolation considering the existing opportunities for genetic flow at the micro-geographic level.

Preliminary microsatellite marker analysis conducted on mullets from five (5) Basque estuarine populations and Cadiz as an out-group, has already revealed that we are facing a panmictic population. It is likely that the genetic structure among the different groups from estuary to estuary is low or non-existent. Microsatellite markers for mullets from Thermaikos Gulf (Thessaloniki, Greece) are currently being analysed to confirm this. The next step for this task involves the use of otolith microchemistry to analyse migration patterns and will possibly be done in conjunction with the Interdisciplinary Centre of Marine and Environmental Research (CIIMAR) in Porto, Portugal. Interpreting the population genetic patterns and the processes that generate them in catadromous species is complex, but essential for proper management and effective conservation of these species. It could thus explain the sensitivity/resistant responses of this species to pollutant exposure.

Unravelling the role of the novel cancer related protein TEDC2 in cell division

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KEY WORDS: E2F, TEDC2, cancer, centrosome

The cell cycle is defined as the series of events that take place in a cell leading to duplication of its DNA and division of cytoplasm and organelles to produce two daughter cells. The E2F transcription factors are known to play a critical role in the control of cell-cycle progression through the transcriptional regulation of their target genes, and deregulation of E2F factors is commonly associated with tumor progression. However, we don't yet know the full set of E2F target genes that are involved in cell cycle control. With this in mind, we have carried out a bioinformatic analysis to search for novel genes of unknown function whose expression in tumors correlates with that of E2F factors. We have identified *TEDC2* (Tubulin Epsilon and Delta Complex 2) as a gene whose expression is amplified in many tumors concomitantly with E2F genes. Interestingly, increased expression of TEDC2 in breast tumors is associated with worse prognosis. High throughput genomic and proteomic analyses have reported that TEDC2 localizes to the centrioles and forms a heterotetrameric complex together with TEDC1, epsilon-tubulin (ε-tubulin) and delta-tubulin (δ-tubulin), suggesting a role for TEDC2 in cell division. However, little is known about its regulation and function.

The generation of YFP-TEDC2 fusion protein constructs has allowed us to define more precisely the cellular localization of TEDC2. We have found that TEDC2 localizes not only to centrioles but also to the pericentriolar region and to the cytokinetic ring of the midbody. We have analyzed its E2F-dependent regulation. We show that different E2F factors regulate *TEDC2* transcription through specific motifs that are located in its promoter. To study TEDC2 function, a transient siRNA-mediated silencing methodology was used. Depletion of TEDC2 causes an early centriole splitting, suggesting a role for TEDC2 in the stabilization of the linker that connects the pair of centrioles. The untimely separation of centrioles triggers a DNA-damage response, a G1-phase arrest and a senescent phenotype in p53-proficient untransformed cells. By contrast, p53-deficient tumor cells, such as HeLa, progress through the G2/M phase, but engage in an abnormal metaphase/anaphase with lagging chromosomes that triggers a mitotic catastrophe and subsequent cell death.

Taken together, our results suggest that TEDC2 is an E2F-regulated cell cycle protein that plays a critical role as a stabilizer of the centriolar structure affecting cell division. These findings have provided us valuable insights on the mechanism underlying TEDC2 involvement in cancer progression, which are being currently analyzed.

Is Ankylosing Spondylitis a single disease? A clinical and genetic perspective

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KEY WORDS: ankylosing spondylitis, non-radiographic axial spondyloarthritis, genetics.

Currently, there is a debate on whether non-radiographic axial spondyloarthritis (nr-axSpA) is a different form of ankylosing spondylitis (AS), an early form of AS, or whether both are two expressions of the same disease due to the fact that some patients with nr-axSpA will develop AS after years of disease, whereas other patients with nr-axSpA will suffer the disease for decades and probably for life. In this context, we have analysed clinical manifestations and a set of 43 risk SNPs localised in genes involved in the pathogenesis of spondyloarthritis (SpA) in a sample of 62 patients diagnosed with axial spondyloarthritis from the University Hospital of Basurto (Bilbao, Basque Country, Spain) in order to evaluate the hypothesis that AS and nr-axSpA are subsets of a single disease. The DNA samples were genotyped through *SNP Type Assay*, using the *BioMark HD* platform of *Fluidigm*. Among the clinical characteristic we found statistically significant differences between the patients with AS and nr-axSpA in the age at diagnosis, the disease duration, the presence of syndesmophytes and the BASMI index. In relation to genetic markers, we only found statistically significant differences in *HLA-B27* allele frequencies. Despite the high genetic heterogeneity observed among the patients, it is worth highlighting that some of the most important risk SNPs associated with AS, located in *ERAP1*, *ERAP2*, *IL-23R*, *GPR25* and 2p15, appeared at high frequencies in all the patients. We have observed that AS and nr-axSpA have a common genetic background; therefore, from the genetic perspective, it could be hypothesised that the two entities constitute two different expressions of the same disease. The present study shows the importance of genes involved in the pathogenesis of AS, such as *HLA-B27*, *ERAP1*, *ERAP2*, *IL-23R*, *GPR25* and intergenic region 2p15, whose role may influence the onset, development and severity of the disease. However, the pathogenesis of SpA is very complex, indicating the involvement of environmental factors (smoking and obesity), in the triggering of the disease, so that patients with different genotypes would have the same pathogenic phenotype.

Magnetosomes and magnetotactic bacteria as magnetic hyperthermia agents

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KEY WORDS: magnetotactic bacteria, magnetosomes, magnetic hyperthermia.

Magnetotactic bacteria (MTB) are a group of non-pathogenic microorganisms able to synthesize membrane-enclosed magnetic nanoparticles called magnetosome that present exceptional magnetic properties. For this reason, both magnetosomes and MTB have been proposed in the last few years for several biomedical applications.

We mainly focus on the study of one of these applications, magnetic hyperthermia, a technique that combines magnetic nanoparticles and external alternating magnetic fields to locally increase the temperature of tumours to try and kill or, at least, debilitate cancer cells. Following this idea, we want to present whole magnetotactic bacteria as ideal hyperthermia agents for cancer treatment.

For this purpose, first we verified that cancer cells (in this case human lung carcinoma cells) could internalize MTB by different microscopic techniques as well as flow cytometry and magnetic measurements. Then, we checked if these bacteria could cause a cytotoxic effect on cells by a combination of live/dead stains and flow cytometry. Finally, we assessed the effectivity of magnetic hyperthermia on lung carcinoma cells (A549 cell line) by applying an alternate magnetic field (435 Oe, 150 kHz, 45 minutes) to cells that have previously internalized MTB, and checking cell viability afterwards.

Our first results are very promising as they show that human lung carcinoma cells internalize magnetotactic bacteria without suffering any decrease in their viability and that the magnetic hyperthermia treatment is effective as it reduces significantly the number of living cells present in the culture [1].

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Analysis of mechanisms involved in *Vibrio harveyi* adaptation to stress and their regulation by antisense RNAs

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KEY WORDS: *Vibrio* spp., RNA, transcriptome, post-transcriptional regulation.

BACKGROUND

In the era of global warming and ecological awareness, evidence unequivocally points towards human activities as the driving force of the recent climate changes that are relentlessly deteriorating the Earth's biosphere. In recent studies, global warming has been linked to the recent spread of infectious diseases, including those caused by members of the genus *Vibrio*, a large group of ubiquitous aquatic bacteria. Previous studies highlighted their capacity to survive under different adverse conditions including starvation, drastic temperature shifts and solar radiation. Previous studies disclosed that the resistance to stress can be controlled at the post-transcriptional level through regulation of gene expression mediated by small RNAs (sRNAs). These regulatory molecules specifically recognize their target mRNAs and subsequently alter their stability and/or translation.

OBJECTIVES

The aim of this project was to use *Vibrio harveyi* as a model organism to discover novel putative sRNAs potentially involved in adaptation of this marine bacterium to changing environments.

MATERIALS AND METHODS

Total *Vibrio harveyi* RNA was isolated and subjected to differential RNA sequencing to map transcription start sites (TSS) within the genome. The data obtained were further analyzed *in silico* and a number of new sRNAs were identified and validated by northern blotting.

RESULTS AND CONSLUSIONS

Differential RNA sequencing revealed 3900 TSS in total. They were placed in 4 arbitrary groups including:

- Intergenic TSS preceding genes on the same strand (group A)
- Intergenic TSS mapped downstream of genes located on the opposite strand (group B)
- Introgenic TSS mapped within genes on the same strand (group C)
- Introgenic TSS mapped within genes on the opposite strand (group D)

Study of regions flanking TSS associated with canonical mRNAs (group A) revealed motifs possibly associated with sigma factor recognition sequences normally present in -35 and -10 regions.

Due to its nature, group B TSS could be associated with new genes overlooked in the annotation of the reference genome. Indeed, bioinformatic analysis revealed a number of putative protein-coding and sRNA genes. Expression of some putative sRNA genes (23 in total) was further validated by northern blotting. The result of this analysis confirmed the existence of several unknown putative sRNAs.

We also found that TSS in group C defined transcripts whose transcription could be initiated within the protein-coding sequences yielding either leaderless mRNA or their truncated forms potentially encoding protein isoforms.

Finally, some TSS in group D were likely associated with *cis*-encoded antisense RNAs whereas others could represent the results of pervasive transcription.

FISIKA ETA INGENIERITZA ELEKTRONIKA

FÍSICA E INGENIERÍA ELECTRÓNICA

Klima-aldaketa
Cambio Climático

NPG/TRIS system and their carbon-based composites as phase change materials for thermal energy storage

Sergio Santos[1,2,*], *Stefania Doppiu*[1], *Gabriel A. López*[3], *Nevena Marinova*[2], *Elena Palomo del Barrio*[1] *and Elena Silveira*[2]

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KEY WORDS: Phase change material; thermal energy storage; latent heat storage; neopentyl glycol; TRIS; plastic crystals; globular polyols; subcooling.

Phase Change Materials (**PCMs**) are nowadays key solutions for thermal energy storage (**TES**). These latent heat-based storage materials have high storage density and an isothermal operation temperature. Globular-shape polyols as neopentylglycol, pentaerythritol or pentaglycerol have been studied as potential TES systems due to the different phase transitions they show. In this study, we propose a binary mixture of Neopentylglycol (**NPG**) and Tris[hydroxymethyl]aminomethane (**TRIS**) as a system presenting different transitions, five eutectoids, one peritectic transition and the melting process, that can be potentially used to store thermal energy. The phase diagram of the NPG-TRIS binary system was determined using DSC, and NMR analysis. The results show that the alcohols mixture show a high degree of undercooling, mostly in their eutectoid transitions. For this reason, different strategies, mainly based on the synthesis of carbon-based composites by dispersion of increasing amount of expanded graphite (**EG**) were applied. This study allowed to optimize the amount of graphite to be added reaching an improvement of the subcooling degree from $\Delta T = 120^{\circ}C$ to $\Delta T = 80^{\circ}C$. Regarding the TES performance, the TRIS-enriched zone has the most promising behavior reaching relatively high enthalpies of transition up to 250 J/g (eutectoid transition), in a temperature range between 100ºC and 130ºC.

Advanced atomistic simulation of materials and interfaces

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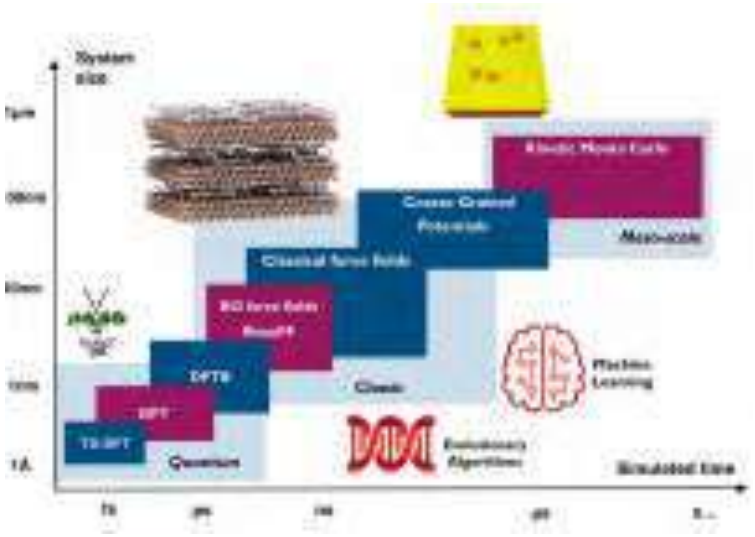
KEY WORDS: Molecular Dynamics, Machine Learning, Materials, Interfaces,

Technological advances are often bounded by the performance of the involved materials. As a consequence, material science is nowadays one of the most active areas of basic research, boosting the properties of existing materials or even seeking for new ones. In that scenario, atomistic simulations are an excellent tool, complementary to experiments, which helps us to understand what is going deep down in our material, right from the atomic scale.

Our research aims to find relationships between atomic scale structure and macroscopic properties in a wide range of systems, with a special focus on sustainable materials for energy storage and construction. For that, we use different molecular simulation methods, from density functional theory (DFT), to (kinetic) Monte Carlo, but mainly advance Molecular Dynamics with empirical potentials. Recently, we are increasing that set of simulation techniques including Machine Learning and advanced sampling methods like evolutionary algorithms:

1. **Evolutionary Algorithms.** There are several methods to explore the potential energy surface of a given compound. The brutal force method would be a random search where atoms are placed randomly and their energies are calculated to compare them. In order to be more efficient, Evolutionary Algorithms use the best structures of a randomly generated set and use them to create a new generation. Every new generation is created by applying variation operators (heredity, permutation, mutation,…) to the best structures of the previous generation. This algorithms mimic the evolution in biological populations over successive generations.

2. **Machine Learning.** The main problem that the above-mentioned methods face is that their precision and computational cost are inversely proportional. Therefore it is not possible to tackle the most demanding problems using the most precise methods. In this regard, machine learning provides a way to overcome the problem by directly learning the complex relation between an atomic configuration and the resulting properties (e.g., energies or forces). Once this mapping is learned from a set of DFT calculations, it can be used to compute those properties for new atomic structures several orders of magnitude faster.



Spin and relativistic effects in electron-phonon interaction

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KEY WORDS: many-body physics, electron-phonon, single atom magnet, spin-orbit coupling.

Theoretical condensed-matter physics involves the use of mathematical and computational models in order to understand and describe the physical properties of materials. In this context, *ab initio* calculations allow the prediction of material properties with the application of quantum mechanics, without requiring the knowledge of fundamental material properties. However, solving many-body problems is a challenging task, requiring the use of wise approximations and complex mathematical tools, as well as high performance computing.

In our research group [1] we develop efficient numerical methods and implement novel theoretical and computational techniques, such as Fermi Surface Harmonics [2], for solving interesting and challenging problems in solid state physics. In this sense, we focus our interest in the theoretical study of low energy electronic excitations (electron-phonon interaction, superconductivity, impurities etc.) and their impact on the properties of materials such as electrical or spin transport.

We are particularly interested on the many-body interactions that lead to collective oscillations of the electronic charge and/or spin density (plasmons and spin-plasmons) [3] and collective oscillations of the crystal lattice (lattice vibrational modes or phonons). We also study how these collective oscillations affect the electron dynamics, that is, the electron-plasmon and electron-phonon coupling. For this purpose, we employ a formulation of the many-body problem based on Green's functions, obtained by solving the Dyson equation, which incorporate the many-body interactions by treating the interacting particles as dressed independent particles with modified or renormalized properties [4-5].

Among other research lines, we study materials where strong spin-orbit coupling introduces new and interesting physics [6-7]. In these materials the spin is at the origin of exceptional spin-related conduction properties, as happens in the promising field of spintronics. Nevertheless, such features can be strongly influenced by many-body effects.

Another investigation line of the group is to analyze the effect of atomic vibrations (phonons) on the stability of magnetic impurities [8], of crucial technological interest with applications as high density storage devices. Breakthrough experimental studies have recently shown that it is possible to create stable magnetic quantum states in individual adatoms. While the role of electronic interactions on the magnetic stability has been thoroughly investigated theoretically, the coupling with phonons has attracted much less attention, in a certain degree, due to the complexity of the problem. To overcome this difficulties we have to combine different techniques developed on the group, in order to be as efficient as possible and make the calculations feasible.

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Shape memory alloys for aero-space applications: mechanical and microstructural properties

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KEY WORDS: shape memory, superelasticity, aerospace, micrsotructure, mechanical properties

Shape Memory Alloys (SMA) are a family of intelligent materials exhibiting the exceptional mechanical properties of shape memory and superelasticity. The shape memory effect is produced thanks to a reversible first-order phase transition between two solid phases, the high temperature austenitic phase, and the low temperature martensitic phase. The martensite in SMA can be easily deformed to a low temperature shape, but the whole deformation disappears once the material is transformed back into its austenite form, or high-temperature shape, by heating. This reversible change of shape can be also induced by the application of a stress at constant temperature and in this case the stress-induced martensite gives place to the superelastic effect. The amount of strain recovered is exceptionally high for a metallic alloy (it can be around 10%), as well as the work output per unit volume ($1x10^7$ J/m^3). These properties allow SMA to have a huge variety of applications, in sectors such as the biomedical (e.g. stents, prosthetics...), robotics, sensors and actuators in cars, aircrafts and satellites, or miniaturization of electro-mechanical devices.

My PhD. is being developed in the frame of the Research Group on Physical Metallurgy, which is specialized in the synthesis of copper based SMA. Specifically Cu-Al-Ni ternary alloys and Cu-Al-Ni-X quaternary alloys (where X can be Ga, Mn, Be, Au...), are produced as poli-crystals and single-crystals. The concentration of the alloying elements controls the properties of the final material, which determine the temperature range and possibilities of its applications. However, to master the functional properties of SMA, a deep knowledge of the relationship between microstructure and mechanical properties is crucial and consequently this is one of the main activities carried out in our research group. For example, the microstructural characterization through scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), as well as by X-ray diffraction is deeply approached. In addition, the thermal properties via differential scanning calorimetry (DSC) and mechanical properties by stress-strain measurements are also performed.

Some of the goals of our research group have already been accomplished, and our materials are being applied in an aerospace actuator REACT (http://react-space.com) developed in the frame of a European H2020 project. We are proud of our SMA, which are already flying in real space missions, and new space actuators are being developed in our group. At present we are also working on the applications of SMA at micro and nano scale, being this field a promising one in which we are worldwide pioneers [1-4].

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A System-on-Chip-based Intelligent system for real-time assessment of fuel consumption

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KEY WORDS: driving style, advanced driving assistance systems, computational intelligence, artificial neural networks, machine learning, self-organized maps, fuel economy, eco-driving.

Pollution is a main concern in worldwide cities. Private transportation plays an important role in emitting toxic gases identified in urban areas' air, with consequences in both citizens health and global warming. With the aim of reducing these affections, several local governments have restricted private traffic in urban areas, and national and transnational institutions have deployed environmental regulations forcing car manufacturers to develop more ecological automobiles.

However, even though traffic restrictions and environmentally friendly means of transport are a reality, their effects on reducing greenhouse effect gasses have been found not to be as significant as expected. In that sense, it has been observed that individual's driving style plays a more important role on emitting polluting agents than the ecological rating of the vehicle itself. With these assertions in mind, it seems reasonable that if we could assess the fuel-consumption efficiency of individuals, their driving styles could be corrected to increase their ecological friendliness.

Despite several fuel economy-intended systems have been implemented in cars, such as gear recommendation or eco-driving scoring, convenient to achieve the objective of reducing the polluting agents' emissions, personalized assessment of ecological behavior might further help motorists to achieve outstanding fuel consumption results by means of driving style recommendations. These recommendations, based on each individual's driving behavior, are intended to re-educate drivers if they follow incorrect driving patterns.

In this line, we propose an intelligent system able to classify driving behavior depending on fuel efficiency features and to give advice according to them. This Advanced Driving Assistance System (ADAS) has been developed using real-world data from an instrumented car from the University of Sabançi, particularly, the data stream from its CAN-bus (e.g. speed, throttle pedal, brake pedal or accelerations). These data were collected through driving sessions along a pre-defined driving path combining urban areas, interurban roads and highway stretches.

The characterization of driving styles (DS) is performed by means of Self-Organized Maps (SOMs), an intelligent unsupervised machine learning (ML) algorithm able to automatically group drivers according to the way they drive. This ML algorithm has been chosen because it relies on a two-dimensional representation of a high-dimensional complex system, known as map, suitable for qualitative evaluation of main driving behavior features. Finally, a hybrid, fully parallel hardware/software, Xilinx ZynQ Programmable System-on-Chip (PSoC)-based implementation has been chosen to deploy the car-boarded SOM assessment solution, achieving real-time performance rates.

Unveiling atomic-scale features in nanoplasmonics

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KEY WORDS: light, nanophotonics, plasmon, atomic-scale features, picocavities, EELS, SERS.

Traditional optical systems are diffraction-limited and therefore their ability to resolve nearby points is proportional to the wavelength of light. Nevertheless, recent advances in theory and fabrication techniques have allowed overcoming this limit. Nanophotonics aims to control light on length scales smaller than its wavelength by harnessing the interaction of light with matter. For instance, metallic nanostructures host collective excitations of conduction electrons (plasmons), which interact with incoming electromagnetic radiation, producing evanescent waves that decay in a region of few nanometers and allow the control and production of light at the nanoscale. At resonant wavelengths the metallic nanostructures show remarkable absorption and produce intense electromagnetic field enhancement and localization around their surface.

Furthermore, atomic-scale features play a major role on the near-field distribution around the surface. We have studied theoretically, with the aid of both classical continuous and quantum atomistic descriptions, the optical response and near-fields of nanoparticles presenting such atomic-scale features. The results show subnanometric field localization around the atomic-protrusions, creating plasmonic picocavities, driven by an off-resonant atomic-scale lightning rod effect.

The field enhancement and localization produced by plasmonic nanostructures has been widely used to boost the light-matter interaction in molecular spectroscopy, thus amplifying the measured signal. Moreover, the presence of picocavities, e.g., at the gaps of nanoparticle-on-mirror structures, has allowed the detection and study of single molecules within surface enhanced Raman spectroscopy (SERS), a technique for the study of vibrational excitations in molecules. With our models we have addressed such picocavities, as well as sudden increases observed in the background signal of SERS, named *flares*. We address these *flares* as local changes in the atomic structure of the metallic structure, that produce a local change in the electron density and thus in the dielectric function, which increases the penetration of the electromagnetic field into the metallic nanostructure.

Apart from light, the excitation of plasmons can also be achieved by other means, such as electron beams. The recent achievement of subnanometric spatial resolution with electron microscopes has motivated the theoretical study of the effect of atomic-scale features in electron energy loss spectroscopy (EELS), showing the great dependence on the orientation of the nanoparticle with respect to the electron beam, and the excitation of confined bulk plasmons, which cannot be excited with light.

Magnetotactic bacteria as sources of biogenic model magnetic nanoparticles and microrobots for hyperthermia treatments

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KEY WORDS: magnetotactic bacteria, magnetism. biogenic nanoparticles, anticancer, hyperthermia, drug delivery

Magnetotactic bacteria (MTB) are microorganisms with the ability to align and orient themselves in the presence of the Earth`s magnetic field. This special property, known as magnetotaxis, arises thanks to the presence of one or several chains of intracellular magnetic nanoparticles. The different species of magnetotactic bacteria synthesize perfectly stoichiometric magnetite nanocrystals, with genetically controlled sizes and shapes, surrounded by a biocompatible membrane, making them ideal for studying their magnetic properties as a biogenic model and also for biomedical use. Thus, the project is oriented in two complementary directions: first, the thorough study of the magnetic properties of the magnetosomes as a model that can be extrapolated to other nanoparticle systems, and second, the exploitation of magnetotactic bacteria for biomedical applications.

On the one hand, the high quality of magnetosomes makes them a perfect model system to investigate the relation between structure and magnetic properties, and to define experimental methods and characteristics for the appraisal of nanoparticle systems. This will be accomplished by comparing the magnetosomes of different species of MTB: *Magnetospirillum gryphiswaldense, Magnetospirillum magneticum and Magnetovibrio blakemorei*. These systems will be studied supported by analytical and modelling methods, in order to assess the influence of the structure, morphology and arrangement of the nanoparticles on their magnetic properties, and reproducibility.

On the other hand, we propose a novel and ambitious initiative, oriented towards exploiting the living bacteria as self-propelled biorobots for cancer treatment, using their tendency to navigate along definite magnetic directions and oxygen gradients. Ideally, guided inside the body by external magnetic fields towards hypoxic tumor regions, they can produce a therapeutic action both by releasing heat (hyperthermia) and therapeutic drugs (drug delivery). In our recent work, we have proven that the biological structure of the chains of magnetosomes is ideal to maximize the hyperthermia efficiency. To test this approach, we have built a laboratory station composed of microfluidic channels mimicking human blood vessels in which the bacteria can be remotely controlled by using a magnetotaxis setup, while their position and movement is tracked by an optical microscope able to follow the movement of the bacteria along the microfluidic channels.

Loop Quantum Gravity effects in gravitational collapse

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KEY WORDS: Loop Quantum Gravity, gravitational collapse, black holes.

One of the most significant open problems in theoretical physics is the understanding of the quantum behaviour of gravity. Although individually, General Relativity and Quantum Mechanics are very successful theories, we lack a fundamental description of phenomena when both, gravitational and quantum effects, are expected to be strong. For instance, black hole singularities, the origin of the universe or the underlying nature of spacetime itself at very small scales.

Loop Quantum Gravity, following the canonical quantization program, provides one of the most appealing frameworks to describe quantum gravitation. In the cosmological sector, for instance, loop techniques show how the Big Bang is replaced by a quantum bounce at very early times. These computations have been extended to black hole interiors, and the collapse seems to stop before the classical singularity is reached. However, most of them are homogeneous studies, and thus they cannot provide a complete realization of the actual collapse of a star.

The objective of our research is to obtain a consistent loop-based model of collapsing matter fields and check whether it avoids the formation of a singularity, in contrast with the classical case.

MATEMATIKA

MATEMÁTICAS

Klima-aldaketa
Cambio Climático

On the development of prediction models for complex survey data

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KEY WORDS: complex survey data, prediction models, sampling weights.

Survey data are becoming increasingly well known among researchers and technicians from different fields. In order to mention some, analysts in areas such as the social and health sciences have to deal with this type of data on a daily basis. Survey data are data collected by sampling the finite population, by means of some complex sampling design. One of the differences between complex survey data and simple random samples, are the sampling weights, which are related to the complex sampling design and indicate the number of units that each sampled observation represents in the finite population. Therefore, the straightforward application of the most common analysis techniques, which are commonly designed to be applied to simple random samples, is usually not appropriate for complex survey data.

In particular, complex survey data are commonly used to develop prediction models as data derived from a simple random sampling. However, the effect that a complex sampling design may have in the modelling process should be carefully checked. One of the most discussed topics in this area is the estimation of parameters of prediction models. In the context of logistic regression models for dichotomous response variables, in particular, the pseudo-likelihood function (Binder, 1983) has been proposed as a modified version of the likelihood function that incorporates the sampling weights in the estimation process of the model parameters. However, it is not yet clear if this method outperforms other alternatives when estimating logistic regression model parameters to complex survey data. Therefore, a simulation study has been conducted in order to compare the performance of three different methods when estimating the model coefficients for a dichotomous response variable: a) the unweighted ordinary logistic regression model, b) the generalized linear mixed model with random intercept for each sampling stratum, and c) the weighted logistic regression model.

Nevertheless, in addition to the estimation of model parameters, there are many aspects that should be taken into account in the development of prediction models in order to end up with a valid model: the selection of the predictors, the functional relation between outcome and predictors, imputation of missing values and evaluation of calibration and discrimination, among others. Therefore, we believe it is necessary to consider the design of the survey, especially the sampling weights, throughout the process of development and validation of a prediction model, beyond the estimation of its parameters. In particular, we have studied the impact that the sampling weights may have in the imputation process of a relevant missing predictor variable and we propose a new approach to impute the missing values of a dichotomous predictor variable in the context of complex survey data.

The goal of this work is twofold. On the one hand, we will present an overview of the progress we have made so far on the issue of the development of logistic regression models for complex survey data and we will show the results we have obtained. On the other hand, we will describe the challenges we aim to face in the future.

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Deep Learning approaches for solving inverse problems

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KEY WORDS: Geosteering, Deep Learning, Inverse Problems.

One of the main tasks of subsurface drilling is to reach a certain target within the Earth's subsurface. Hydrocarbons industries' objective is to maximize hydrocarbon extraction while minimizing costs. This is the reason why oil companies want to drill through the oil reservoir as much as possible. To carry out this task, we want to create a map of the subsurface which will allow us to drive the drilling process.

We perform the drilling process using a Logging-While-Drilling (LWD) tool. This is a logging device that simultaneously drills and records logging measurements (through installed transmitters and receivers) for their real-time interpretation. Thus, if we are able to properly interpret (invert) these measurements, we will characterize the materials near the borehole and we will be able to guide the drilling process, for example, avoiding porous rocks filled with salty water or traveling longer distances within the oil reservoir.

Recently, LWD tools became more efficient, improving the gathering of data. Thanks to this development, we are now able to perform *geosteering*. In this process, the well trajectory is corrected based on real-time inversion of the results obtained using downhole measurements. This new possibility of work requires a real-time interpretation of data.

At the industry of hydrocarbons, some 3D numerical simulators of borehole resistivity measurements were developed during the past decades. However, the simulation of 3D problems is computationally expensive, especially, when performing real-time inversion. Thus, we need to develop a method that provides accurate simulations and inversion results with a low computational cost, i.e., in real-time.

Deep Learning is a branch of Machine Learning. It is inspired by the structure of brain cells (neuronal connections) and we call this algorithms artificial neural networks (NN). This technique seems to be an adequate alternative to deal with the aforementioned problems. We train a NN that taking measurements as input data simulates the subsurface properties. This optimization process could be performed with existing data or with synthetically created data. Then, during *geosteering* operations, we can quickly evaluate the already trained NN with our current data and obtain an accurate map of the subsurface properties.

Vanishing viscosity limit of conservation laws

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KEY WORDS: conservation law, vanishing viscosity limit.

This will be an introductory talk about a technique called vanishing viscosity limit. The main idea here is to regularise an ill-posed PDE with a higher order term and after solving the regularised problem, we compute the limit of the regularising term tending to zero in order to get a solution for the first problem.

If time permits, we will briefly mention the kind of non-local regularisation which we have been studying.

Joint work with: Carlota M. Cuesta

Commutators in finite p-groups

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KEY WORDS: Group theory, commutators, commutator subgroup.

A commutator of a group G is an element of the form $xyx^{-1}y^{-1}$, where x and y are two elements of G. These elements are fundamental in group theory, in particular in the theory of solvable and nilpotent groups, as they provide a lot of information about the structure of the group. The subgroup of G generated by all the commutators is called the derived subgroup of G and it is denoted by G'.

At first glance, one may think that all the elements in G' are commutators, but this is not true in general. Indeed, even though G' is generated by all the commutators, it may happen that the product of two of them is not a commutator anymore. However, we can add some restriction to the group G so that we can ensure that G' consists only of commutators.

In this talk, we will see that if G is a finite p-group such that its derived subgroup can be generated by three elements, then all the elements of G' are commutators or, equivalently, that the product of two commutators is again a commutator.

GEOLOGIA

GEOLOGÍA

Klima-aldaketa
Cambio Climático

Climate changes in the past: mid-Cretaceous Oceanic Anoxic Events and their expression in shallow-marine environments

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KEY WORDS: Cretaceous, OAE, *Lithocodium-Bacinella.*

Earth´s climate has changed cyclically at a variety of time-scales throughout the planet's 4500-million-year history, ranging from ice ages to long periods of warm climate referred as interglacials. The mid-Cretaceous was a time of prevailing extreme greenhouse conditions at a global scale. This global warming led to weak latitudinal temperature gradients, the absence of permanent ice-caps in the poles and mean sea-level about 100 to 200 metres above present sea-level. There were also smaller-scale climatic fluctuations within the mid-Cretaceous, which include a number of geologically short-lived hyperthermal events that gave rise to the so-called Oceanic Anoxic Events (OAEs). The most widespread mid-Cretaceous OAEs took place in the early Aptian (OAE 1a), at the Aptian/Albian boundary (multi-event OAE 1b) and during the latest Cenomanian (OAE 2). These periods record dramatic changes in ocean circulation and chemistry, as well as in the marine biota. As a result, organic-rich black shales were deposited globally and synchronously in deep-sea basins. However, the potential expression of the OAEs in shallow-marine neritic environments is still a matter of controversy.

Various authors have reported platform-wide ecological shifts from metazoan-dominated ecosystems to microbial carbonate production as a response to major palaeonvironmental perturbations coeval with the OAE 1a and OAE 1b. Our research aims to clarify whether the repeated biotic replacements observed in the latest Aptian urgonian limestones of the Cuchía area (Cantabria, Spain) may be related to the coetaneous multi-episodic OAE 1b. The sedimentary facies analysis reveals intermittent *Lithocodium-Bacinella* mass-occurrences within a thick limestone sequence typically made up of rudists, corals and orbitolinids. The *Lithocodium-Bacinella* units reach thicknesses of few tens of metres and show distinct bacinellid fabrics developed under different palaeobathymetric conditions. These stratigraphic intervals contain scarce rudists and corals, but instead include outstanding oyster-like *Chondrodonta* patch reefs up to 3.3 metres thick and several tens of metres wide. Isotopic analyses will help attribute a precise chronostratigraphic assignment to these microbialites, which is essential to emplace them within a global context of palaeoclimatic and palaeoceanographic changes.

Anthropogenic dynamics from the Holocene to the Anthropocene on the Cantabrian coast (Nortern Iberia)

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KEY WORDS: Paleopalynology, Estuaries, Holocene-Anthropocene.

Paleopalinology is the study of fossil remains as pollens,spores and non-pollen palynomorphs that have survived to this day thanks to an extraordinary capacity for conservation. Through paleopalinology we can detect several anthropic dynamics (deforestation, selective plantations,the existence of livestock cabins,the natural or anthropic origin of fires, the relationship between periods of dryness and humidity and even the presence of foreign invasive species). On natural deposits (peatbogs, lakes, estuarine contexts) palepalinology has been applied in the reconstruction of the Pleistocene and Holocene ecosystems.

The Anthropocene concept refers to the recent history of our planet characterized by a rapid and profound geological change provoked by numerous human activities and reflected in the sedimentary record. This impact can be studied through a great variety of proxies as, for example, fosil pollen in estuarine settings. The objective of this work is to reconstruct the process of anthropization of the coastal vegetal landscape on the eastern Cantabrian coast (northern Iberian Peninsula).

Different sedimentary records have been studied: Long cores (±16 m) that extend to Holocene dates, and short cores (50 cm) dated approximately in the last 200 years.

The general dynamics shown during the most recent times suggest a progressive growth of forest areas, since the arboreal pollen of the current taxa from the Cantabrian coastal vegetation (e.g., *Alnus, Betula,* deciduous *Quercus* and *Pinus sp.*) increases through time. Other anthopogenic taxa as *Cerealia* t., Poaceae (whose expansion is often linked to deforestation and infrastructure construction) and *Sordaria* t. appear with significant percentages in some parts of the cores, suggesting the presence of intense agricultural activities and livestock animals.

Human activities have left a clear signal on the recent paleopalynological record of this region. Firstly, with the agricultural and timber exploitation that caused a reduction of the arboreal species in favour of the herbaceous taxa. Secondly, with the abandonment of these activities the arboreal forests recovered naturally their spaces appearing forms like *Alnus* that usually grow in humid environments near coastal areas or river courses. Finally, the recovery of forest spaces, especially during the last 200 years, probably linked to the replanting began in the 19th century and exacerbated with the “National Reforestation Plan” carried out during the 1940s.

Evaluation of land cover effects on hydrological functionality of soils: adaptation measures from the territory (Bidasoa catchment, Western Pyrenees)

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KEY WORDS: soil, hydrological functionality, soil-moisture, climate change, adaptation.

The central axis of this Doctoral Thesis project is based on the need to analyse the interactions through the compartments Land Cover-Soil-Water. The project is focused on the analysis of the effect that land cover and associated soil properties have on different hydrological services. Indeed, land use and its management directly affect soil hydrology, which is a key factor in streamflow temporal distribution. A better understanding of the water-soil-vegetation system is essential for reliable hydrological modelling, which results should be considered in developing sustainable land and water management strategies, in a context of adaptation to climate change. This knowledge is of particular relevance in The Pyrenees mountain range, as it is the main source of water resources for a large surrounding region, making this area remarkably vulnerable to the consequences of climate change.

To this aim, a detailed chemical and physical characterization of soil properties consisting of 172 sample points has been conducted at the 681 km^2 Cantabrian Bidasoa catchment (Pyrenees). Analyses reveal a great relation between chemical characteristic and surrounding geology, whilst land cover is the main element affecting physical properties. So as to understand the influence of these factors into the hydrological functionality of soils, a soil-moisture monitoring network was established in July 2019 in a 0.4 km^2 experimental site within the catchment. Four soil-moisture stations and a meteorological one were installed within the same geological setting, same rainfall conditions and similar soil texture characteristics (silt-loamy texture and about one meter deep), but different land covers (pine forest, oak forest, grassland and fernery). Continuous soil-moisture data obtained to date show that soil-moisture dynamics are deeply influenced by top vegetation cover. Superficial soil-moisture in grassland exhibits the highest variations, ranging from 16.2 to 36.6 %, as they closely mirror precipitation patterns. Pine and oak forests present similar variation trend, varying from 33.9 to 42.8 % and from 35.3 to 41.9 %, respectively. Soil-moisture at fernery goes from 30.5 to 36 %. Maximum values, occurring during very heavy and continuous precipitation in November 2019 (647 mm registered from 1 to 24 November), are considered as a proxy for saturated soil conditions. In all the plots, fluctuations in soil-moisture diminish significantly with increasing soil depth. However, considerable differences are found in the vertical soil-moisture profile across land covers. In both forest plots, a decreasing trend of soil-moisture within the profile is observed, while grassland and fernery show an increasing trend. Preliminary results show that soil water infiltration is different among different land covers. In fact, soil with grassland cover seems to retain more water than tree cover, where infiltration to deeper layers could be faster.

All of this knowledge will give insight into the hydrological functionality of soils under different vegetation types. Longer records of soil-moisture dynamics in the area would contribute to better assess the linkages between water, soil and vegetation and, in turn, to improve hydrological modelling in humid mountainous areas. This understanding is necessary for a better consideration of the adaptation measures that should be taken from the territory.

Analysis of cliff instabilities in the Basque Coast, for a respectful management in areas of high geological value

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KEY WORDS: instabilities, geoheritage, specific management.

The study of instability processes, especially in cliffs that require special protection, is fundamental for the proper management of geoheritage. This study, is all the more important in the context of climate change, since the more and more frequent meteorological events (torrential rains, temperature fluctuations…) are considered to be major external factor causing slope instability. New work methodologies innovate by using modelling in the analysis of these events, but on a wide scale. This thesis aims to develop a methodology for the study and management of coastal environment of high geological value. To this end, coastal cliffs, their dynamics and evolution will be studied in detail in the western coast of the Bay of Biscay.

In this way, new Technologies such as drones or GPS systems are used to create three-dimensional models that allow process simulations. In order to do so, the discontinuity planes and the rock resistance parameters will be calculated in the field, and numerous laboratory tests will be carried out to find out the origin of the instability processes.

The first step has been to carry out this study in Zumaia, in the Basque Coast Geopark, which conserves a practically natural environment with an active geological dynamic. In its northern limit, the coastal cliffs evolve, and numerous gravitational processes take place, with the development of different forms of instability. These processes are very common in all types of slopes, both natural and constructed, and are determined by geological, geomorphological and environmental conditions.

Within the laboratory and field tests, the following stand out:

- Schmidt's hammer
- Slake Durability Test
- Point Load Test
- Uniaxial Compressive Strength
- Triaxial Compressive Strength

In addition, thin section of rocks that present different resistance results will be made, to provide more data to the specific study of the materials, and to know in detail the origin of the instabilties.

In short, the aim is to develop a methodology based on the specific study of the processes and not on the large number of unknowns that exist today in the world of engineering geology.

Geomicrobiological interactions and mineral neoformation in sediments of acid mine drainage environments.

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KEY WORDS: acid pit lakes (APLs), acid mine drainage (AMD), mineral neoformation, metal-microbe interaction.

BACKGROUND

Spain has a long history of intensive sulfide mining. This activity took place in the SW part of the Iberian Peninsula related to the Devonian-Carboniferous Iberian Pyrite Belt mining district, composed of ~80 volcanogenic massive sulfide ore deposits. Similarly important was the SE La Unión-Sierra de Cartagena mining district with late-Tertiary Pb-Zn-Fe ore deposits. These mineralizations have abundant sulfides, sulfosalts and arsenic sulfides (e.g., pyrite (FeS_2), sphalerite (ZnS), galena (PbS), chalcopyrite ($FeCuS_2$), arsenopyrite (FeAsS)), which after open-pit exploitation, become exposed to oxidation, releasing high acidity, sulfate and metals (e.g. Fe, Al, Zn, Cu, As, Pb, Cd), enabling continuous long-term pollution known as acid mine drainage (AMD). Extensive knowledge is available on bacterial communities living in acid pit lakes, as well as on mineralogical processes during chemical neutralization. Nevertheless, mineral neoformation related to biological activity (i.e., bio-mineralization (direct) and bio-induced (indirect) mineralization) is generally disregarded. The mineralogy and crystal chemistry of sulfide minerals formed during microbial sulfidogenesis is especially poorly studied.

OBJECTIVES

The main aim of this work is the identification and characterization of neoformed mineral phases arising from microbial-metal direct (biomineralization) or indirect (bio-induced mineralization) interaction, as well as metal mobility during the neoformation and early diagenesis. Finally, geochemical modelization will be performed.

MATERIALS AND METHODS

A great variety of limnological, mineralogical, geochemical and ecological techniques are being continuously used[1]. Original water and sediments were gathered to build incubation columns[2], which proved to be highly useful for laboratory investigation of natural systems. This approach allows us to obtain detailed information on the evolution of geochemical conditions of the natural systems and the mineralogical response. Even more, we may change environmental conditions and evaluate their impact, revealing those factors exerting the greatest control. The use of classical mineralogical techniques (e.g., optical microscopy, XRD, XRF) is rather limited due to extremely small size and low crystallinity of neoformed minerals. Thus, electronic microscopy (e.g., SEM, TEM, STEM)[3,4], along with synchrotron-based techniques (XAS: X-ray absorption spectroscopy) have to be used.

CURRENT RESULTS

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ACKNOWLEDGEMENTS

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Submerged marine terraces identification and an approach for numerical modeling the sequence formation in the Bay of Biscay (northeastern Iberian Peninsula)

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KEY WORDS: marine terrace, submerged sequence, digital bathymetric model, TerraceM, numerical modeling, Bay of Biscay.

Submerged sequences of marine terraces potentially provide crucial information of past sea-level positions. However, the distribution and characteristics of drowned marine terrace sequences are poorly known at a global scale.

Using bathymetric data and novel mapping and modeling techniques, we studied a submerged sequence of marine terraces in the Bay of Biscay with the objective to identify the distribution and morphologies of submerged marine terraces and the timing and conditions that allowed their formation and preservation. To accomplish the objectives a highresolution bathymetry (5 m) was analyzed using Geographic Information Systems and TerraceM ®.

The successive submerged terraces were identified using a Surface Classification Model, which linearly combines the slope and the roughness of the surface to extract fossil sea-cliffs and fossil rocky shore platforms. For that purpose, contour and hillshaded maps were also analyzed. Then, shoreline angles, a geomorphic marker located at the intersection between the fossil sea-cliff and platform, were mapped analyzing swath profiles perpendicular to the isobaths.

Most of the submerged strandlines are irregularly preserved throughout the continental shelf. In summary, 12 submerged terraces with their shoreline angles between approximately: -13 m (T1), -30 and -32 m (T2), -34 and -41 m (T3), -44 and -47 m (T4), -49 and -53 m (T5), -55 and -58 m (T6), -59 and -62 m (T7), -65 and -67 m (T8), -68 and -70 m (T9), -74 and -77 m (T10), -83 and -86 m (T11) and -89 and -92 m (T12). Nevertheless, the ones showing the best lateral continuity and preservation in the central part of the shelf are T3, T4, T5, T7, T8, and T10. The age of the terraces has been estimated using a landscape evolution model. To simulate the formation and preservation of submerged terraces three different scenarios: (i) 20-0 ka; (ii) 128-0 ka; and (iii) 128-20 ka, were compared. The best scenario for terrace generation was between 128 and 20 Ka, where T3, T5, and T7 could have been formed.

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KIMIKA

QUÍMICA

Klima-aldaketa
Cambio Climático

Rotational Spectroscopy unveils Chemistry at the molecular level

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KEY WORDS: Rotational spectroscopy, high resolution, structural determination

Gas phase microwave spectroscopy is able to unveil subtle structural and dynamical effects directly related to the chemical physical properties exhibited by a system, by isolating it from interactions with solvent or crystal packing. Moreover, by coupling these techniques with supersonic expansions, we can access the native conformational and aggregation preferences of molecules and intermolecular complexes.

The Spectroscopy Group at the University of the Basque Country (UPV/EHU) has built several microwave spectrometers along years. The more recent one is the chirped-pulsed FT-microwave spectrometer (CP-FTMW) equipped with a customized multi-valves system. [1] The second one is a cavity based FT-MW spectrometer coupled with an UV ultrafast laser vaporization system. [2] Both set-ups are cutting-edge in the field of microwave spectroscopy.

In order to illustrate our strategy, we present recent results focused on solving various structural problems of Chemistry at the molecular level.

Figure 1. Microwave facilities available at the University of the Basque Country (UPV/EHU).

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Shortcuts to adiabaticity applied to quantum technologies

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KEY WORDS: shortcuts, quantum technologies.

Advances in achieving exhaustive control over individual quantum systems has sparked the field of quantum technologies, that bears the promise of developing quantum devices that outperform theirs classical counterparts. We design fundamental processes that underlie such devices using shortcuts to adiabaticity, a tool box that allows us to design processes that mimic the result of an adiabatic (very slow) evolution in a finite time, avoiding detrimental effects such as decoherence and accumulated time. Shortcuts have been applied in a variety of contexts, such as quantum state preparation, quantum computation and quantum thermodynamics.

Polyoxometalate-metalorganic hybrids with selective sorption properties towards CO_2.

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KEYWORDS: Polyoxometalates, SCSC transitions, Gas sorption.

Polyoxometalates (POMs) are a well-known family of metal-oxo clusters of d-block early transition metals in their highest oxidation states which presents a wide structural and compositional diversity with remarkable applications in a number of fields such as catalysis, material science or biomedicine. The possibility of combining the inherent properties of POMs (magnetism, luminescence or catalysis) with the characteristics related to open-framework materials, such as their highest internal surface area, has gained attention in recent years with the aim of generating multifunctional hybrid materials. In this sense, the self assembly of POMs with copper(II) complexes of macrocyclic polyamines constitutes an excellent method for designing these POM-based porous materials.

Following this synthetic strategy, the aqueous reaction between Na_2WO_4 and $[Cu(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) complexes at pH = 8.3, has resulted in an covalent 3D network with the general formula $[\{Cu(cyclam)\}_3(W_7O_{24})]\cdot 15.5\ H_2O$ (**1**). This open-framework is constructed by hybrid layers of heptatungstate anions which are linked to four neighbouring clusters by octahedral-shaped metalorganic complexes. Additional complexes connect these layers, which allow the structure to exhibit interconnected channels of square-like voids where all the hydration water molecules are hosted. Crystal structure of **1** showed the ability to undergo two sequential thermally-triggered single-crystal-to-single-crystal transformations (SCSC), which lead to a partially dehydrated phase **1s** and a totally dehydrated **1a**. These phase transitions involve rupture and formation of coordination bonds as well as changes in the geometry of some [Cu(cyclam)] moieties. The anhydrous **1a** presents permanent microporosity with the ability to selectively adsorb CO_2 over N_2 [1].

Recently, the combination between $[Mo_7O_{24}]^{6-}$ polyanion and $[Cu(cyclam)]^{2+}$ complexes in water at pH = 6, results in the isostructural analogous of **1** based on a polymolybdate anion , namely $[\{Cu(cyclam)\}_3(Mo_7O_{24})]\cdot 15.5\ H_2O$ **(1-Mo)**. This new Mo-based system is expected to present the similar attractive properties as those shown by **1**. Finally, it is worth mentioning that Mo presents some advatages over W, such as: i) its faster and reversible redox activy. This property could be exploited for the generation of electrochemical energy storage systems; ii) its lower molecular weight and iii) the fact that it is not considered as a critical raw material. Therefore, the fact of developing a new material with the ability of selectively absorb CO_2 over N_2 opens up a new perspective to synthetize novel devices that could be helpful to face greenhouse effect and selectively reduce the amount of atmospheric CO_2.

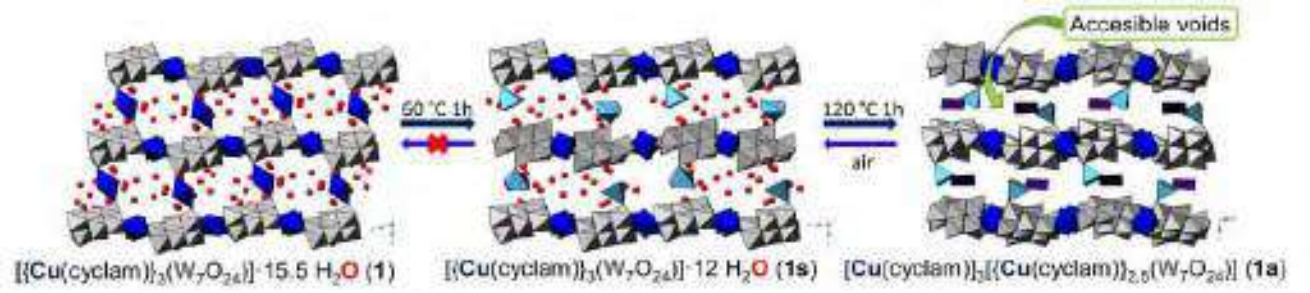

Figure 1. Scheme of the thermally-triggered SCSC transformations of **1**, highlighting their reversibility, structural changes and the permanent porosity of **1a**.

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Nanosystem design, synthesis and characterization for biomedical applications

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KEY WORDS: functionalization, hiperthermia, magnetic nanoparticles

Nanotechnology addresses the design, manufacture and application of nanostructures and nanomaterials. But, in addition to analyzing the materials and structures that are framed on that scale, it also combines the physical properties and dimensions of the materials. At present, there have been many biologists, chemists, physicists, doctors and engineers who have been interested in the application of these materials, as they can be the main incentives of the next industrial revolution.

It is note to mention the great interest of nanomaterials in biomedicine area, and especially magnetic nanomaterials. This kind of nanoparticles present applications as drug delivery systems, contrast agents for RMI or in cancer therapies, as in the case of magnetic hyperthermia. This therapy is based on the heating capacity of magnetic materials under an A.C. magnetic field. The control of the temperature in the range between 40 and 46°C, would yield apoptosis of cancer cells, without damaging healthy cells. Thus, by placing the magnetic nanoparticles on the tumour side and applying the magnetic field in turns, the death of the tumour cells occurs as a result of the increase in temperature.

For all these purposes the selection of the material is a critical factor [1]. The lack of toxicity and the ability to biodegrade easily in the human body is essential to ensure posterior success in clinical trials, being magnetite materials the most used ones. What is more, a proper functionalization can increase their biocompatibility, together with providing functional groups to attach biomolecules with special features [2]. In fact, specific functionalizations are essential to reach certain parts of the body that are otherwise inaccessible or to anchored drugs to be delivered to specific areas of the body. In this way it can be assigned a specific surface for each treatment and application to be used.

Although this seems straightforward at first sight, the effectiveness of the nanosystems is directly related to the homogeneity of nanomaterials (size, shape, composition, etc.). Therefore, the aim of the work performed by our group in the last years has been targeted to the optimization of magnetic nanomaterials for being applied in magnetic hyperthermia. So, herein we present different preparation methods and functionalizations to synthesize nanoparticles with homogeneous characteristics. Several in-vitro and in-vivo tests carried out to date will be accompanied.

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A more sustainable approach to diaryldiacetylenes

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KEY WORDS: diaryldiacetylenes, molecular oxygen, polyethylene glycol.

Conjugated 1,3-diacetylenes have attracted much attention due to their extensive use in pharmacologically active compounds, advanced materials and optoelectronic devices.[1] A number of synthetic approaches to these appealing compounds can be found in the literature. However, in many cases stoichiometric amounts of harmful oxidants and other reagents are required as well as volatile and relatively toxic organic solvents.[2]
Following our research on the development of new catalyst systems that allow more efficient transformations in sustainable reaction media,[3] we wish to present an advantageous procedure for the preparation of diaryldiacetylenes based on the use of molecular oxygen as the sole oxidant and polyethylene glycol as the solvent. The latter polymeric glycol has been reported as a safe and environmentally benign alternative to other more traditional solvents, but never combined with dioxygen to promote an oxidative coupling leading to diaryldiacetylenes. In addition, the remarkably active catalyst system employed can be used in very small amounts so that the metal content in final products is minimized.

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A cascade approach to potentially bioactive pyrrolo[1,2-*a*]indoles

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KEY WORDS: cascade reactions, cycloisomerization, cross-coupling.

The preparation of potentially bioactive compounds often relies on long linear stepwise sequences requiring stepwise work-up and purification stages. Thus, waste of resources and relatively low overall yields for the target molecule remain common challenges to solve. In this regard, cascade reactions are those chemical transformations in which the starting substrate is designed to undergo a reaction whose product becomes the substrate for the next step, and so on, until a stable product under the reaction conditions is obtained. In the last years, cascade reactions initiated by the cycloisomerization of alkynoic acids have demonstrated to be a powerful tool for the construction of different polyheterocyclic compounds.[1]
Among *N*-fused indole derivatives, pyrrolo[1,2-*a*]indoles are attractive targets due to their presence in natural products and pharmaceuticals such as the melotonin analogue, tetrahydrobenzopyridopyrrolizinone or the pyrrolodione displayed in Figure 1.[2] We wish to present our research on a new cascade reaction from alkynoic acid derivatives and 2-haloanilines involving metal-catalyzed cycloisomerization and Heck-type reactions.

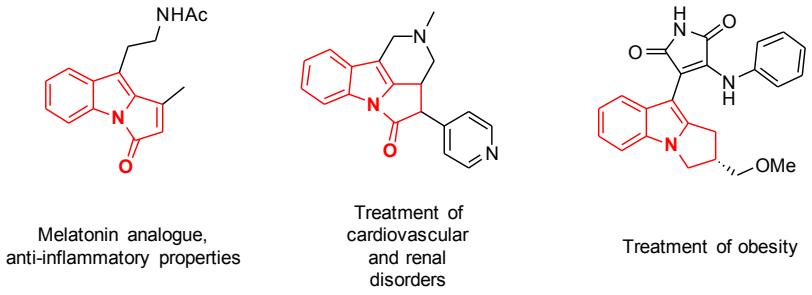

Figure 1. Some bioactive pyrrolo[1,2-*a*]indole derivatives.

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Feasibility of passive dosing methods for in vitro toxicological tests in order to evaluate the risk of petroleum hydrocarbons in accidental spills

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KEY WORDS: Accidental oil-spills, Arctic environment, Ecotoxicological assessment, Water Accommodated Fraction, Passive dosing.

Marine traffic in arctic seas shows a growing trend and the effects on the arctic environment are a matter of increasing concern, especially due to the high probability of accidental oil spills (1). As a consequence of the environmental threats, international institutions and governments are fostering the study of marine oil spill response technologies in the cold climate area and the assessment on the impacts on fish, invertebrates and macro algae of naturally and chemically dispersed oil, in situ burning residues and non-collected oil using highly sensitive biomarker methods.

One of the typical approaches to study the toxicological effect of oil emulsions in marine biota is the use of the water accommodated fraction (WAF) prepared according to standard procedures (2) . In addition to this, the assurance of long and stable exposures to very hydrophobic compounds such as the polycyclic aromatic hydrocarbons (PAHs) for in-vivo and in-vitro tests requires the use of sensitive and precise analytical techniques.

In order to overcome the difficulties of classical approaches, we have explored the feasibility of the passive dosing approach. Within this context, the main aims of this PHD thesis were to study the features of the WAF prepared according to the agreed procedures and to study the feasibility of a passive dossing method to run in-vitro assays.

All the analysis were carried out by gas chromatography coupled to mass spectrometer detection in order to analyse PAHs and lineal aliphatic hydrocarbons. First of all, two method were compared, fractionation (3) and direct analysis of the oil. The first method shown losses on the more volatiles compounds (small alkanes) in contrast to direct analysis which those losses were not seen. Three oils were analysed with this method. IFO, Marine Diesel Oil (MDO) and Northen Naphthenic Oil (NNA). Naphthenic related compounds presented the highest concentration in all samples with a concentration between 1143 to 4774 µg/g. The rest detected PAHs were detected between 4 and 872 µg/g. Higher concentrations of all PAHs were obtained in IFO samples.

Regarding to the preparation of the WAF, a small and handy procedure was designed allowing the preparation of up to 130 ml of WAF at different temperatures and including the loading of a small sheet (1 cm^2) of polydimethylsiloxane (PDMS) as a passive sampler. The kinetics of the oil-water-PDMS sheet partitioning was studied and it was concluded that the steady state was achieved after 150 h of soft stirring. The composition of the WAF at this steady-state was measured by solid-phase microextraction (SPME). Finally, the stability of the WAFs without and with dispersant (CE-WAF) at room temperature was also studied and, according to the p results, the most abundant PAHs are lost in the early five hours in the case of WAF. On the contrary, CE-WAF present higher stability during the first 35 hours and about 50 % of the concentration was loss.

Based on the loaded PDMS sheets during the preparation of the WAFs, the feasibility of these sheets to run in-vitro tests is being studied. The preliminary results show very low concentrations of the most abundant PAHs in both the sheets and the obtained water solutions, but compared to the standard WAFs longer stable exposures were observed. In addition to this, sea-urchin embryo test was carried out using the passive dosing strategy.

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From Earth to Mars, Raman spectroscopy's journey: Development of analysis methodology, testing with Martian meteorites and scientific implementation in SuperCam

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KEY WORDS: Mars, meteorites, Raman spectroscopy.

Raman spectroscopy is one of the main techniques that will land on Mars in the next year, as it is present in three different instruments of the upcoming missions from NASA and ESA to Mars, Mars2020 and ExoMars2020, respectively. This technique will analyze the mineralogy and chemistry of Martian rocks, which might help to find fossilized microbial life, or biosignatures, on the Red Planet.

Besides the mineralogical characterization of a rock, Raman spectroscopy can also be useful to assess several fundamental parameters that might help in the study of the Martian surface and geological history. During my PhD, I have developed several new analytical methods to obtain additional information from the Raman spectra. For instance, a calibration has been established to estimate the pressure suffered by calcites after a shock through its remaining residual stress. This might provide clues about the different meteorite impacts that an area of Mars suffered in the past and also about its magnitude. Regarding the mineralogical composition, Mars is rich in igneous rocks, mainly pyroxenes and olivines, due to the planet's volcanic past. In order to determine the metallic content of the minerals present in these rocks, a calibration model that estimates de Fe and Mg content in olivines through Raman band shifts has been developed. Finally, in the event that organic compounds are found on Mars, a classification model was designed to determine by Raman spectroscopy the different organic types in a complex mixture.

In order to prove the validity and effectiveness of the developed methodologies, several meteorites were analyzed as test samples. For instance, in the Martian meteorite NWA 6148 a bubble containing a mixture of several organic compounds was found and, using the classification model mentioned above, it was observed that they were a variety of short (~10-16 C), saturated, carboxylic acids. In addition, type II calcite was observed in the sample thanks to the developed model, which estimated a residual stress of 0.34 ± 0.06 GPa, consistent with the impact with Earth's surface. Raman spectroscopy was proven as a useful technique not only due to these facts, but also because it was used to discover new mineral phases not observed before in the meteorite's parent body. Such is the case of the tridymite (a low pressure and high temperature polymorph of silica) found in the meteorite EET 83227 coming from 4 Vesta or the Co_3O_4 observed in the NWA 6148 coming from Mars.

All these new tested methodologies will be used to study the surface of Mars through the three different Raman instruments that are flying to Mars in the upcoming missions: the Raman Laser Spectrometer (RLS) from ExoMars2020 (ESA) and the SHERLOC and SuperCam from Mars2020 (NASA). As a member of the scientific group of SuperCam, during my PhD I contributed to the scientific calibration and optimization of this instrument in Los Alamos (NM, USA). During this process a collection of more than 100 mineral samples were analyzed with all the techniques of SuperCam (LIBS, Raman spectroscopy, VISIR and luminescence) to assess its quality parameters. Regarding Raman, the collected data was processed and analyzed, obtaining results for parameters such as the reproducibility intra-day and inter-day (RSD smaller than 1% for every mineral studied), which will allow SuperCam to differentiate between similar phases of the same mineral group, or relative intensities of calcite comparing SuperCam results (0.44:0.11:1) with a commercial instrument (0.40:0.11:1).

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Performance of $NiAl_2O_4$ catalyst in the steam reforming of raw bio-oil

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KEY WORDS: Steam reforming, Bio-oil, Hydrogen.

The steam reforming (SR) of bio-oil obtained by pyrolysis of lignocellulosic biomass is a promising route for sustainable hydrogen production, with a low environmental impact because of neutral CO_2 balance. One of the main problems of bio-oil SR is the deposition of carbonaceous material that causes rapid catalyst deactivation. In order to improve catalyst stability, research effort has been focused on the development of new catalysts resistant to deactivation and with ability to be completely regenerated. A bulk $NiAl_2O_4$ (33 % Ni) catalyst was selected in a previous work for its efficient regenerability [1]. The aim of this work is to establish an optimum reaction temperature of enhancing the H_2 production and attenuating deactivation of this catalyst in the SR of raw bio-oil.

The raw bio-oil, obtained by flash pyrolysis of pine sawdust, was supplied by BTG Bioliquids BV. The bulk $NiAl_2O_4$ catalyst (33 wt% Ni) was synthesized by the co-precipitation method, calcined at 850 ºC for 4 h and sieved between 150-250 µm. Fresh and deactivated catalysts have been characterized by N_2 adsorption-desorption (porous structure), transmission electron microscopy (TEM) and X-ray diffraction (XRD) (metal properties) and temperature programmed oxidation (TPO) (amount and nature of the coke). The catalytic runs were performed in an automated reaction equipment (Microactivity Reference) provided with two steps (thermal+catalytic) in series [2]. The controlled deposition of pyrolytic lignin in the thermal step at 500 ºC minimizes operation problems and catalyst deactivation in the subsequent catalytic step. The latter has been carried out in a fluidized bed, with steam/carbon (S/C) molar ratio of 6 and space time of 0.15 gcatalyst/gbio-oil. Prior to each reaction, the catalyst is reduced *in situ* (with 10% v/v of H_2 in N_2) for 4 h at 850 ºC.

The evolution with time on stream (TOS) of bio-oil conversion and H_2 yield for different reaction temperatures (Figure 1a) show a slower and similar deactivation rate at 600 and 700 ºC, whereas the deactivation is faster at 650 ºC. This unusual result differs from that previously reported in bio-oil SR with Ni/La_2O_3-αAl_2O_3 supported catalyst [3], whose deactivation was attenuated by increasing temperature in the 600-700 ºC range. This different kinetic behavior suggests different deactivation mechanism for bulk $NiAl_2O_4$ and Ni/La_2O_3-αAl_2O_3 supported catalysts.

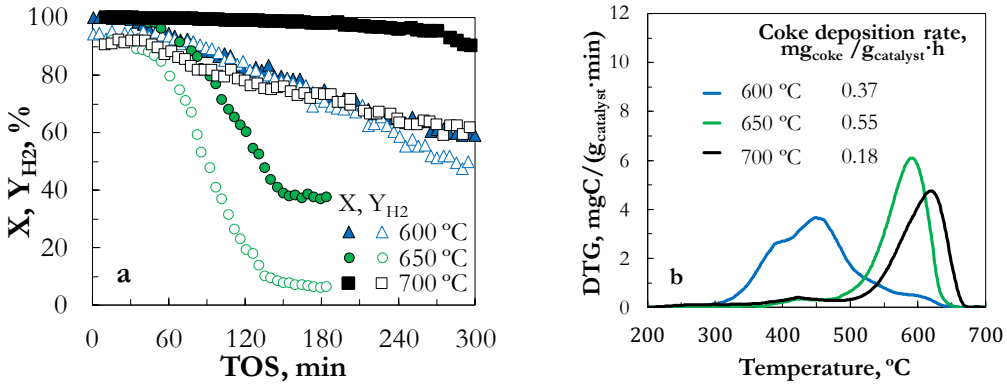

Figure 1. Effect of temperature on the evolution with TOS of conversion and H2 yield (a) and on the TPO profile of the deactivated catalyst (b). Reaction conditions: S/C = 6, space time of 0.15 $g_{catalyst}/g_{bio\text{-}oil}$.

The XRD analysis of deactivated catalysts evidences that Ni sintering is incipient at 650 ºC and noticeable at 700 ºC. TPO analysis (Figure 1b) shows the formation of two different types of coke, which depends on the reaction temperature. An encapsulating coke that burns at low temperature is deposited at 600 ºC, whereas at 650 and 700 ºC a more condensed coke is deposited on the support, which partially blocks the porous structure. Both types of coke contribute to catalyst deactivation. The lower deactivation observed at 700 ºC compared to 650 ºC is explained by the promotion of coke gasification and a lower impact of this coke on the catalyst activity.

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Innovations on biomass steam gasification using spouted bed technology

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KEY WORDS: Spouted bed, Biomass, Gasification, Syngas

In the current energy scenario, an efficient use of clean renewable energy sources is mandatory to tackle the global warming and climate change. Biomass stands out as one of the best alternative energy candidates to produce heat, power and biofuels without contributing to a net rise in CO_2 level. Amongst all the thermochemical routes to convert biomass into valuable products, gasification is the most promising one, as it may allow a sustainable production of syngas, which could be used as fuel or intermediate in the production of other fuels and chemicals. Different biomass gasification technologies have been developed (downdraft, updraft, fluidized beds, fixed bed and rotary kiln), but fluidized beds are undoubtedly those mostly used [1].

Spouted beds are especially suitable for biomass valorization and they have been widely used in different thermochemical processes, such as pyrolysis, torrefaction or gasification. However, this technology involves short gas residence times, which is an excellent feature for minimizing undesired secondary reactions but a serious drawback for gasification, as short residence times hinder tar cracking reactions and limit the gasification efficiency [2]. The fountain confined spouted bed (Figure 1) is an interesting innovation for improving tar cracking efficiency. This novel gas–solid contact regime is characterized by the cyclic, vigorous particle movement of conventional spouted beds and has several advantages over the fluidized bed reactor (e.g., greater versatility in gas flowrate, higher heat transfer rates between phases, and low segregation). Gas residence time is therefore increased, and the gas-solid contact is improved, especially operating under an enhanced fountain regime, which favours tar conversion. Furthermore, this regime greatly improves the gas-solid contact in the fountain, and thereby significantly promotes tar cracking and reforming reactions. Moreover, the fountain confiner provides a noticeable increase in the applicability range of conical spouted beds, which means it can operate with fine materials, avoiding the elutriation of the bed material, and confines the gases generated, forcing them to follow a longer path [3].

As a result of a better gas solid contact, tar content was reduced from 49.2 g Nm^{-3} under conventional spouting regime (without confiner) to 20.6 g Nm^{-3} under fountain enhanced regime (with confiner), with the reduction of heavy PAHs being especially remarkable (from 31.75 wt% to 10.19 wt%). In the same line, the gas and H_2 productions and carbon conversion efficiencies were also greatly improved when operating under enhanced fountain regime. Gas and H_2 productions increased up to 1.3 Nm^3 kg^{-1} and 5.0 wt%, respectively and carbon conversion attained a value of 83.6%. Therefore, the use of a fountain confiner together with a fountain enhanced regime greatly increases the implementation possibilities of the spouted bed technology for biomass gasification.

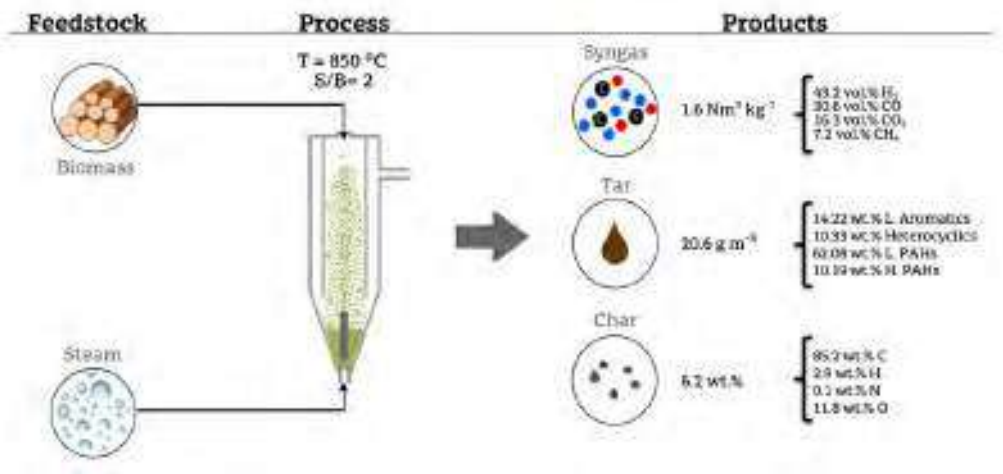

Figure 1. Scheme of the gasification process on conical spouted bed under the fountain enhanced regime and the main results.

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Direct CO_2 valorization to olefins using a In_2O_3-ZrO_2/SAPO-34 catalyst

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KEY WORDS: CO2, olefins, OX/ZEO catalyst

The viable valorization of CO_2 consists in its conversion into value-added products (to compensate the cost of its capture and storage) through routes capable of activating the stable structure of CO_2. Among these routes, the best prospects are those of the catalytic production processes of liquid fuels and raw materials of the petrochemical industry (olefins and aromatics) [1]. In the new direct route of olefin production a bifunctional OX-ZEO (metallic oxide-zeolite) catalyst is used. The metallic function catalyzes the synthesis of methanol/DME and the acid function converts in situ these oxygenates into olefins [2]. This route is very effective to shift the thermodynamic equilibrium of methanol/DME synthesis, favoring the conversion of CO_2. In this work, the effect of reaction conditions on products distribution and yield is studied for feeds composed of H_2, CO and CO_2 mixtures, using a In_2O_3-ZrO_2/SAPO-34 catalyst. In_2O_3 is active for methanol synthesis due to its capability to adsorb CO_2 in the surface oxygen vacancies and its limited capacity for the hydrogenation of C=C bonds and for methane formation. The role of ZrO_2 structural promoter is to attenuate the sintering of In_2O_3. In addition, SAPO-34 is selective to light olefins. A mechanism with format ions as intermediates in the synthesis of methanol/DME and the hydrocarbon pool mechanism for the conversion of these into hydrocarbons is reasonably justified in this process [3].

The runs have been carried out in a fixed bed reactor (Microactivity Reference, PID Eng. Tech.) connected on-line to a Varian CP4900 micro gas-chromatograph for the continuous analysis of the products. A wide range of reaction conditions has been tested: H_2/CO_x molar ratio in the feed, 1-3, and $CO_2/(CO+CO_2)$ molar ratio, 0-1; temperature, 375-425 ºC; pressure, 20-40 bar; space time, 1.25-10 $g_{cat}h(mol_C)^{-1}$; time on stream, up to 60 h.

After an induction period, the catalyst shows a stable trend, and no significant deactivation has been observed up to 60 h of time on stream (TOS). As an example, in Figure 1, the influence of the H_2/CO_x ratio in the $H_2+CO+CO_2$ feed on product yield and selectivity can be observed (after 24 h TOS), under fixed operating conditions: 400 ºC, 30 bar, 5 $g_{cat}h(mol_C)^{-1}$, CO_2/CO_x ratio of 0.5. The results evidence that increasing the H_2/CO_X ratio in the feed from 1 to 2 leads to a significant upgrade of the pursued production of olefins (yield depicted in Figure 1a), with no influence on product distribution (Figure 1b), being olefins selectivity around 70 % in all cases. However, further increasing the H_2 content in the feed does not give way to significant improvements. This result encourages considering the direct synthesis of olefins from syngas + CO_2 a feasible route for valorizing CO_2 together with syngas obtained from biomass gasification (which has a lower H_2/CO_x ratio). Besides, it has been concluded that space time and reaction pressure have a favorable effect on olefins yield, and 400 ºC has been set as the most suitable reaction temperature for boosting olefins production.

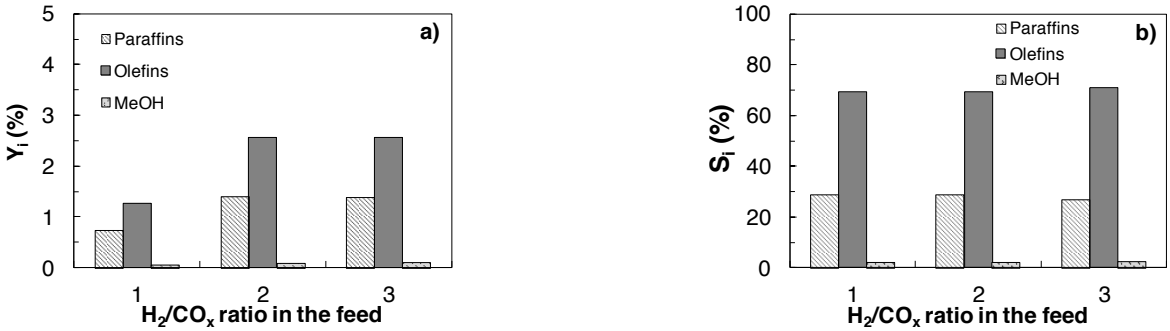

Figure 1. Products yields (a) and selectivity (b) values for different H_2/CO_x ratios in the $H_2+CO+CO_2$ feed. Reaction conditions: 400 ºC, 30 bar, 5 $g_{cat}h(mol_C)^{-1}$, CO_2/CO_x ratio of 0.5, TOS, 24 h.

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Towards a renewable energy model: CO_2 capture and methanation

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KEY WORDS: CO_2 valorization, CO_2 methanation, renewable hydrogen, catalyst, reactor, operational strategies.

The work summarized in this contribution is focused on the development of an efficient system **to maximize conversion of CO_2 *via* hydrogenation to produce synthetic natural gas** as a convenient way to store large amounts of intermittent energy produced from renewable sources for long periods.

In recent years, the exploitation of CO_2 as a carbon source has gained special attention as easy way to mitigate the negative effects of the emission of this greenhouse gas. One of the most promising alternatives is the catalytic hydrogenation of CO_2 to methane through Sabatier reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$).

This reaction is exothermic ($\Delta H = -165$ KJ mol^{-1}, at 298 K) with high equilibrium conversion between 25 and 400 ºC, also with 99% CH_4 selectivity. Such a thermodynamic feature makes the management of heat of CO_2 methanation a difficult task, especially at the pilot and commercial scale, but also makes CO_2 methanation more significant in terms of energy efficiency and economic viability.

Over the last years, the TQSA research group has focused its efforts on the development of catalytic systems for the different operational strategies and designing a reactor system for enhancing the temperature control, cost efficiency and methanation operational flexibility under dynamic operation conditions.

Two main operational strategies have been explored: **continuous CO_2 methanation and cyclic CO_2 adsorption and methanation**. Numerous catalysts based on group VII metals (such as Fe, Co, Ni, Ru and Rh) have been studied for both operational strategies. Among them, Ni-based catalysts are the most widely reported due to their high activity and selectivity to methane, and low price. Ni nanoparticles (NPs) are usually distributed over high surface area supports, such as Al_2O_3, SiO_2 or CeO_2. Despite alumina is the most studied support, there are evidences of the higher catalytic activity with ceria-based support in the continuous operation.

Recently, we have developed **Dual Function Materials (DFMs)** to achieve CO_2 methanation from diluted streams without needing a previous stage of sequestration and concentration. The DFMs contain an additional alkaline or alkaline earth metal (Na, Ca, etc) that adsorbs CO_2. In this technology, the operating conditions are modified at regular intervals to **switch between capture (adsorption) and methanation (hydrogenation) modes**. During the adsorption step, a gas stream containing CO_2 is admitted to the reactor and CO_2 is stored as carbonates onto the basic sites, such as Na or Ca. Once the catalyst is saturated with CO_2, H_2 is admitted to promote the decomposition of carbonates and their subsequent hydrogenation to CH_4 onto Ni sites. Na has shown excellent properties to adsorb CO_2 and then release it during the hydrogenation period.

Different mechanisms have been proposed for the CO_2 methanation reaction, forming various reaction intermediates, with several controlling factors. The purpose of these mechanisms was to provide the best catalytic system with which methanation should be performed in the industries. Several conditions were also studied, such as mechanisms under conditions of low and high temperatures. Several challenges were encountered; the major challenge being the development of a catalyst able to perform methanation at relatively low temperature to economize the project, while yet another challenge is to find an appropriate support, as well as a proper promoter. We have also to make concordance between molecular level mechanisms and global reaction kinetic model. In agreement with molecular mechanism, the model based in the formiate route with two active sites acting for dissociation of H_2 and dissociation of CO_2, resulted the best to describe the observed reaction rate for the optimum Ni/CeO_2 formulation in continuous operation. On the other hand, concerning to the dual system for adsorption/hydrogenation process we have proposed a complete reaction scheme to describe CO_2 adsorption. We were able to define the kinetic equations capable of describing the formation rate of each reactant and product, based on the reaction scheme previously reported.

Valorisation of biomass-derived compounds over transition metal catalysts

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KEY WORDS: hydrogen; catalysts; aqueous phase reforming; hydrodeoxygenation; biomass.

The increasing emission of greenhouse gas due to fossil fuel use has led us to a climate crisis. This fact drives to the development of environmentally friendly technologies. Biomass is considered the fourth largest source of energy in the world, currently supplying more than 10% of primary energy. The transformation of biomass and compounds derived is a promising and sustainable process to obtain fuels and value-added chemicals. Due to its widespread availability, renewable nature, neutral relation to global warming and easy storage and transportation, the potential of biomass to meet the need for world energy has been widely recognized. Therefore, the transition to a bio-based economic model would greatly solve environmental, economic and political problems driven by the current fossil-based economic model.

In recent decades, several catalytic processes have been developed and improved for upgrading biomass into valuable fuels and chemicals. Among these processes, Aqueous Phase Reforming (APR), introduced in 2002, produces hydrogen and other value-added chemicals from biomass derived feedstock under significantly mild reaction conditions. APR can be carried out in a single-step chemical reactor, though various chemical reactions like Water-Gas Shift (WGS) reaction, dehydration, carbon bond cleavage, etc could also compete. With proper catalysts, APR generates H_2 without the necessity of evaporate large amount of water, representing major energy savings. Furthermore, APR minimizes undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures. Likewise, it is one of the most technically feasible approaches to produce H_2 streams with trace amounts of CO. In general, oxygenated hydrocarbons such as sugars (glucose, fructose) and alcohols (sorbitol, xylitol, glycerol, ethylene glycol, ethanol, and methanol) can be valorised into hydrogen and carbon dioxide among other gaseous and liquid products. Another interesting process is the aqueous phase Hydrodeoxygenation (HDO) using in-situ generated or co-feeding hydrogen to produce high value-added fuels and useful chemical building blocks.

Considering the importance of H_2 in a society inclined to the use of clean and renewable energy, our research has focused, firstly, in the development of active catalysts for obtaining H_2-rich streams from the APR of biomass-derived glycerol; and in parallel, in the production of high value-added chemical products via HDO using in-situ generated hydrogen. The interest of the project is oriented to the non-conventional design (preparation, composition and activation protocol) of new transition metal cost-effective catalysts (Co, Ni) whose catalytic behaviour can be comparable to that of the benchmark noble metal catalysts.

To gain knowledge on catalyst structure-activity relationships, a deep physico-chemical characterization, involving a wide number of techniques, is carried out on the synthesized materials, with special emphasis on the characteristics of the metal nanoparticle (crystallite size and dispersion) and the surface acid-base properties. The evaluation of the catalytic performance is carried out in a bench-scale fixed-bed up-flow reactor and the reaction products analysed by chromatographic methods.