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26-27 abril

# Zientzia eta Teknologia Fakultateko VIII. Ikerkuntza Jardunaldiak

## VIII Jornadas de Investigación de la Facultad de Ciencia y Tecnología



eman ta zabal zazu



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del País Vasco

Euskal Herriko  
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Dear colleagues,

On April 26 and 27, 2023, the "VIII Research Days" of the Faculty of Science and Technology took place with a remarkable success.

The first Conference was held in 2008 and continued in a biannual basis until the VII Conference, the previous one, which had to be postponed from March to September 2020 due to the COVID19 pandemic, and was finally held virtually.

The VIII Conference began on April 26 with a continuous session of posters in the "Grande Salle" of the Faculty maintained throughout the whole Conference. 67 posters from different research groups of the Faculty were presented. The influx of students and staff throughout the two days of the Conference was continuous and at certain times very numerous.

The inaugural conference entitled " Más vale ciento volando: emprender desde la ciencia " given by the President of the IUPAC and Professor at the University of Alicante, Javier García Martínez, had a very good reception and raised a multitude of questions from the audience. This good reception continued with the 43 oral communications that were given in parallel on April 27 by doctoral students. It is noticeable that in all the rooms there was a large influx of public. On this day, a round table was also held on the research career. The speakers, postdoctoral researchers of the Faculty, showed the different ways for the development of the research career. The Conference ended with the award ceremony for the best Poster that corresponded to the Hidro-Ingurumeneko Prozesuak Ikertaldea (HGI) group, belonging to the Department of Geology.

We sincerely believe that the objectives of the Conference, which were the following ones:

- (1) establish a meeting place that enables the knowledge of the research lines developed by the different research groups of the Faculty in order to encourage synergies between different disciplines;
- (2) offer an alternative to disseminate to the Society the research carried out in the Center;
- (3) offer the young researchers the possibility of orally disseminating the research they carry out (in many cases their public baptism) and
- (4) awaken the students' interest in the research and the possibilities it offers.

They have been more than fulfilled and the participation of the staff and students of the Faculty in the Conference was specially remarkable.

Therefore, I must conclude by stating that the "VIII Research Conference of the Faculty of Science and Technology" has been a success. Likewise, I sincerely express my gratitude to the Vice-Rectorates of Campus of Biscay and Research for the grants received and to all the attendants and organizers of the Conference for taking part.

Fernando Plazaola  
The dean of the Faculty of Science and Technology

Lankideok,

2023ko apirilaren 26 eta 27an Zientzia eta Teknologia Fakultatean egindako VIII. Ikerketa Jardunaldiek arrakasta handia izan zuten.

Jardunaldiak 2008an hasi ziren, eta bi urtean behin egin dira, ezustekorik gabe, VII. Jardunaldietara arte. 2020an, COVID19aren ondorioz, martxotik urte horretako irailera atzeratu behar izan ziren, eta, hala ere, pandemiak gogor jarraitzen zuenez, modu birtualean egin behar izan genituen.

VIII. Jardunaldiak apirilaren 26an hasi ziren: Fakultateko Grande Salle aretoan posterrak egon ziren jardunaldiek iraun zuten denbora osoan, eta Fakultateko hainbat ikerketa talderen 67 poster egon ziren ikusgai. Fakultateko ikasleen eta langileen joan-etorria etengabea izan zen aretoan, eta une jakin batzuetan jende ugari ibili zen posterrak ikusten.

Jardunaldiei hasiera emateko hitzaldia, "Más vale ciento volando: emprender desde la ciencia", Javier García Martínez jaunak, IUPACeko presidente eta Alacanteko Unibertsitateko katedradunak, egin zuen: oso harrera ona izan zuen eta hainbat galdera egin zizkioten auditoriumean bildutakoek. Harrera ona izan zuten ere apirilaren 27an doktoregoko ikasleek emandako 43 komunikazioek. Areto guztietan bildu zen lagun ugari. Egun horretan, ikerketa ibilbideari buruzko mahai-inguru bat ere egin zen. Hizlariak Fakultateko doktorego ondoko ikertzaileak izan ziren, eta ikerketa ibilbidean aurrera egiteko hainbat aukera jarri zituzten mahai gainean. Jardunaldiak amaitzeko, Geologia Saileko Hidro-Ingurumeneko Prozesuak Ikertaldeak (HGI) poster onenaren saria jaso zuen.

Hauek ziren jardunaldien helburuak:

- (1) Fakultateko ikertaldeek ikerketa ildoak ezagutzera emateko topagune bat sortzea, diziplina desberdinen arteko sinergiak bultzatzeko;
- (2) ikastegian egiten den ikerketa gizarteari zabaltzeko beste bide bat eskaintzea;
- (3) ikertzaile gazteei beren ikerketaren berri ahoz zabaltzeko aukera eskaintzea, askotan jendaurrean egindako bataioa izan baita, eta
- (4) ikaslearen interesa piztea ikerketarekiko eta ikerketak eskaintzen dituen aukerekiko.

Horiek izanik, bada, helburuak, guztiak bete dira, soberan bete ere, eta goraiatzekoa da Fakultateko langile eta ikasleek jardunaldietan izan duten parte hartzea.

Beraz, bukatzeko, adierazi nahi dut Zientzia eta Teknologia Fakultateko VIII. Ikerkuntza Jardunaldiak arrakasta handidunak izan direla. Eta eskerrak eman nahi dizkiet Campuseko errektoreordetzei eta Ikerketaren arloko Errektoreordetzari eman diguten laguntzagatik, eta, era berean, eskerririk asko ere parte hartu duten guztiei eta antolatzaileei.

Fernando Plazaola  
Zientzia eta Teknologia Fakultateko Dekanoa

Estimadas compañeras,  
Estimados compañeros,

Los días 26 y 27 de abril de 2023 se celebraron con notable éxito las "VIII Jornadas de Investigación" de la Facultad de Ciencia y Tecnología.

Las Jornadas comenzaron su andadura en 2008 y se celebraron bianualmente sin contratiempos hasta las VII Jornadas, las anteriores, en las que debido a la pandemia del COVID19 hubo que retrasarlas de marzo de 2020 a septiembre del citado año. Además, como la pandemia no remitía las Jornadas se tuvieron que realizar de manera virtual.

Las VIII Jornadas comenzaron el 26 de abril con una sesión continua de pósteres en la Grande Salle de la Facultad que duró hasta la finalización de las Jornadas. Se presentaron 67 pósteres de diferentes grupos de investigación de la Facultad. La afluencia de estudiantes y de personal de la Facultad a esta sesión continua de pósteres fue continuada a lo largo de la duración de las Jornadas y en determinados momentos muy numerosa.

La conferencia Inaugural de título "Más vale ciento volando: emprender desde la ciencia" impartida por el presidente de la IUPAC y catedrático de la universidad de Alicante, Javier García Martínez, tuvo una muy buena acogida que trajo una multitud de preguntas del auditorio. La muy buena acogida continuó en las 43 comunicaciones orales que se impartieron paralelamente el 27 de abril por estudiantes de doctorado. Conviene indicar que en todas las salas hubo una gran afluencia de público. Este día también se celebró una mesa redonda relativa a la carrera investigadora cuyos ponentes fueron investigadores postdoctorales de la Facultad y que puso sobre la mesa variadas vías para el desarrollo de la carrera investigadora. Las Jornadas finalizaron con la entrega del premio al mejor Poster que correspondió al grupo Hidro-Ingurumeneko Prozesuak Ikertaldea (HGI) del Departamento de Geología.

Creo sinceramente que los objetivos de las Jornadas:

- (1) establecer un lugar de encuentro que posibilite el conocimiento de las líneas de investigación que desarrollan los distintos grupos de investigación de la Facultad para favorecer sinergias entre diferentes disciplinas;
- (2) ofrecer otra vía para difundir a la Sociedad la investigación que se realiza en el Centro;
- (3) ofrecer a los investigadores jóvenes la posibilidad de difundir oralmente la investigación que realizan, que en muchos casos ha sido su bautismo en público y
- (4) despertar el interés del estudiantado por la investigación y por las posibilidades que ofrece.

Se han cumplido con creces y la participación del personal y estudiantes de la Facultad en las Jornadas ha sido encomiable.

Por tanto, he de concluir afirmando que las "VIII Jornadas de Investigación de la Facultad de Ciencia y Tecnología" han sido un éxito. Así mismo, agradezco a los Vicerrectorados de Campus y de Investigación por las ayudas recibidas y a todas y todos los participantes y organizadores de las Jornadas.

Fernando Plazaola  
Decano de la Facultad de Ciencia y Tecnología

ABSTRACTS

IDATZIZKO

KOMUNIKAZIOAK

COMUNICACIONES  
ESCRITAS



BIOZIENTZIAK

BIOCIENCIAS

# Nutrition Management in Plant and Soil (NUMAPS) research group

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KEY WORDS: Agriculture, nitrogen, nutrient, plant molecular biology, plant nutrition, plant physiology, soil microbe.

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Plant growth and crop yield depends on nutrient acquisition. Besides, carbon (C), hydrogen (H) and oxygen (O), plants need fourteen different mineral elements that they acquire from soil. Among these mineral elements, the position of nitrogen (N) is unique since it is an important component of nucleic acids, proteins, nucleotides (including ATP), etc. Indeed, N availability is a main determinant of crops yield. Thus, N fertilizers are intensively applied in agriculture and its global demand is continuously increasing. Without drastic changes on agricultural practices or human diet, N fertilizers demand will double for 2050. Unfortunately, agriculture systems have very low N use efficiency (NUE) and more than 50% of the applied N is not used by the crops and hence, is lost to the environment and causes environmental pollution. Main pathways for N losses are nitrate (NO<sub>3</sub><sup>-</sup>) leaching and runoff, ammonia (NH<sub>3</sub>) gas volatilization and nitrous oxide (N<sub>2</sub>O) emission, a powerful greenhouse gas. These N losses provoke eutrophication of freshwater, NO<sub>3</sub><sup>-</sup> pollution, soil acidification, contribute to global warming, degrade air quality ecosystem and contribute to biodiversity loss in many ecosystems. However, these huge N losses also mean that there is extensive room for improvement in agricultural systems NUE. For instance, through using and/or breeding crops with higher NUE, improving agricultural practices such as better adjusting the N dose and by the use of N fertilizers that promote N retention in the soil

In this general framework, the main objective of the Nutrition Management in Plant and Soil (NUMAPS) research group is to improve plants NUE in agricultural systems. At present NUMAPS group is composed of 6 permanent researchers, 6 postdoctoral researchers and 3 PhD students.

To reach this general objective the NUMAPS group is divided in three research lines.

1. Environmental and productive implications of nitrogen fertilization: focus on nitrification inhibitors and greenhouse gases emissions.
2. Molecular and metabolic mechanisms associated with plants nitrogen use efficiency.
3. Management of organic fertilization combined with microbial inoculants as a tool to improve crops yield and quality

To develop these research lines we use a wide array of different techniques that include plant growth under controlled environmental conditions (hydroponics, in vitro, etc.), field trials, greenhouse gases emission determination (gas chromatography), plant physiology monitoring (photosynthesis, growth, etc.), metabolic analysis (enzyme activities, chromatography), plant transformation (CRISPR/Cas9, overexpression, etc.) and “omics” (metagenomics, transcriptomics by RNASeq, proteomics, metabolomics), among others.



# Terrestrial flora and vegetation as sentinels of global change

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

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Our group has evolved over the last 30 years, from an initial focus on diversity, mapping and classification of vegetation to later incorporate taxonomic, functional and phylogenetic diversity of plant communities, monitoring and ecological modeling of biodiversity in the face of global change. We use a variety of botanical, statistical and laboratory techniques, including modeling and various in-house and international databases about plant communities, nested vegetation plots and climate databases. Students and professional researchers in our group contribute to field, laboratory and computational research to promote community classification and mapping, ecological analysis and modeling. All this activity is aimed at strengthening the foundations for rational ecosystem management and conservation.

We have recently launched a **Sentinel Network for Global Change Monitoring** where we use plant diversity patterns to track changes occurring at different scales and monitor the responses of different plant communities. So far, we have incorporated monitoring plots in different habitats of the territory with conservation interest:

## **Coastal Habitats Management and Conservation**

We have selected dune and estuarine habitats, which are naturally subjected to strong environmental stress, coupled with a strong human impact and the threat of rising sea levels and increased storms. In this type of habitats, the above-mentioned impacts are compounded by the expansion of several invasive species that, favored by global change, already threaten many habitats and highly specialized native species.

## **Forest Diversity and Management**

We have selected two types of forests that are highly fragmented and isolated in the territory: the Navarre-Alava island forests and the sub-Cantabrian riparian ash forests. The selected plots are located in climate transition zones where a greater impact of climate change is expected. We study effects of environment and forest management on plant diversity across different scales. 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 Restoration and Monitoring**

Peatlands not only represent a valuable fossil record where we can study events that occurred thousands of years ago, but also respond rapidly to changes that are occurring today. 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. For this, we use field sampling, plot data and GIS to analyse and model the distribution of grassland diversity at multiple scales for conservation and management, and predict potential climate and land use changes impacts.

# Marine ecology

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KEY WORDS: marine ecosystems, plankton, harmful algae, invasive species, ecosystem health, time series, climate change

The main research lines are:

1. Long-term changes in plankton ecosystems of the Basque coast in relation to climate and local anthropogenic actuations. We analyse the time series of plankton and environmental variables obtained from monitoring program carried out in marine and brackish waters, and hydrographic and climatic data series obtained from local and international public sources.
2. Detection and impact of harmful microalgae and invasive species. We are exploring the presence and effects of toxic microalgae and non-native zooplankton species in the Basque coast from data obtained in ongoing projects and the monitoring programs.

## RATIONALE

Time series are useful tools to identify and analyze long-term changes in ecosystems in relation to climate change and local human perturbations, and to forecast future changes. Plankton time series inform on the changes in composition, abundance and phenology of the low trophic levels of the pelagic food webs, which support fisheries and commercial filter-feeding shellfish, in response to environmental changes. Plankton seems to be a better indicator of climate change and other local scale environmental perturbations than higher trophic level animals because planktonic population dynamics are not affected by harvesting, as it is the case of several fish and marine mammals.

We initiated plankton time-series in the neritic and transitional zones of two emblematic estuaries of the Basque coast (Bilbao and Urdaibai) in 1998. These have allowed us the identification and analysis of the causes of changes in the basic environmental properties of water masses (temperature, dissolved oxygen, transparency) and plankton communities (phytoplankton biomass, zooplankton abundance and composition) during the first two decades of the present century. They also allowed us to record the arrival of non-native zooplankton species with overall greatest colonization success in the estuary of Bilbao than in the estuary of Urdaibai, having a greater impact on the abundance, structure and diversity of the zooplankton community of the former one, where they have become dominant in the brackish habitat. Recent checking of these non-native species in other estuaries of the Basque coast revealed an irregular spread related in part to the inherent estuary capability to host them.

Phytoplankton communities are analyzed in the context of different environmental monitoring programs. In the one hand, phytoplankton community changes are a primary symptom to the trophic status changes of aquatic ecosystems. On the other hand, phytoplankton species and communities respond to other environmental impacts such as climate change and the increase of pollutants. The response of selected microalgae to different environmental parameters and emerging pollutants such as nanomaterials are being studied.

Also, toxic microalgal species are a concern both for the recreational use of the marine environment and for the development of the incipient bivalves' aquaculture on the Basque coast. Among the former, we have the case of the warm-water benthic dinoflagellate genus *Ostreopsis*. The analysis of a bloom that generated pruritus cases in bathers in 2021 revealed the presence for the first time in the Bay of Biscay of the toxic species *O. ovata*, which has been causing problems in the Mediterranean Sea during the last decades. Regarding poisoning of mussels, PSP (Paralytic Shellfish Poisoning) associated with the genera *Alexandrium* and *Centrodinium*, and YSP (Yessotoxin Shellfish Poisoning) associated with the genera *Protoceratium* and *Lingulodinium* are being evaluated, and the trophic relationships of the dinoflagellate genus *Dinophysis*, causative of DSP (Diarrhetic Shellfish Poisoning), with cryptophyte algae are also being addressed.

# Biodiversity, Ecosystem services and Ecophysiology of Stress and Pollution in Plants: “BEZ-EKOFISKO Group”

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KEY WORDS: Ecophysiology, agroecosystems, Biomarkers, forestry systems, soil pollution, Didactics of experimental science, Biotic, Abiotic, Stress, Biodiversity, Nature-based solutions, Ecosystem services

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BEZ-EKOFISKO is a consolidated research group distinguished with the highest grade of the Basque Government classification for Scientific Groups (IT1648-22). It is led by **Raquel Esteban** and **Ibone Ametzaga-Arregi** and is composed of 13 Ph.D. and 5 Ph.D. students. The composition of the group is consistent with its objectives and activities, which are sustained on 3 **pillars**: i) quality research, ii) training of excellent research staff and iii) education, dissemination and communication of science. The **main challenge** of BEZ-EKOFISKO is to investigate the essential ecophysiological processes of plants in response to natural/anthropic environmental conditions and integrate this response at the level of the ecosystem, its effect on biodiversity and ecosystem services. For this purpose, our activity is based on **6 strategic lines of research** (exposed above), which are interconnected with each other, aligned with the RIS3 strategy and framed within the United Nations International Scientific Program. Our group develops and uses cutting-edge **methodologies** in its research such as genomics, proteomics, non-invasive techniques, physiology, biochemistry, ecosystem health, and Geographic Information Systems. Our research generates knowledge to understand the essential ecophysiological processes and identification of mechanisms (genetic, molecular, biochemical, physiological) in response to biotic and abiotic environmental stresses (climate change, fungal infections, or extreme weather conditions) and anthropic stresses (pollutants, heavy metals, organic, antibiotics). The study of these mechanisms allows us to 1) identify biomarkers of loss of plant health, particularly those related to photoprotection and oxidative stress, 2) develop novel biotechnological and methodological tools (e.g. remote stress detection indices, plant toxicity bioassays to determine the ecotoxicological effects of pollutants...), 3) select species tolerant to natural/anthropic conditions, 4) develop friendly environmental remediation strategies 5) monitor short- and long-term forest health and degraded and/or contaminated sites, and 6) implement physiological parameters to assess tolerance caused by natural stress conditions. This knowledge enables us to 7) identify functions and assess the conservation status of ecosystems and their impact on biodiversity in the landscape, 8) develop and apply indicators to quantify the goods and services from a social (health and well-being of people and organisms), ecosystem (environmental) and economic (creation of green employment) point of view. We also aim to develop knowledge and tools for planning and management, as well as to anticipate future scenarios on the consequences of climate change, land use and its consequences on ecosystem functions and, consequently, on the flows of services derived from them. In this way, human impacts on ecosystems will be minimized, favoring their conservation and guaranteeing the provision of services, maintaining a resilient landscape and the health and well-being of ecosystems and the population. 9) University and pre-university education, dissemination and social awareness of citizens in these concepts is an essential aspect and a transversal task that is considered one of the priority-lines of our group. Our **research lines** are: 1) Ecophysiology of stress 2) Phytomanagement and recovery of degraded soils 3) Sustainable management 4) Biodiversity protection 5) Development of transversal tools and 6) Education for sustainability. Our group has **national and international prestige and recognition**, so it has great weight and international competitiveness, as evidenced by all our activities and merits: i) research stays in internationally renowned laboratories during their predoctoral, postdoctoral, and visiting professorships, ii) international projects and networks, iii) presentations to international congresses, and iv) joint authorship with prestigious researchers (e.g. in the last six years, the BEZ-EKOFISKO group has maintained an intense collaboration with other groups, which is reflected in the list of publications and participation in projects with more than 24 countries involved), v) teaching at other prestigious universities and, finally, vi) our research is currently carried out in collaboration with relevant national and international scientists and institutions. Our group participates in postgraduate **training by teaching courses** in several Masters and Doctorate Programs with Quality Mention from the Ministry of Education. We are committed to **outreach** activities.

# Lipid-protein interactions in autophagy

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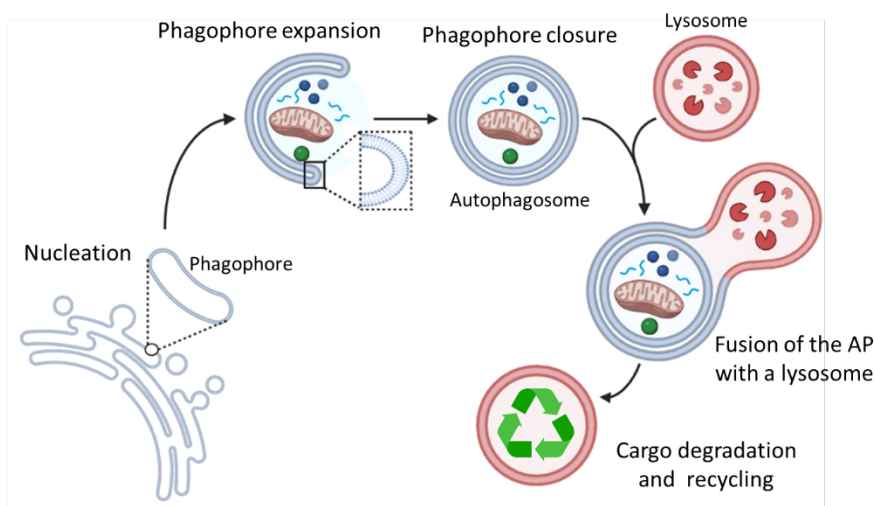
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KEY WORDS: autophagy, lipid-protein interactions, LC3/GABARAP.

Autophagy (from the Greek auto-, "self" and phago "to eat") is a cellular recycling system typical of eukaryotes. Through this process, cells isolate certain cytoplasmic components and disassemble them for subsequent reuse as new building blocks, in response to the metabolic situation. Thus, autophagy provides nutrients under starvation conditions (non-selective autophagy), but it also acts as a quality control system by which misfolded proteins and damaged or unnecessary organelles can be selectively eliminated (selective autophagy). Errors in the autophagic process compromise cellular homeostasis and are related to numerous pathologies such as infectious and neurodegenerative diseases, muscular dystrophy, lipid storage disorders, cancer, etc.

There are three types of autophagy: macroautophagy, microautophagy and chaperone-mediated autophagy. Macroautophagy is the best characterized at present. It was first described in mammals when it was observed that entire organelles could be "devoured" by a double-membraned vesicle, named the autophagosome (AP).

The AP is a membrane organelle, and new lipids are required for its formation and expansion from an initial membrane (also called phagophore). A large number of specific proteins and lipids are involved in the process, and membrane fusion and fission events occur, as well as changes in the curvature and architecture of the membranes involved. Once formed, the AP fuses with lysosomes, after which its inner membrane and contents (cargo) are rapidly degraded. All these events are possible because protein-protein and protein-lipid interactions are established. These interactions are particularly important in selective autophagy, since it depends on the activation of specific signals that indicate to the autophagic system the organelle or cellular component that should interact with the AP membrane to be degraded. It has been described that LC3/GABARAP family proteins are very important for the formation of the AP and therefore for the autophagic process to function correctly. The mechanism by which they carry out this function is not yet fully understood, but it is known that they interact with specific lipids present in the AP membrane.



The general objective of our research group is to understand the activity of this family of proteins in autophagy and to characterize the different functions of each member. Our research lines focus on studying the interactions that these proteins establish with different lipids and lipid membranes and how these regulate their activity. For this purpose, we study lipid-protein interactions in autophagy both *in vitro* and in eukaryotic cell cultures, using cloning techniques, purification of recombinant proteins, formation of different types of membrane model systems (liposomes, monolayers, etc), handling and maintenance of eukaryotic cell lines or confocal microscopy, among others.

# Proteomics of ubiquitin pathways and neuronal diseases

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KEY WORDS: Ubiquitination, Proteomics, UBE3A.

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The coordinated activity of ubiquitin E3 ligase (E3) and deubiquitinating (DUB) enzymes is crucial for maintaining the appropriate balance of protein ubiquitination required for cellular homeostasis. In fact, deregulation of many of these enzymes is implicated in a number of diseases, including cancer and rare neurological diseases. Therapeutic strategies that can modify the biological activity of these enzymes and thus, restore appropriate ubiquitination levels of cellular proteins are therefore currently emerging; in particular, those targeting DUB enzymes. However, due to the insufficient understanding of the role of protein ubiquitination in neurons, the development of selective drugs for therapeutic purposes has been limited.

Our lab has developed different strategies for the isolation and identification of ubiquitinated proteins *in vivo*. Using these approaches, we have reported basal ubiquitin landscapes under physiological conditions in the nervous systems of flies and mice, as well as identified several E3 ligase enzymes' substrates. Moreover, we have identified the substrates of several DUBs, an information that we have integrated in a newly developed interactive database (DUBase: Deubiquitinating Enzyme's Substrate Database), together with another 650 high-confidence manually reviewed DUB substrates. All in all, we have proved that our strategies are very efficient for the analysis of the cellular ubiquitome from different tissues, organisms and conditions.

# Molecular Biology of Cancer

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KEY WORDS: Cancer, Cell Cycle, DNA repair, Genomic instability, Gene knockout, Genomics, Proteomics, Therapy.

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The main characteristic that defines cancer is the alteration of cellular homeostasis. The mechanisms underlying this alteration include deregulation of the cell cycle, defects in DNA repair, metabolic rewiring and genomic instability, among others. Our research group focuses on the detailed characterization of these mechanisms and how their alterations contribute to malignant transformation. Our ultimate goal is to use the knowledge acquired to apply new treatment strategies to the clinical practice, either by identifying markers of prognosis, or by identifying and characterizing new therapeutic targets.

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 Plan de Ciencia, Tecnología e Innovación Euskadi 2030, 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.

By applying genomic and proteomic approaches, together with classical methods of genetic and biochemical analysis, we are identifying and characterizing 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, metastasis and resistance to chemotherapy. As an example of our research outputs, we have discovered recently that aggressive prostate cancer cells depend on the activity of E2F proteins to keep their DNA stable and prevent cell death. We have shown that inhibiting the activity of these cell cycle regulatory proteins kills prostate cancer tumor cells in culture and enhances the effect of other drugs typically used in the clinic as anti-tumor therapy *in vivo* and *in vitro*. Our results highlight the importance of targeting E2F as a promising strategy for the treatment of prostate cancer.

# ONE-HEALTH OMICS

## GENOMICS and HUMAN and ANIMAL HEALTH

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KEY WORDS: genomics, infectious diseases, vaccines, adjuvants, autoimmunity, RNA-seq, miRNAs, non-coding RNAs, metagenomics, women health

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With the ongoing developments of high throughput sequencing machines and advancement of modern bioinformatic tools at unprecedented pace, the high-throughput-next generation sequencing technologies are revolutionizing the human and animal genomes researches by approaches such as RNA sequencing, metagenomics or personal genomics. The non-protein coding region of the genome, also named the “dark side” of the genome, has remained unknown until recently, when due to the development of these novel sequencing technologies, characterization of non-coding RNAs (ncRNAs) has emerged. The importance of the ncRNAs has become increasingly apparent and our knowledge on the significance and contribution of ncRNAs in disease pathogenesis is expanding rapidly.

The main objective of our research group is deepening in the study of the mechanisms of infectious diseases as well as other complex ones using omics methodologies. Our research includes in depth knowledge of specific pathogens and diseases, along with carefully selected samples and optimally developed model systems. Among the specific objectives, and in relation to the host-pathogen interactions, the followings are addressed:

Line 1:

- Detection and characterization of genomic elements, both protein-coding genes and non-coding RNAs, involved in the immune response against infectious agents.
- Characterization of the Immune response to vaccination and vaccine adjuvants by transcriptomic analysis.

Line 2:

- Metagenomic analysis of the cervico-vaginal microbiota as a modulator of infectious diseases in women.

These studies 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 the sequencing of different RNA molecules. Moreover, the analyses of the second line can provide information for the diagnosis of cervico-vaginal diseases in women.

# Human Evolutionary Biology

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KEY WORDS: Wolf, Dog, Ancient DNA, Domestication syndrome, Prosociality, Pigmentation, melanoma, microbiome, adaptation, bioinformatics, exome

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## ORIGINS OF WOLF DOMESTICATION: PALEOGENOMIC ANALYSIS IN THE CANTABRIAN FRINGE

Dogs are known to be the first species domesticated by humans, although the geographic and temporal origin of this process is still under debate. During the last glacial period, large ice caps forced populations to retreat to refuges in southern Eurasia, such as the Franco-Cantabrian (Iberian Peninsula), where population density increased and hunter-gatherer human populations had to coexist with other species (such as the wolf), emerging interactions that contributed to the generation of a favorable niche that would trigger the domestication of the wolf. The most widely accepted hypotheses (self-domestication of the wolf and active selection by Upper Palaeolithic hunter-gatherers) indicate the existence of a human-wolf social interaction factor. Humans from this period underwent technological and cultural changes that reached their greatest development in the Magdalenian - a contemporary period of the oldest dog fossils found to date, such as the one found at the Erralla site (Zestoa, Gipuzkoa). The study carried out by us indicated that the Erralla specimen represents one of the earliest domesticated dogs in Europe, in the Lower Cantabrian Magdalenian period (17,410-17,096 cal. BP, direct AMS 14C dating). Our ongoing research is based in the paleogenomic analysis of the remains of wolves and dogs from the Mousterian to the Bronze Age sites in the Basque Country. In the initial stages of the domestication process, the changes in the behavioral traits are manifested before the morphological ones. The natural selection could favor, among others, the genes involved in the decrease of the aggressiveness, both on the part of the wolf and the human being. Another objective is to analyze genetic variants of those genes that could influence the generation of this domestication niche that favored the origin of the dog.

## SKIN PIGMENTATION, MELANOMA AND POPULATION GENOMICS

Natural selection, our demographic history and chance all shape our genetic diversity and consequently determine our ability to adapt to the environment. Understanding these forces help us understand our survival as a species. These adaptations are the result of a tinkering process, and some of them, while being good enough to allow us to reach reproductive age, have actually undesirable consequences for human health. Thus, for instance, light-skinned individuals are at a higher risk of developing a skin cancer. Therefore, we are trying to identify the 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 Next Generation. We analyse the variability in melanoma patients and healthy individuals in order to discover early markers of melanoma diagnosis and prognosis. For instance, we use Digital PCR so to assess the mutational load of BRAF V600E in melanoma biopsies. Bioinformatics is part of our tool-box in this regard. Another branch of our research group focuses in the study of population genomics and environmental adaptations of human populations. On the one hand, we have an interest in Africa, the cradle of humankind. Precisely, we are investigating Cameroon due to its extraordinary genetic, ethnic and linguistic diversity, and the wide variety of subsistence strategies of its inhabitants. Taking advantage of next-generation sequencing techniques, we are analysing the genetic diversity and population structure in this country, as well as their microbiome. On the other, we also have an interest in the genetic history of the Basque population.

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# Bio-Surveillance through AI and Human Rights

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KEY WORDS: body surveillance, human rights, cyber security, artificial intelligence.

Digital technologies and connectivity are fundamentally changing the way people and societies live. The EU is determined that the *Digital Decade* will be the time to consolidate the EU's digital sovereignty. Digitalisation is presented and promoted in all areas of social life and governance. AI-Biosurveillance is a **coordinated project** involving experts in Physical Anthropology and Telematic Engineering, together with experts in different social sciences (Law, Sociology, Political Science) from the UPV/EHU, the UGR, the Institute of Police Sciences (UAH) and the Basque Police Forensic Science Unit (Ertzaintza). It has received a grant from the MICCIN in the 2021 call for Ecological and Digital Transition Projects: TED2021-129975B-C21 (PR. L. Escajedo and F. Balaguer) and C22 (PR. Eduardo Jacob).

The overall objective of the coordinated *AI-BioSurveillance* project is to **generate, transfer and disseminate knowledge that contributes to the protection of the fundamental rights in face of the irruption of mass biometric surveillance.**

The term **biometric recognition** has become widespread over the last two decades, almost synonymous with automated recognition systems that are able to verify the identity of individuals by capturing and processing specific bodily features (such as fingerprint or iris patterns, hand or facial geometry, dynamic aspects of a signature or voice spectrum).

The basis of such recognition is an **automated association between**, on the one hand, *a person's social (or civil) identity*, and, on the other hand, *unique anatomical-physical or dynamic characteristics that can be captured from their corporeality*. Since the beginning of the twentieth century, such technologies have been presented as recognition systems based on the premise that *"the body never lies"*

Despite the closeness between the use of biometrics in Forensic Anthropology and automated recognition systems, there are important differences in terms of reliability and accuracy. **The human body is not easily biometrisable, and the architecture of automated biometric recognition systems has shortcomings.** Capturing body data, extracting the most unique attributes, transforming this information into digital information, comparing stored patterns and making decisions after the comparison are among the most critical elements of these systems. Statistically, some people are predestined to be discriminated against. In some cases, because they belong to groups for which false acceptance or rejection errors are high.

**Mass biometric surveillance, which is the focus of this work, represents a quantum leap in terms of risks to individual rights:**

- 1) It is possible to train biometric recognition systems to perform screening tasks, in the sense of looking for specific people or people who fit certain profiles. Profiling, or the application of profiles to identify a person or fit them into a certain group or set, can be very valuable for businesses and governments, but the potential for such profiling to be excessive with respect to fundamental rights is great.
- 2) Everything that legislators, courts and jurists have expressed about the risks of video surveillance in public spaces needs to be re-read and reoriented to the new public spaces, mostly virtual, in which people are not only exposed, but overexposed.
- 3) Mass biometric surveillance can generate in people a **psychological feeling of permanent surveillance**. Thus, even if they are purely symbolic mechanisms, mass surveillance systems can lead to people's submission to power or powers, be they political, economic or even simulated.

# Complex Disease Precision Medicine Network

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KEY WORDS: Personalized medicine, childhood cancer, targeted therapy, molecular profiling, NGS technologies, DNA methylation profiling, cost-effectiveness.

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Personalized medicine is currently emerging as a tool that seeks to make the treatment of complex diseases more effective. However, there is still a need of biomarkers to guide treatment decisions and assess response to treatment. Genetic and molecular characterization of each individual or subgroup of patients could help to overcome this situation, refining the diagnosis, improving risk-adapted management strategies and providing elements to better assess the response to treatment and disease surveillance.

In order to build the conceptual basis on which developing precision therapies, we aim to broaden our knowledge about complex diseases such as cancer, mainly analyzing the molecular profile of poorly characterized subtypes (especially those with unknown prognosis, intermediate diagnosis or non-determinant) and its intratumoral heterogeneity. The current possibility of performing an integrative approach that includes all data sets generated from omics studies for the identification of specific genomic signatures may be crucial to develop more specific and less harmful therapies. In addition, the genetic and molecular information obtained from these new data sets will be assembled with previously generated knowledge and clinical information, for the identification of potential new biomarkers. After the identification of biomarkers in tissue samples, in those cases in which it is particularly relevant, the suitability of liquid biopsies for identifying these markers will also be tested.

Our objectives to deal with all these important aspects are instrumentally divided in four key milestones:

- Definition of the genetic and epigenetic profile with diagnostic implications of childhood acute lymphoblastic leukemia/lymphoma, pediatric medulloblastoma and diffuse large B-cell lymphoma, through RNAseq and functional studies
- Definition of the map of intratumoral heterogeneity in medulloblastoma through single cell RNAseq and deconvolution analyses
- Identification of prognostic biomarkers and response to therapy in pediatric cancer through the study of the potential of non-coding RNAs as risk markers or new therapeutic targets
- Evaluation of the translational impact of using liquid biopsy in diagnosis and follow-up in cancer

This project is possible thanks to the collaborative effort between the UPV/EHU and the 4 University Hospitals with the highest volume of patients in the Basque Country, such as Cruces, Basurto, Donostia and Araba. The establishment of this Collaborative Network in our Community is being key in improving the diagnosis of cancer and the implementation of various ongoing projects and implementation of clinical trials, emphasizing the importance of collaboration between basic researchers (UPV/EHU) with clinical researchers (UPV/EHU-Osakidetza). However, these ongoing tasks must be consolidated and intensified to ensure progress in the diagnosis and treatment of these diseases. It is also very important to point out the teaching work that the group performs, tutoring doctoral theses, participating in postgraduate programs and training postdoctoral researchers.

# Agri-sciences and Just Ecological Transition in the EU: Regulatory Challenges

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KEY WORDS: EU integration of Agri-Sciences, Regulatory Issues, Just Ecological Transition.

Major strategic objectives of the *European Green Deal* (2019) are projected in Plant Science (from fundamental research to applied R&D for the production and distribution of crop products). Agri-sciences are identified, among other things, as instruments that will enable more sustainable food production, better use of land and a reduction in the use of pesticides, while protecting pollinators.

To respond, it is crucial to enable agri-scientists and agri-innovators across the EU to collaborate in knowledge generation and application. To respond, it is crucial to enable agri-scientists and agri-innovators across the EU to collaborate in knowledge generation and application. But these developments are threatened by a number of outstanding regulatory hurdles and tasks that the EU has been dragging behind it since the 1990s.

1. **Low awareness of the importance** and properties of plants and plant material.
2. **Difficulties in realising pan-European projects** with collaboration between academia and industry.
3. **Inadequacy of some regulatory frameworks** (due to obsolescence and incorporation of decision-making models that are not based on scientific evidence).

Many of these difficulties are **due to the following factors**. First, agri-science R&D is an area of intersecting competencies (agriculture, environmental protection, agri-food market, consumer protection). Second, that in some of these areas, notably agriculture, MS have preserved a much greater margin of policy autonomy than in other economic sectors, even allowing some forms of protectionism. Both factors have led to many "dysfunctions" in the European integration of agri-sciences.

Focused on the thematic priority of the Bioeconomy, *VegEquity project (Plant Breeding and EU integration, MICINN, PID2021-12379600B-C21 DER)* is a **scientific-legal research project whose mission is to generate, transfer and disseminate knowledge** that contributes to providing greater legal security to the Spanish and European plant breeding sector.

Here is a list of the main agri-science regulatory frameworks that the EU has recently reformed or is in the process of reviewing:

- 1) The use of biotechnologies in plant breeding: the regulation of GM plants and plants modified by new genomic techniques (such as CRISPR).
- 2) Plant Reproductive Material.
- 3) Novel food and feed.
- 4) The storage, **use and exchange of genetic information and germplasm** for scientific purposes.
- 5) Organic farming.
- 6) Plant Health.
- 7) Legislation on new plant varieties and other forms of intellectual property protection.

# Hologenomic Tools for Sustainable Agriculture, Food Safety, and Biodiversity Conservation

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KEY WORDS: bioinformatics, genomics, host-microbiota interactions, metagenomics

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The studies developed by **Applied Genomics and Bioinformatics** research group are of an applied nature, nourished by basic or fundamental studies, to respond to challenges raised in sectors of great importance for the Basque Country and Europe: the APICULTURE, FISHING, FOOD and VITICULTURE industry. Our research is oriented towards characterizing the taxonomic and functional composition of microbial communities in diverse environments, the genomic and transcriptomics characterization of eukaryotes at the individual and population level, and the study of host-microbiota interactions (hologenomics). Our lines of research include the search for resilience factors in honey bees (*Apis mellifera*), understanding the genomic composition of the anchovy (*Engraulis encrasicolus*) to provide insights into the evolutionary forces that led to different ecotypes, comprehending how host-microbiota interactions influence animal performance and productivity traits, and deciphering soil and grapevine microbiota impact on vine health and grape/wine quality. In short, our work is aimed to provide the necessary scientific knowledge to promote sustainability, productivity and resilience throughout the agri-food sector.

**APICULTURE SECTOR:** Locally adapted honey bees have been shown to have greater survivability and resilience. We seek to conserve the genetic resources of local bees in the Iberian Peninsula to preserve the adaptive potential on which to build agricultural production systems resilient to future needs and to cope with global environmental change. To do so, we are supporting the Breeding Program of the *A. m. iberiensis* honey bee led by ERBEL to provide local bees to commercial beekeepers. In addition, we are leading two projects at national (ECOAPI) and European (BEEGUARDS) level, where we study the contribution of the bee genome and its associated microbiota to varroa mites resistance (an external parasite causing several diseases to honey bees worldwide), in order to provide alternative and sustainable solutions that will favor more resilient bees.

**FISHERIES SECTOR:** The European anchovy (*Engraulis encrasicolus*) is a commercially important fish species in the Basque Country, and understanding its genomic makeup is essential for developing sustainable practices and conserving wild populations. Our population genomics and adaptation studies of the anchovy involve the assembly of the first reference genome for the species at the chromosome level, based on PacBio HiFi reads and Hi-C data.

**FOOD INDUSTRY:** The HOLOFOOD European project aims to obtain in-depth knowledge on how host-microbiota interactions affect animal performance. Microbial communities are considered active participants in animal development and welfare, and understanding microbial functional dynamics can help us design microbial solutions to improve the quality and sustainability of animal production.

**VITICULTURE INDUSTRY:** The use of natural compounds to replace (or reduce) chemical fertilizers and pesticides in agriculture has significant environmental benefits and can contribute to the development of more sustainable agricultural practices. In the **Metabotrytool** Euroregional consortium we study the biogeographical distribution of grape microbiota seeking for a microbial bioindicator to anticipate the appearance of the pathogenic fungus botrytis (*Botrytis cinerea*). In the national project **SEAWINES**, we are testing the bioestimulant and antifungal capacity of seaweed and their effect on soil, grape and must microbiota in an attempt to enhance grapevine tolerance to diseases by using fewer chemicals without impairing grape and wine quality.

# Bacterial resistance to stress.

## Mechanisms of *Vibrio* persistence in aquatic systems

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KEY WORDS: *Vibrio*, ocean warming, environmental reservoirs.

Climate change causes an increase in the surface temperature of marine systems affecting the communities that inhabit them. Among these communities there are pathogenic bacteria that belong to the genus *Vibrio*. These bacteria adapt and survive in changing environments and are being detected in aquatic systems where their presence was not previously known, thus indicating that the members of the genus *Vibrio* can serve as biomarkers of global warming. Some adaptation mechanisms have been proposed to facilitate the persistence of *Vibrio* spp. They include induction of the viable but nonculturable state (VBNC), morphological changes and/or association with plankton, mollusks or fish, which could act as reservoirs of vibrios. Our group studies these mechanisms of persistence and factors that facilitate *Vibrio* spread in the time of climate change.

1. In particular, for the last 3 years, our group has been studying the temporal/spatial distribution of *Vibrio* spp. in the coastal, estuarine and open water of the Bay of Biscay. During the last year we have sampled water in the Bay of Plentzia to carry out its analysis for the BlueAdapt and Hobe projects. We are determining the presence of free-living bacteria of the genus *Vibrio* in water as well as in phyto- and zooplankton, algae and mollusks. This analysis is complemented by the enumeration and/or detection of other bacteria widely used as indicators of contamination.
2. In addition, we study the survival patterns developed by a laboratory *V. harveyi* strain and other environmental *Vibrio* species isolated from seawater. Our results indicate that survival of *Vibrio* spp. under starvation conditions is a temperature-dependent process, which is accompanied by a reduction of cell length, decrease of pathogenicity, proteomic changes and, occasionally, leads to the acquisition of the VBNC phenotype. In a similar way, solar radiation and other essential abiotic factors, such as salinity, also affect survival of *Vibrio* spp. Interestingly, we observed differences in the survival patterns of laboratory and environmental strains attributable to the complexity and diversity of *Vibrio* genus.
3. We also determined the capacity of mollusks to act as a reservoir of *Vibrio* spp., accumulating these microorganisms in their tissues (digestive glands, gills and gonads). Our results show that mollusks could actively remove *V. harveyi* from seawater or simulated estuarine water at 12°C and 20°C. In few minutes *Vibrio* reached its maximum density in the organs, where was retained for several hours or days. Afterwards, the bacterial content decreased progressively. In addition, we demonstrated that mollusks could concentrate *Vibrio* in the pseudofaeces which could be a mechanism of *Vibrio* dissemination.

The techniques and methodologies used include enumeration and isolation of indicator bacteria as well as *Vibrio* spp., enumeration by epifluorescence microscopy and/or fluorescence *in situ* hybridization (CARD-FISH), analysis of bacterial proteome, etc.

# Fungal pathogens and their infectious diseases

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

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The incidence of fungal infections has been increasing globally in the last years. Actually, infections caused by microscopic fungi affect millions of individuals every year, mainly immunocompromised patients, with mortality rates that 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 antifungal drugs. Therefore, the Fungal and Bacterial Biomics (MICROBIOMICS) 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 *Aspergillus*, *Scedosporium/Lomentospora*, and *Candida*, with the aim of understanding their virulence mechanisms. In fact, in 2022 the World Health Organization published the fungal priority pathogens list, with *Candida auris*, *Candida albicans*, and *Aspergillus fumigatus* inside the Critical Priority Group and *Scedosporium/Lomentospora* in the Medium Priority Group due to their high antifungal resistance and virulence.

Currently, the MICROBIOMICS research group is mainly researching into the following three lines:

1. **Study of the infections caused by the most prevalent airborne pathogenic filamentous fungus, *Aspergillus fumigatus*.** For that, we use CRISPR-Cas9 gene-editing technique 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 in different animal (mouse and *Galleria mellonella*) and cell line models, immunological techniques, sequencing and bioinformatics are frequently used. Moreover, we have recently started a new research line focused on studying the prevalence of environmental *A. fumigatus* strains and their resistances to antifungals.
2. **Identification of new diagnostic and therapeutic targets of the group *Scedosporium/Lomentospora*.** The group *Scedosporium/Lomentospora* presents high resistance to almost all antifungal treatments available, which make them very dangerous for immunosuppressed patients to whom they cause very high mortality rates. Moreover, they are the second more prevalent filamentous fungi found in cystic fibrosis patients. To accomplish this research line goals, we combine several omics technologies and currently, we have designed a serologic ELISA based method to detect *Scedosporium/Lomentospora* in cystic fibrosis patients and monitor them. Moreover, we have also developed a serologic rapid method with higher specificity and sensitivity.
3. **Study of *Candida spp.* interactions with host cells and environment.** In this sense, we have studied the molecular mechanisms underlying inflammatory responses of endothelial cells against *C. albicans* as well as its implication in cancer and metastasis promotion *in vitro* and *in vivo*. On the other hand, we assess the effect of environmental factors affecting the resistance mechanisms and virulence of the emerging fungus *Candida auris*. In fact, we have identified the proteins involved in the tolerance to oxidative stress, as well as their role in the resistance of the phagocytosis process in RAW 264.7 murine macrophages.

Summarizing, the MICROBIOMICS 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.

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# Effects of environmental stress on adaptation and survival of *Vibrio harveyi* and *Escherichia coli*

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KEY WORDS: Climate change, gene expression analysis, *anaerobic conditions*, small regulatory RNAs

The ubiquitous presence of microorganisms is largely conferred by their unique abilities to adapt and survive under adverse and continuously changing conditions. We use the well-known Gammaproteobacteria, *Escherichia coli* (*E. coli*) and *Vibrio harveyi* (*V. harveyi*), as model organisms to study microbial responses to stress (e.g., elevated temperature, low pH, limitation of oxygen 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, temperature, 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 employing advanced 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. Development and use of advanced 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 employed to determine the interannual dynamics of the *Vibrio* populations in seawater sampled in the Bay of Plentzia. The results of this analysis will further be used to assess the risk of the climate-dependent appearance and spread of *Vibrio*-associated diseases.

## 3. Gene expression analysis of *Escherichia coli* under limitation of oxygen

The ability of enterobacteria to colonize the mammalian hosts is dependent on their capacity to adapt and thrive in low-oxygen environments. We are utilizing a combination of transcriptomic and proteomic tools to discover transcriptional and post-transcriptional mechanisms that facilitate *E. coli* thriving under oxygen-limited conditions. In particular, we are interested in learning more about the role of small regulatory RNAs and their possible contribution to gene expression.

Some of the most recent results include:

- Characterization of the long-term physiological and phenotypical responses of *V. harveyi* at different pH (7.0, 7.5, 8.0, 8.3 and 8.5) that mimic the pH of the world ocean in the past, present and future;
- *In silico* design of specific PCR primers that enable to improve differentiation of *Vibrio* species;
- Addressing the multifaceted roles of *E. coli* non-coding small RNAs and oxygen-dependent sensing in global gene expression control;
- Determining the key gene clusters associated with cellular responses to fluoride and define its ATP-dependent stabilizing effects on transcripts containing repetitive extragenic palindromic sequences.

# Global effects of climate change on marine microbial community

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KEY WORDS: marine microbes, global warming, climate change, imbalance, metabolism, adaptation.

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The ecological role and biodiversity of marine microbial communities that include many pathogenic species are essential not only for biogeochemical cycles but also for the health of aquatic ecosystems. Owing to the global change that our planet is undergoing, the ocean is becoming warmer. This process has different impacts on oceans, and is more profound in marine surface coastal waters. Therefore, these areas of the global ocean are of particular interest to analyse the response of marine microorganisms to global warming from the ecological and health perspectives.

From an ecological perspective, the function and metabolism of marine microbial communities will be affected, thus altering the heterotrophic production, respiration and enzymatic activities in surface waters, especially in areas with tropical and subtropical climates. However, these processes are differentially affected by temperature, thus causing an imbalance in marine biogeochemical cycles. On one hand, the different temperature sensitivities of several extracellular enzymatic activities that hydrolyze specific compounds present in dissolved organic matter will lead to stoichiometric shifts toward more nutrient-poor organic matter and, as a consequence, cause the expansion of low-nutrient regions in the ocean. Moreover, although both bacterial production and respiration in coastal waters positively respond to raising temperature, the effect on respiration is greater. The unequal increase in these two parameters in response to global warming would provoke changes in the functioning of the microbial loop and carbon cycle in marine coastal systems. In a warming scenario, these two key processes regulating the carbon cycle will increase their rates; however, this increase will be more intense during the cold season than during the warm season.

From a health perspective, an increase in temperature can exacerbate the presence and survival of some pathogens such as *Vibrio* spp. Temperature promotes different adaptation patterns depending on the species and/or the origin of the bacteria, and increases the ability of *Vibrio* to attach to biotic surfaces and spread to new areas. As their ability to survive and be transported through ocean currents increases in the time of global warming, it would lead to an increase in the presence of *Vibrio* in coastal waters.

Since there are only a few reports addressing the impact of climate change on microbes in marine environments, the aim of our study is to monitor the effects of climate change on marine microbial communities in order to be able to reveal and predict possible imbalances in the biogeochemical cycles as well as problems in the health of ecosystems.



# Soil health and quality improvement in soils amended with sewage sludges after application of bioremediation and phytomanagement strategies

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KEY WORDS: phytomanagement, bioremediation, heavy metals, sewage sludges, *in situ*.

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Landfills and waste disposal points of the Basque Country are summarized in the inventory of soils that support or have supported potentially polluting activities or facilities (Law 4/2015). It has been found that “Landfill 17” located in Gernika-Lumo has received sewage sludges (from the local WWTP) for decades as amendment with agricultural purposes. In order to decontaminate and recover soil functionality, a combination of biological technologies (bioremediation, vermiremediation and phytoremediation) in the context of phytomanagement strategies was applied *in situ*. In parallel, chemical analysis of pollutants and toxicity bioassays on plants, earthworms and soil microbial populations were carried out in order to assess the effectiveness on soil remediation and soil health recovery.

Soils chemical analysis showed a great decrease in main pollutants (Cd, Cr, Ni, Pb, Benzo(a)pyrene and Dieldrin) in all treated plots as compared with the untreated plot (MN8). Earthworm and plants bioassays guide to conclude that MN8 was the one with worst soil quality and health. Microbial parameters do not present a remarkable difference among plots. In conclusion, the results obtained showed that phytomanagement strategies involving combined biological technologies can be used to remediate sewage sludges landfills with mixed contamination and to recover soil health.

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# Microfluidics Applications

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KEY WORDS: Microfluidics, device, monitoring, cell biology, sensors and actuators.

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The Microfluidics Cluster UPV/EHU is a multidisciplinary group from the University of the Basque Country (UPV/EHU) working at the Faculty of Science and Technology in Leioa and at the Faculty of Pharmacy in Vitoria-Gasteiz. Our work investigates on two main areas of microfluidic technology: **Cell Biology**, which involves the generation of devices for a better control of cell microenvironment, and **Sensors and Actuators**, which are used as microtechnological tools for the analysis and control of human samples (blood, sweat, ...), the environment and roots exudates from plants.

As for **Cell Biology**, our group focus on the generation of devices for cell monitoring. To achieve this goal, different materials such as PEDOT:PSS or hydrogels are used. For instance, PEDOT:PSS is an electroactive porous polymer that conducts electricity. When cells attach into the pores of the PEDOT:PSS it is possible to monitor cell adhesion by impedance measurements.<sup>1</sup> Another microfluidic device developed in our group is SCADA. This device has a pattern of fibronectin, which is a cell adhesion protein, in the channel. When cells are flowed at a constant they continuously pass through the protein pattern and get attached forming a single cell pattern array.<sup>2</sup> Therefore, SCADA enables the monitorization of single cells, allowing the possibility to explore the effects of different toxics on them. Finally, the CELLSTUDIO platform is a device where multicomponent cell patterns can be achieved. This platform enables the control of hundreds to thousands of different and independent cell colonies in a single device. These colonies are surrounded by functionalized microspheres that actuate as sensors for the monitoring of proteins secreted by the cells. CELLSTUDIO provides cellular monitorization in a controlled microenvironment for a better understanding of cell fate and behavior.<sup>3</sup>

Regarding **Sensors and Actuators**, we have developed an alginate-based biosystem for the detection of different biomarkers. For that, different enzymes were encapsulated in alginate microspheres for the colorimetric detection of lactate, glucose and cholesterol in different human samples.<sup>4</sup> In this way, the concentration of the different biomarkers can be determined according to the obtained color intensity. In addition, magnetic particles can also be added to the alginate microspheres to give them magnetic properties. Apart from that, in the area of plant biology the Microfluidics Cluster UPV/EHU has developed a paper-based microfluidic device for the detection of root exudates and its location along the root. The device enables the collection of the released substances and the integration of sensors for their detection and monitoring thanks to the platform design. Finally, another field in which the group is expanding is the generation of biosensors that take advantage of the plasmonic signal of gold nanoparticles, functionalized with a receptor, when they adhere to tiny chemically modified optical fibers (105 µm in diameter) for a specific analyte.<sup>5</sup>

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<sup>3</sup> E. Azuaje-Hualde, *et al.* Biotechnol. Bioeng., 2021, 118:2626-2636.

<sup>4</sup> S. Garcia-Rey, *et al.* Sens. Actuators B, 2023, 133514.

<sup>5</sup> A. Calatayud-Sanchez, *et al.* Scientific Reports, 2022, 12, 9566.

# Integrated assessment of ecosystem health and pollution in aquatic and soil environments

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KEY WORDS: Environmental Toxicology, Ecosystem Health Assessment, Biomonitoring, Cellular and molecular biomarkers, Emerging pollutants, One Health

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The [Cell Biology in Environmental Toxicology + One Health](#) (CBET+) Consolidated Research Group is an active partaker in the study of environmental health status with a vast experience in the use, development and application of early warning **biomarkers** of pollution at molecular, cell and tissue levels and understanding of the adverse outcome pathways (AOPs) exerted by pollutants. The employed biomarkers include exposure and effect biomarkers together with the use of standard and novel *in vitro* and *in vivo* toxicity tests, bioassays and omics based approaches. The use of model species, such as zebrafish or earthworms, and in-field sentinel species (bivalves, fish, terrestrial gastropods...) provides integrated data for the determination of not only the environmental health status but also the toxicity pathways involved and toxicity profiles exerted by both legacy pollutants and emerging ones, which are less studied. All this information allows getting closer to the all-inclusive concept of **One Health**, which recognizes that even human health is closely connected to the health of our shared environment.

Since the early 80's, the group has been investigating the biological effects of pollutants in both terrestrial and aquatic ecosystems with a common conceptual and methodological approach (biomarkers + bioassays + bioanalytical chemistry). More notably, since the early 90's the group has been involved in the **monitoring of biological effects** of pollution along the Bay of Biscay, Mediterranean coast, North Sea, Baltic Sea, the Arctic and Wider Caribbean region, being recognized internationally as a reference group in environmental biomonitoring programmes. More recently, the group has also focused on the determination of toxicological effects of **emerging pollutants** such as endocrine disruptor substances, nanomaterials, micro- and nanoplastics and pharmaceuticals.

Together with studies on the marine environment, the research group has also paid attention to soil and sediment environments, starting with studies on the effects of metals in sentinel organisms both in the laboratory and in the field (including chronically polluted areas such as abandoned mines and volcanic areas). In the last years, the research activities of the group also include the study of the effects of emerging substances of concern, such as metal-bearing nanomaterials and antibiotics, in collaboration with other groups and organizations, in order to obtain an integrated assessment of soil/sediment health status.

The current activities of the group include several national and international projects but, most notably, the CBET+ group is the promotor of two of the most outstanding marine research facilities of the Basque Country such as the Spanish node of the [European Marine Biological Resource Centre](#) (EMBRC) and the [Biscay Bay Environmental Biospecimen Bank](#) (BBEBB) both located at the PiE-UPV/EHU.

CBET+: <https://www.ehu.eus/es/web/cellbiologyinenvironmental toxicology/presentacion>

BBEBB: <https://www.ehu.eus/PIE/bbebb-2/>

EMBRC: <https://www.embrc.eu/>

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# Assessing the environmental impact of micro- and nanoplastics, novel bio-based polymers and other emerging pollutants on aquatic biota

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KEY WORDS: environmental toxicology, nanoplastics, microplastics, bioplastics, pharmaceuticals.

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For more than 20 years the “Cell Biology in Environmental Toxicology-CBET+” Consolidated Research group investigates the impact of diverse pollutants and other environmental stressors on the health of ecosystems. In the last years, in collaboration with our partners, we are carrying out several research projects aiming to understand the fate and effects of nanomaterials, micro and nanoplastics (MNPs), and other emerging contaminants, such as pharmaceuticals, on aquatic biota. For that, we employ a combination of field studies and laboratory experiments, mostly with invertebrates and fish, in which we assess responses from the molecular to the organism level to understand mechanisms of toxic action and to build Adverse Outcome Pathways. Further, we apply a battery of bioassays with microalgae, invertebrate and fish embryos and adults, and *in vitro* assays with isolated invertebrate, fish and human cells, useful for risk assessment.

We participate in the **CAS6 project** (Towards a technological platform for nanoplastics -NPs- detection). The *in vivo* experimental studies with mussels and copepods dietarily exposed to NPs of different sizes and chemical composition, including metal-doped polystyrene (PS) NPs, contributes to better understand the fate, impact and life cycle of NPs. After studying the effects of standard PS micro and nanoplastics (MNPs) and their potential role as carriers of other environmental pollutants, in the **FIERA project** (Fate and impact of environmentally realistic nanoplastics and of novel bioplastics in the aquatic environment) we address the challenge of assessing the impact of plastics found in the Bay of Biscay. For that, we monitor the presence of MNPs in diverse species and we work to obtain realistic NPs whose toxicity will be tested using the biomarkers and bioassays mentioned above. In the related **PLASFITO project** (Fate and effect of the microplastics, nanoplastics and additives coming from the degradation of fishing gears during their life cycle. Study in the Bay of Biscay) we specifically focus on MNPs from fishing nets. Moreover, the concern about the increasing detrimental effects of plastics in the environment is leading to the development of bio-based polymers, whose safety is still to be proved. Within FIERA, we test novel bio-based polymers used as pressure sensitive additives and biopolymers, such as polylactic acid, already used in food packaging and, therefore, present in the environment. Also addressing the problem of bio-based polymers, in the **ENSURE2 project** (Environmental Safety of polyurethanes from renewable sources and from recycled plastics: hazard assessment based on a battery of alternative methods) we synthesize partially renewably sourced and partially recycled waterborne polyurethane dispersions without and with nanocellulose, and investigate their environmental hazard. On the other hand, MNPs can reach human beings through consumption of polluted bivalves and fish. Thus, in the **MIKRONANOPLAS Project** (Microplastics in molluscs and fish of interest for human consumption in the Basque Country) we determine the occurrence of MNPs in selected commercial species to assess their potential risk for human health. Moreover, *in vitro* toxicity studies with human cell lines will contribute to the risk assessment. Finally, the **OMICS4TOOL Project** (What role can play omics as a tool for risk assessment and environmental monitoring?) aims to document the applicability of the three omics approaches (transcriptomics, proteomics and metabolomics) in risk assessment and environmental monitoring. For that, the response of mussels to a chronic low-dose exposure to the anti-depressant fluoxetine is studied. This pharmaceutical, as many others, can behave as an endocrine disruptor in different organisms. Interestingly, in our ongoing projects we address the potential impact of plastic additives, such as phthalate esters and bisphenol A, which are also well known endocrine disruptors. \*Work funded by the Basque Government grant to consolidated research groups (ref. IT1743-22) and projects CAS6 (DG JRC, S.4 Unit), PLASFITO (Euskampus EUSK22/03), FIERA (PID2021-128600OB-I00, MCIN/AEI/ 10.13039/501100011033 and “ERDF A way of making Europe”), ENSURE2 (TED2021-131147B-I00, MCIN/AEI /10.13039/501100011033/ NextGenerationEU/PRTR), MIKRONANOPLAS (GV/EJ, PA22/01) and OMICS4 TOOL (ANSES, 21-EST-072).

# Reproduction and sex differentiation in aquatic organisms under environmental stress

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KEY WORDS: endocrine disruption, intersex condition, oocyte molecular markers.

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Reproduction in teleost fish is highly diverse. Sex determination and differentiation mechanisms are very flexible and subjected to external environmental factors such as oxygen or food availability, changes in temperature, behavioural cues and exposure to chemicals termed endocrine disrupting compounds (EDCs). In many circumstances exposure of teleost fish to xenoestrogenic EDCs leads to the development of oocytes in testes (intersex condition). We have described intersex testes in mullets (*Chelon labrosus*) from different estuaries in the SE Bay of Biscay, with up to 83% of males in Gernika or 60% in Pasaia harbour showing feminization. This has been associated to xenoestrogenic EDCs detected in the bile of fish, suggesting exposure to chemicals discharged from Wastewater Treatment Plants.

In our research group, we develop markers of intersex condition by studying the molecular pathways mediating oocyte differentiation, that can then be used as proxies of xenoestrogenicity. Most teleosts are broadcast spawners and little is known about the molecular determinants that define oocyte quality and reproductive output. Changes during oogenesis include growth through the incorporation of nutrients and molecules (proteins, RNA, hormones and polysaccharides) in the oocytes that will be necessary for embryonic development in case of successful fertilization. Transfer RNAs (tRNAs) and 5S rRNA stored in nucleoprotein particles can constitute up to 90% of the RNA content in the ovaries of teleost fish and by far are the predominant RNA molecules in previtellogenic oocytes, which are the typical ones in intersex testis. Possibly, this accumulation in the growing oocytes will help in a rapid ribosome assembly in the case of fertilization, allowing protein synthesis during early embryo development. These RNAs are all produced by RNA polymerase III and we are now interested in studying the signalling mechanisms/pathways that integrate the nutritional status into ribogenesis vs autophagocytosis, and the influence of rRNA and tRNA production and accumulation. Such RNA molecules are not only good markers of sex differentiation, oocyte growth and intersex condition but they could also provide tools to explore the possible role of protein synthesis intermediates in defining oocyte quality in teleost fish.

These activities are part of the research line 3 of the Consolidated Research Group Cell Biology in Environmental Toxicology + One Health (CBET+), funded by the Basque Government (ref. IT1743-22).

# One Ocean - One Health: A paradigm to face the challenge of Sustainable Development Goals (SDGs) at Plentzia Marine Station (PiE-UPV/EHU)

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KEY WORDS: Ocean Health, Sustainability, Services, Antimicrobial resistance

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The In 2015, all the countries in the United Nations adopted the 2030 Agenda for Sustainable Development. It sets 17 Goals, which include 169 targets. The areas of work in which a One Health approach is particularly relevant include issues aligned with the following research lines developed at PiE-UPVEHU:

**ENVIRONMENTAL HEALTH:** The motto of Plentzia Marine Station (PiE-UPV/EHU) “Ocean and health” is related to holistic concept of “One health”, which has become globally adopted by the scientific and political communities in the past five to six years. It implies that connections between human beings, animals, plants, microorganisms and their shared environment are essential to obtain the best health and well-being. In other words, human health is linked to environmental health, and the ocean, which is our focus, is an integral part of such environment. Health must be understood comprehensively in order to protect the environment.

**SUSTAINABLE AQUACULTURE.** One of the fields with most potential for improving aquaculture sustainability is research of innovative aquaculture feeds based on alternative ingredients and on omnivorous or herbivorous aquaculture species. PiE-UPV/EHU together with GAIKER and KARDALA is gaining knowledge since 2017 on intensive culturing of the omnivorous mugilid thicklip grey mullet *Chelon labrosus* as alternative to the traditional farmed carnivorous species (AKURA project, Basque Government). In addition, SLOW ALGA Project began in 2021 with the aim of taking advantage of the biological characteristics of algae from the Basque Coast to explore the possibility of creating new products or natural additives to support the Basque gastronomic industry and generate healthy feeds with high nutritional value. The discovery of new compounds in the two aspects of exploitation of marine resources for food/culinary and biotechnological, can imply the development of an efficient and sustainable economy, which stimulates the country's economic growth and social well-being.

**ANTIMICROBIAL RESISTANCE<sup>1</sup>:** Research groups from the Basque Science and Technology Network (Neiker, BC3) and different research groups from the UPV/EHU are integrated in the Joint Research Laboratory on Environmental Antibiotic Resistance. Within this JRL, the aim is to share experience and scientific interests to offer holistic solutions to a problem that affects the one-health context. Moreover, the European project BlueAdapt (“Reducing clinical health risks in blue environments: Adapting to the climate change impacts on coastal pathogens”), led by and with the participation of PiE-UPV/EHU contributes to this topic. All the research groups at PiE-UPV/EHU contributing interdisciplinary research under the projects HOBE (Strategic Projects Oriented to the Ecological Transition) and BlueAdapt (Horizon) establishing Plentzia Bay as a one health observatory, where the transition from land to sea can be studied through aspects as the horizontal gene transfer of antibiotic resistance genes between land and marine microorganisms.

**LABORATORY SERVICES:** The European Marine Biological Resource Centre (EMBRC<sup>2</sup>) is a European Research Infrastructure (RI) established in 2018 to advance fundamental and applied marine biology and ecology research promoting the development of blue biotechnologies. This is achieved by enabling access of researchers to service facilities, and technology platforms in 45 marine stations in 9 European countries. PiE-UPV/EHU, founding member of EMBRC and Spain representative, provides access to marine ecosystems in the Basque country as will for instance in September/October 2023 when researchers of EMBL and Tara Foundation will visit us during the TREC expedition to explore the land-sea transitions across the European coastline.

<sup>1</sup> <https://www.jrl-environmental-antibiotic-resistance.eu/>

<sup>2</sup> <https://www.embrc.eu/>

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# Assessing the environmental impact of micro- and nanoplastics, novel bio-based polymers and other emerging pollutants on aquatic biota

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KEY WORDS: environmental toxicology, nanoplastics, microplastics, bioplastics, pharmaceuticals.

For more than 20 years the “Cell Biology in Environmental Toxicology-CBET+” Consolidated Research group investigates the impact of diverse pollutants and other environmental stressors on the health of ecosystems. In the last years, in collaboration with our partners, we are carrying out several research projects aiming to understand the fate and effects of nanomaterials, micro and nanoplastics (MNPs), and other emerging contaminants, such as pharmaceuticals, on aquatic biota. For that, we employ a combination of field studies and laboratory experiments, mostly with invertebrates and fish, in which we assess responses from the molecular to the organism level to understand mechanisms of toxic action and to build Adverse Outcome Pathways. Further, we apply a battery of bioassays with microalgae, invertebrate and fish embryos and adults, and *in vitro* assays with isolated invertebrate, fish and human cells, useful for risk assessment.

We participate in the **CAS6 project** (Towards a technological platform for nanoplastics -NPs- detection). The *in vivo* experimental studies with mussels and copepods dietarily exposed to NPs of different sizes and chemical composition, including metal-doped polystyrene (PS) NPs, contributes to better understand the fate, impact and life cycle of NPs. After studying the effects of standard PS micro and nanoplastics (MNPs) and their potential role as carriers of other environmental pollutants, in the **FIERA project** (Fate and impact of environmentally realistic nanoplastics and of novel bioplastics in the aquatic environment) we address the challenge of assessing the impact of plastics found in the Bay of Biscay. For that, we monitor the presence of MNPs in diverse species and we work to obtain realistic NPs whose toxicity will be tested using the biomarkers and bioassays mentioned above. In the related **PLASFITO project** (Fate and effect of the microplastics, nanoplastics and additives coming from the degradation of fishing gears during their life cycle. Study in the Bay of Biscay) we specifically focus on MNPs from fishing nets. Moreover, the concern about the increasing detrimental effects of plastics in the environment is leading to the development of biobased polymers, whose safety is still to be proved. Within FIERA, we test novel biobased polymers used as pressure sensitive additives and biopolymers, such as polylactic acid, already used in food packaging and, therefore, present in the environment. Also addressing the problem of biobased polymers, in the **ENSURE2 project** (Environmental Safety of polyurethanes from renewable sources and from recycled plastics: hazard assessment based on a battery of alternative methods) we synthesize partially renewably sourced and partially recycled waterborne polyurethane dispersions without and with nanocellulose, and investigate their environmental hazard. On the other hand, MNPs can reach human beings through consumption of polluted bivalves and fish. Thus, in the **MIKRONANOPLAS Project** (Microplastics in molluscs and fish of interest for human consumption in the Basque Country) we determine the occurrence of MNPs in selected commercial species to assess their potential risk for human health. Moreover, *in vitro* toxicity studies with human cell lines will contribute to the risk assessment. Finally, the **OMICS4TOOL Project** (What role can play omics as a tool for risk assessment and environmental monitoring?) aims to document the applicability of the three omics approaches (transcriptomics, proteomics and metabolomics) in risk assessment and environmental monitoring. For that, the response of mussels to a chronic low-dose exposure to the anti-depressant fluoxetine is studied. This pharmaceutical, as many others, can behave as an endocrine disruptor in different organisms. Interestingly, in our ongoing projects we address the potential impact of plastic additives, such as phthalate esters and bisphenol A, which are also well known endocrine disruptors. \* Work funded by projects CAS6 (DG JRC, A/05), PLASFITO (Euskampus EUSK22/03), FIERA (PID2021-128600OB-I00, MCIN/AEI/ 10.13039/501100011033 and “ERDF A way of making Europe”), ENSURE2 (TED2021-131147B-I00, MCIN/AEI /10.13039/501100011033/ NextGenerationEU/PRTR), MIKRONANOPLAS (GV/EJ, PA22/01) and OMICS4 TOOL (ANSES, 21-EST-072).

# Understanding disorders of the visual system and promoting repair and regeneration

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

The GOBE (Grupo de Oftalmología Experimental, [www.ehu.es/gobe](http://www.ehu.es/gobe)) is a multidisciplinary research group interested in eye research. Ophthalmologists, biologists and biochemists integrate the group. Currently, GOBE have 26 members: 17 doctors and 5 PhD, 1 Master Student and 3 undergraduates. 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 27 years in which 40 Doctors has been formed, 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. We also have close collaborations with the industry like Sylentis, IMG-Pharma and Tecnalia as well as Technological Institutions like CIDETEC and POLYMAT. The group is currently funded by Grupos Consolidados A-Gobierno Vasco (IT1510-22), ELKARTEK (KK-2021/00023), MINECO-Retos (PID2019-111139RB-I00) and PIBA (2020\_1\_0026). We have at present projects in collaboration with companies PUE, Elkartek and Hazitec. Two of our projects have end up in clinical therapies. Some of our methods and technologies developed are being used internationally. 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.

## 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 analysing 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 analysing the epiretinal membranes obtained from patients with retina detachment as well as we are studying the equilibrium of the cell adhesions that could be affected in inflammatory diseases like diabetic retinopathy and uveitis.





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

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

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

- Automatic bilingual video subtitling applied to the plenary sessions videos that the Basque Parliament posts in its website (<https://www.legebiltzarra.eus/portal/web/eusko-legebiltzarra>), 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 collaborations with other research groups. Finally, we also devote great efforts to academic training (PhD and Msc Theses).

## ACTIVE PROJECTS

- Basque Government Research Group Aholab-GTTS (IT1704-22): 2022-2025 (60.000 euros)
- Spanish MINECOR under national plan of R+D+I (PID2019-106424RB-I00): Unsupervised methodologies for leveraging public domain data in state-of-the-art automatic speech recognition: from high- to low-resource languages (OPEN-SPEECH). 2020-2024 (35.000 euros)

## RESEARCH ACTIVITY IN THE LAST 8 YEARS (2015-2023)

- Basque Government Research Group Aholab-GTTS (IT1355-19): 2019-2021 (100.000 euros)
- Projects, contracts and research fellowship: 6 (200.000 euros)
- More relevant publications: 14 (5 JCR journals, 9 peer-reviewed conferences)
- Thesis: 2 presented
- Organization of international Workshops:
  1. Odyssey 2016: The Speaker and Language Recognition Workshop (<http://www.odyssey2016.org>)
- Organization of international competitions:
  1. MediaEval<sup>(1)</sup> - The Query-by-Example Search on Speech Task (QUESST) (2015).
- Participation in international competitions:
  1. NIST<sup>(2)</sup> Language Recognition Evaluation (2015)
  2. NIST Language Recognition Evaluation (2017)
  3. NIST 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, based on automatic transcriptions of speech.
- Kalaka-3: database for the development of language recognition systems.
- ICT- COST 278: TV broadcast news database in Spanish and Basque for audio segmentation and speaker diarization.

<sup>(1)</sup> MediaEval Benchmarking Initiative for Multimedial Evaluation.

<sup>(2)</sup> NIST: National Institute of Standards and Technology

# Digital Electronics Design Group (GDED): Improving Car Safety and Comfort with a View to Autonomous Driving

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

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The Digital Electronics Design Group (GDED) focuses on two major areas of research aimed at the development of innovative multidisciplinary applications. These areas 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:** System-on-a-Chip (PSoC) 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 driving assistance systems (ADAS), hyperspectral imaging (HSI), comfortable driving, eco-friendly driving, intelligent sensors, internet of things (IoT).

## RECENT APPLICATIONS DEVELOPED BY THE GROUP AND WORK IN PROGRESS

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 incorporation of multispectral cameras in ADAS with the aim of improving road safety is a 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 could 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 deep neural processing, and its integration into FPGA-based PSoCs will allow real-time processing of multispectral images.

On the other hand, ADAS are primarily designed with the aim of increasing driving safety without paying too much attention to passenger comfort or motion sickness. However, the comfort perspective is essential in the future car investigation. In this sense, the GDED developed a methodology based on measured car signals, data processing techniques, and machine learning algorithms in order to identify driver actions that negatively affect passenger motion sickness. Our models are able to identify different driving patterns and associate them with the motion sickness levels suffered by the passenger. Based on these models, the GDED proposed a recommendation system to fix non-comfortable riding situations by adapting driver's actions.

Furthermore, pollution that originates from automobiles is a concern in the current world, not only because of global warming, but also due to the harmful effects on people's health and lives. In this context, the group developed an intelligent PSoC for real-time assessment of fuel consumption to promote eco-driving.

# Magnetism and Magnetic Materials Group

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KEY WORDS: Nanomagnetism, Magnetotactic bacteria, ferromagnetic shape memory alloys, Thin films, magnetic sensors

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The Magnetism and Magnetic Materials Group (GMMM), <https://www.ehu.es/en/web/gmmmt>, 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.

## **Acknowledgments**

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# Microstructural, magnetic & spectroscopic characterization of materials with high technological applications

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KEY WORDS: magnetic hyperthermia, Mössbauer Spectroscopy, Positron Annihilation Lifetime Spectroscopy

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Our interdisciplinary group is focused on the characterization of the different materials by AC magnetometry, Mössbauer Spectroscopy and Positron Annihilation Lifetime Spectroscopy (PALS).

Tumour destruction with magnetic nanoparticles (MNPs) in an AC magnetic field is a promising cancer therapy called magnetic hyperthermia (MH). The specific absorption rate (SAR) value, defined, as the power transformed into heat per unit of mass of MNPs, is one of the most relevant parameters for the treatment. In general, calorimetric methods are used to measure SAR of samples with magnetic nanoparticles, even though there are many factors that can affect the value of SAR measured in this way. Alternatively, SAR can also be measured by AC magnetometry. In this technique, SAR is directly obtained from the area of the AC hysteresis loop of the samples when they are excited by an AC magnetic field. This hysteresis loop area is directly related with the dynamic magnetization of the MNPs, information that calorimetry technique do not provide.

Our group has developed several AC magnetometers since 2015. We recently built an AC magnetometer that works in a frequency range between 100-1000 kHz and capable of applying higher intensities than those existing in current devices. The device is based on a variable parallel LCC resonant circuit fed by a linear power amplifier limited to 1 kW. The geometry of the main coil was carefully designed to reach 90 mT at 134 kHz and 30 mT at the maximum frequency of 950 kHz, in all cases with a high degree of homogeneity in a volume of approximately 100 mm<sup>3</sup>. Additionally, our device incorporates a temperature system for continuously measuring dynamic magnetization between 220 K and 380 K.

NiTi shape memory alloys (SMA) have been implemented in several industrial and biomedical applications due to their mechanical properties such as the shape memory effect (SME) or the superelasticity (SE). The SME is controlled by the so-called martensitic transformation (MT), characterized by the transformation temperature (TT) which determines the working temperature of the material. The TT of these alloys is below 100 °C, limiting their operation temperature for many applications requiring high working temperatures. For such reason, recently, the addition of Hf and Zr has been proposed. The NiTiHf and NiTiZr alloys exhibit good shape memory response and super elastic effect with TTs over 100 °C. The composition of the alloys influence greatly the TT, however, there are other factors that could have an impact in the TT temperature such as the defects. Some authors have reported a decrease in the TT that may be caused by the formation of defects in the sample. We study and characterize the NiTiHf and NiTiZr alloys through positron annihilation lifetime spectroscopy (PALS). This technique allows an exhaustive analysis of the bulk and the different types defects present in these alloys. Our group has studied defects such as monovacancies or divacancies in depth and the different factors that influence the positron lifetime. These calculations and measurements allow a good understanding of the positron annihilation characteristics in these materials and represent a solid background to study the influence of defects in the MT. The optimization of the 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.

Mössbauer spectroscopy is a powerful technique for both structural and magnetic characterization at the atomic level. Although several works can be found, in which <sup>57</sup>Fe MS has been used in Fe doped Ni-Mn-Sn alloys, <sup>119</sup>Sn MS, which makes doping unnecessary and therefore helps to ensure chemical environment of Sn atoms, has been scarcely employed.

# Theory of Nanophotonics

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KEY WORDS: light, nanophotonics, nanoantenna, nanoparticle, surface plasmon, plasmonic picocavity

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Our research is focused on the theoretical description of new physical phenomena arising from the complex light-matter interaction at the nanoscale, in collaboration with experimental groups. This interaction opens up a range of new possibilities in optics, due to the ability of metallic nanoparticles to host collective oscillations of conduction electrons on their surface, so-called "surface plasmons". The energy and momentum exchange between light and plasmons allows to intensify and localize light to a few nanometers around nanostructures, acting as "collectors" or "emitters" of light at the nanoscale. For this reason, metallic nanoparticles are often considered as "optical nanoantenna". Therefore, metallic nanoparticles and nanostructures effectively carry energy from the far electromagnetic field to the near field, making it possible to overcome lens optics, whose resolution and manipulation were limited to the micrometer scale (diffraction limit of visible light). Typical dimensions of optical nanoantenna are in the range of several tens to hundreds of nanometers. However, it is now possible to achieve field localization in nanometer and sub-nanometer regions of space thanks to the fabrication and use of extreme metallic morphologies, such as atomic-scale metal tips or sub-nanometer cavities, called picocavities, configurations of great relevance to the research of our group. Nanophotonics allows to exploit light technology more efficiently, and in this way respond to many social challenges in terms of safety, energy and health.

Our research is articulated around two general lines, that explore the interaction of light with plasmonic nanostructures and their technological applications at two different levels:

**1- Quantum effects in plasmonic nanocavities and picocavities:** We explore the interaction of plasmonic nanoparticles and picocavities with molecules, addressing the emerging quantum effects, to improve the performance of devices and spectroscopies in the following fields: Optoelectronics, Plasmon-enhanced molecular spectroscopies (SERS, Surface Enhanced Raman Spectroscopy and SEIRA, Surface Enhanced Infrared Absorption Spectroscopy) and EELS (Electron Energy Loss Spectroscopy).

**2- Optical response of plasmonic nanoantenna in the visible and near-infrared:** We collaborate with local and international experimental groups on the design of nanophotonic devices based on plasmonic nanoantenna and functional materials for different applications, as all-optical switches, molecular and biological sensors or magnetoplasmonic devices for active control. Two specific research lines in progress are:

- Optical colorimetric sensors based on Au nanoparticle aggregation.
- Nanophotonic devices applying self-assembled colloids for novel on-chip light sources.

We have experience in using analytical and numerical methods to address theoretically the complex light-nanostructure interaction. We use home-made and commercial codes to solve different classical electrodynamics problems, as BEM, MPBEM (Boundary Element Methods), DDA (Discrete Dipole Approximation), LUMERICAL (FDTD, Finite Difference Time Domain method) or COMSOL (Finite Element methods). To address quantum effects in Nanophotonics we use TDDFT (Time Dependent Density Functional Theory) and ab-initio codes based on SIESTA or GPAW, together with optimization codes as BOSS (Bayesian Optimization Structure Search).

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# ICE, Grupo de Instrumentación y Control Experimental / Tresneria eta Kontrol Esperimentalaren Taldea

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KEY WORDS: Automation and control, High frequency instrumentation, Particle sources and accelerators, High frequency circuits, Protonics, Neutronics, Shape memory alloys, Sensors and Actuators

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The **Instrumentation and Experimental Control Group (ICE)** results from the alliance of the **GAUDEE group and the RF and Microwave group**, both integrated into the Department of Electricity and Electronics of the UPV/EHU. Both groups have maintained collaborations since their foundation, over two decades ago, in the field of analysis and control of high-frequency circuits. This collaboration has expanded in recent years through the activity, pioneering in the Basque Country, in Particle Science and Technology and in the founding of the Izpilab joint laboratory, focused on instrumentation and control of ion sources and subsystems for acceleration of particle beams using RF signals. The team has experience in the development of research projects financed in competitive calls, in relevant fields such as Communications, Advanced Manufacturing, Energy and Health.

**ICE's research topics** arise naturally from the evolution of the two groups, whose trajectory can be summarized in the following lines:

- GAUDEE has been working on the development of instrumentation and advanced control of complex systems in very varied fields of application, from high-performance mechatronic and electromagnetic systems, offshore wind generation systems, or signal monitoring and control systems involving RF signals. Another important activity of the group has been in the field of new active or intelligent materials, such as shape memory alloys (SMA) and ferromagnetic shape memory alloys (FSMA), from which the group has designed and manufactured a variety of novel actuators, demonstrating its use in nanometer-precision control loops. Also based on principles such as giant magnetoresistance (GMI) or making innovative use of RF resonant cavities, the group has developed, designed and manufactured new sensors with novel properties and sub-nanometric resolution, and has demonstrated their use in high-speed control systems. precision.

- The RF and microwave group has developed its research work in the area of high frequency circuits and systems and their applications. Its activities can be summarized in two lines of research, the first focused on the analysis and design of circuits and systems and the second dedicated to instrumentation and measurement. The objectives of both include, among others, aspects such as the design of RF subsystems for various purposes, the stability analysis of nonlinear circuits, the experimental characterization of nonlinear noise, or the implementation of transducers, sensors, and subsystems for instrumentation. The group path has been characterized by intense technology transfer activity in an international context, highlighting an international patent, shared with the French Space Agency and licensed to the company AMCAD Engineering, which continues to generate royalties.

The ICE group carries out its **research activities in applied science and technology in which instrumentation and control play a relevant role**, with special emphasis on electromechanical systems and RF and microwaves:

1. Izpilab - Particle Beam Laboratory
2. Advanced analysis techniques, experimental characterization and control of complex circuits and systems
3. Sensors and actuators using new materials and principles

# Speech Interactive Research Group

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KEY WORDS: dialogue modelling, emotion recognition.

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The Speech Interactive (SPIN) research group explores novel ideas in the areas of Dialog Modeling and Spoken Emotion Recognition. Currently, the group is involved in several research projects and doctoral thesis.

Regarding the thesis that are related to Dialogue Modeling, one of them focuses on improving machine learning methods for end-to-end neural dialogue systems. Then, we are also working on a thesis in the field of Natural Language Generation, which is a key module of every dialogue system. Its main contribution is to adequate the generated responses to the emotional state of the user. Last, another thesis explores different techniques to detect emotion from speech and text based on neural networks.

As for the research projects, we would like to highlight four of them. CITA GO-ON aims at developing a system to monitor users habits to prevent the development of dementia and related diseases. Next, EKIN and its continuation BERREKIN are industrial projects where a virtual assistant has been designed to help industrial workers look for specific information in technical manuals. The last two projects are related to emotion recognition. First, in AMIC-PoC an automatic prototype to recognise emotion from TV shows has been developed. Last, in ORKESTA we research on the automatic detection of depression and anxiety indicators.



# Quantum Matter and Quantum Simulations

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KEY WORDS: ultracold atoms, optical lattices, quantum simulations, tensor networks

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In the early 1980s, Richard Feynman proposed the notion of *universal quantum simulator*, referring to a particular category of quantum systems capable of emulating other complex quantum systems. This simulator serves three main purposes: first, to replicate the behavior of otherwise inaccessible systems; second, to manage and examine particular effects that may be concealed; and third, to investigate novel parameter regimes, even those deemed unfeasible.

Currently, ultracold atoms represent one of the most versatile platforms due to their ability to i) finely adjust various system parameters, including interactions, dimensionality, and geometry; ii) create Hamiltonians for other physical systems; iii) prepare diverse quantum states; and iv) perform precise measurements.

Our research group is engaged in theoretical investigations of several of these aspects, which are conducted in parallel and sometimes in conjunction with experiments conducted at international laboratories. Our current research areas encompass a range of topics, including superfluid and supersolid matter, optical lattices and topological matter, digital and analog quantum simulations, and the use of tensor network approaches for simulating quantum systems.

# Computational methods for describing many-body interactions in condensed matter physics

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KEY WORDS: condensed-matter physics, computational methods, low-energy excitations, density-functional theory, spin-orbit coupling, strong correlation

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The computational condensed matter physics group [1] aims at understanding and describing the physical properties of materials that arise from many-body interactions, with focus on vibrations (phonons) and magnetism. Our approach to the problems is ab-initio, that is, we start from a first-principles description of matter that uses only the quantum mechanics of electrons and atomic nuclei. It is evident that solving a many-body problem under this assumption is extremely challenging. Therefore, we need to work with approximate methods, being the popular density-functional theory (DFT) one of our main resources and often a starting point for our methodological developments. Our work as computational physicists involves creating effective numerical techniques and algorithms to solve problems, utilizing high-performance computing resources.

The group's expertise covers different scenarios featuring excited collective oscillations where a correct description of many-body interactions is mandatory: electron-phonon coupling [2-4], spin-phonon coupling, and magnetism in strongly correlated systems [5]. These effects underlie phenomena such as superconductivity, transport, "hidden orders", magnetic exchange interactions, the Kondo effect, etc. Of course, these phenomena cannot be accounted for with a description based on plain DFT. Instead, we employ Green's functions, which incorporate the many-body interactions by treating the interacting particles as dressed independent particles with modified or renormalized properties. Importantly, all our techniques include spin-orbit interactions [6-8], which are a crucial ingredient in the physics of low-dimensional systems, such as 2D materials and magnetic impurities.

Our current efforts are aimed at improving the efficiency of our computational codes, primarily by implementing point group symmetries in our calculations to reduce the computational cost and improve accuracy. Additionally, at the moment we focus on implementing parallelization and concurrency in our codes to take advantage of modern computing architectures and accelerate calculations. Along with these technical improvements, we are also exploring new physical phenomena related to hidden spin properties and relativity in connection to vibrations and strong correlation. By investigating these properties, we hope to get new insights into the behavior of matter.

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# Observing Cosmic Superstrings with Gravitational Waves

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KEY WORDS: Cosmic Strings, Superstrings, Gravitational Waves.

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Cosmic Superstrings are line-like structures that may have been produced in the Early Universe. Their typical energy scale is very high and as the universe expands and cools down, they stay behind as relics of the high energy phase of the primordial universe. They can also be produced in cosmological models of the Early Universe that rely on String Theory. In these models, these cosmic strings are nothing more than a blown-up version of the fundamental strings of Superstring Theory, hence the name of Cosmic SuperStrings. Their discovery by the observation of the gravitational waves they produce would open up a new window into the high energy physics beyond the Standard Model that can not be reached by particle accelerators.

# Research Group on Physical Metallurgy and Advanced Materials

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KEY WORDS: Shape Memory Alloys, Intermetallics, High Entropy Alloys, Additive Manufacturing, Electron Microscopy.

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Materials science opens the third millennium with the challenges of three new paradigms: The emerging Nano Technology and the size effects on properties at small scale, the breaking conception of the new metallic alloys called High Entropy Alloys (HEA) and the new 3D-technologies of materials processing by Additive Manufacturing (AM).

Today, scientific developments of advanced materials are aligned to reduce the greenhouse gas emission sustainably to take care of the planet, while, simultaneously, are looking towards the space exploration, which is opening new opportunities and challenges.

The Research Group on Physical Metallurgy and Advanced Materials (GIMF) activity covers all these paradigms and challenges through four research lines, which are shortly described in our presentation, in collaboration with International Excellence Research Centres as well as with National Technologic Centres.

- **Shape Memory Alloys (SMA):** This family of smart materials constitute the main research line of the GIMF, with is focused on several aspects of relevant scientific and technological interest:

- **High-Temperature SMA** based on the system Cu-Al-Ni [1] for aerospace applications. A space actuator called REACT, built with the alloys developed at GIMF is already flying in space missions.
- **Nano-scale properties** and size effects of SMA. This is a pioneering activity of GIMF, with promising applications in micro electro-mechanical systems (MEMS) [2-4].
- **Ultra-low-temperature SMA** for cryogenic applications. This kind of SMA was recently patented by the GIMF and opens new potential applications in cryogenic systems, for instance in Hydrogen technologies.

- **Intermetallic Ti-Al materials:** This research line is focused on the fundamental aspects of the atomic structure and defects mobility controlling the mechanical properties at high temperature of the Ti-Al alloys that are already flying in the low-pressure turbine of the aeronautic engines [5]. These advanced alloys reduce the weight and increase the efficiency of the engines, contributing to the clean-sky objective.

- **High-Entropy Alloys (HEA):** These newly developed alloys including a nearly equal atomic proportion of five or more elements constitute a new paradigm. The GIMF is working on the fundamental aspects of Fe-Mn-Co-Cr-Ni-Si alloys to improve and understand the low temperature mechanical properties. In addition, we are affording the challenge of developing HEA with shape memory properties [6].

- **Additive Manufacturing (AM):** In collaboration with several research centres, the GIMF is developing a broad activity to produce by AM several advanced materials, including HEA and SMA [7].

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# Physical and mathematical foundations of the structure of the Universe

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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

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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 very compact astrophysical objects and black holes. 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 gravity: dynamics, semi-classical approach and physical consequences.
3. Quantum models of black holes and gravitational collapse. Quantum-gravity effects in the dynamics of the early universe.
4. Mathematical relativity; trapped and umbilical submanifolds, computer algebra, initial data characterisations and exact solutions.
5. Observational tests with large scale astrophysical data, alternate gravity theories beyond Einstein's, and future cosmological singularities.

# Experimental research on the thermo-physical properties of materials

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KEY WORDS: thermo-physical properties, radiative properties, emissivity, dielectric properties

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The study and understanding of the interaction between matter and electromagnetic radiation –in other words, the absorption, emission, and scattering of electromagnetic waves by matter– is key for the research on advanced materials, optimizing the energy and economic cost of industrial processes and addressing major pressing issues such as the climate crisis. In the physics department, the research Group of Thermophysical Properties of Materials (GPTM) approaches this topic by means of three main experimental techniques:

1. **Infrared emissimetry:** the emissivity is the thermophysical property that describes the thermal emission of a material, which depends on the material's composition, temperature, surface condition, as well as the direction and wavelength of the radiation being emitted. To perform these measurements, the HAIRL emissometer is used, an experimental equipment designed at the UPV/EHU and recently updated, which is an international reference in the field.
2. **Thermography:** a powerful tool for non-invasive temperature measurement of objects and surfaces. It works by detecting the heat energy emitted by these objects and converting it into an image or visual representation that highlights variations in temperature. It has a wide range of applications, including electronic fault detection, renewable energy technology and detection of areas of heat loss.
3. **Infrared spectroscopy:** one of the most popular and widespread spectroscopic techniques, radiation-matter interaction is studied by means of reflectivity, absorptivity and transmittance. In this case, infrared spectroscopy is used to study the effect of the nanoscale morphology and structure of heterogeneous materials on their optical properties, in order to tailor their optical behavior by altering their nanostructure.

Moreover, thanks to the multidisciplinary nature of its members, the group covers a considerably broad spectrum of materials science and applied physics, such as physical metallurgy, advanced alloys, electron microscopy, crystallography and structural phase transitions, among others. This extensive knowledge and experience allow us to develop research on complex materials (nanofilms, multilayers, selective absorbers, etc.) for solar applications (thermophotovoltaic and concentrating solar power), next-generation alloys for the aeronautics industry or the optimization of emerging technologies such as additive manufacturing.

In addition, our group collaborates on an ongoing basis with national and international scientific research centers and universities (CNRS, CICenergigune, Tecnalia, Tekniker, UC San Diego, etc.) as well as with companies (ArcelorMittal, Petronor, etc.).



MATEMATIKA

MATEMÁTICAS

# Stochastic Network Optimization for Intelligent Transport and Logistics

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KEY WORDS: stochastic optimization, network applications, risk management.

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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 2021-2023, three of the six strategic actions are focused on: Health: Digital World, Industry, Space and Defense; and, Climate, Energy and Mobility. 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. Energy networks
  - B1. Determination of smart grids (network topology)
  - B2. Multi-Energy Systems (network nodes) in buildings.
- C. Analysis and design of a connected emergency healthcare system and
- D. Logistics
  - D1. Optimization of humanitarian logistics for sustainable disaster relief.
  - D2. Cross-docking infrastructures.

These 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 Applications and Technology 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.
- Polytechnic university of Milan (Italy).st no. Id duo nihil impetus minimum, ex dicat suavitate explicari cum.



# Mathematical and optimisation tools in industry

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KEY WORDS: Optimization. Operations Research. Industrial Mathematics. Call center. Deep learning

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Statistical data analysis, optimisation and deep learning tools are very useful for modelling industrial problems. Here are some examples where these techniques are applied to real models.

Four mathematical models developed in collaboration with institutions and companies are presented. The models have been designed for solving practical problems in real scenarios obtaining significant improvements.

The first model concerns the call center service that manages the internal incidences of a distribution company. 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 categorized 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, every day a calculus of a safety stock can be made guaranteeing the supply and minimizing the loss by outdated.

The target of the third scenario is to efficiently organize the 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 it is currently being developed statistical models for forecasting and optimal allocation of shared-use space in the offices of a medium-sized company. Deep learning techniques for the recognition of digital images for use in autonomous vehicle driving are also being studied with the same company.

# Profinite Groups and Zeta Functions

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Matteo Vannacci <sup>1</sup>  
<sup>1</sup>Matematika Sails

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KEY WORDS: Topological groups, profinite groups, zeta functions.

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Topological groups are the meeting point of Group Theory and Topology. Prominent examples of topological groups are *Lie groups*, e.g. subgroups of  $GL_n(\mathbb{R})$ , which are omnipresent in Physics and other sciences.

Profinite groups are a class of topological groups that appear naturally in Algebra (products of finite groups), Number Theory (absolute Galois groups) and Algebraic Geometry (algebraic fundamental group), among others. Profinite groups also are intrinsic to the study of asymptotic properties of finite groups.

To boot, the use of zeta functions to study algebraic objects is a well-established branch of Mathematics. Just to mention one: Riemann's zeta function. In this poster, we will try to outline how zeta functions come naturally into play when studying groups; in particular, when studying the integers.

The main goal of the poster is to present two proofs of the following classical theorem of Euclid: there are infinitely many prime numbers.

1) The first proof is due to Furstenberg and it is a topological proof. The topology introduced is the profinite topology on the integers and we will see what interesting features of this topology can be transported to other groups.

2) The second proof is due to Euler and it uses zeta functions. We will use this to motivate some recent research on a new kind of zeta function counting representations of profinite groups over finite fields.

# Matrix analysis and applications group

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

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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. Parametrize the spectral filters of general quadratic systems, characterize the eigenvectors of classically damping systems and generalize the phase synchronization method.
2. Design a procedure to effectively construct vibrating and gyroscopic systems with prescribed dynamic behaviour.
3. Complete a polynomial matrix with rows (columns) of bounded degree so that the resulting matrix has some prescribed invariants for a given equivalence relation.
4. Progress on the characterization of the assignment of invariants under state feedback and output injection, for linear control singular systems.
5. Complete the study of the hyperinvariant and characteristic subspace lattices.
6. Generalize Berlekamp-Massey algorithm to obtain matrix generators of minimal length for a given sequence of matrices.
7. Study the regularity of the stratified manifold of controllable and observable linear systems with fixed controllability and observability indices.
8. Obtain a general characterization of the stable  $(A,B)$ -invariant subspaces.
9. Analyse the geometry of the connected components of the pseudospectra and compute their derivatives in the sense of the Hausdorff metric.
10. 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>

# Group on Applied Mathematical Modeling, STATISTICS, and Optimization

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KEY WORDS: statistics, statistical modelling, validation, biostatistics.

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The key objectives of the Group on Applied Mathematical Modeling, Statistics, and Optimization (**MATHMODE**) are: 1) **Develop knowledge** on the numerical simulation of ordinary and partial differential equations, as well as on optimization problems and **statistics**; 2) **Transfer this mathematical knowledge** to the industry, and 3) Train new researchers in the area.

Being **Statistics** one of the main areas of the group, we present below the main lines of research in which we work in the field of statistics.

## Development and implementation of regression models for patient reported outcomes (**PRO**) modeling

- Development of regression models based on the beta-binomial distribution for multidimensional and longitudinal PRO modelling.
- Development of a theoretical framework for joint modeling of PRO and time-to-event data based on non-exponential family distributions, especially beta-binomial distribution.

## Development and validation of prediction models in health-, experimental- and social-sciences

- Evaluation of logistic regression model parameters estimation for complex survey data.
- Development of AUC estimator for complex survey data.
- Variable selection proposal for the development of prediction models with complex survey data.
- Categorization of continuous variables in prediction models.

## Analysis and prediction of patient-centered clinical outcomes

- Development of prediction models for patients with chronic diseases.
- Identification of patient profiles in chronic diseases (e.g. COPD) or infectious diseases (e.g. covid-19).

**Software Development.** We are working on the implementation of the methodology developed in this group into R packages or Shiny Applications.

We have active collaboration with members from public institutions in the Basque Country such as Osakidetza, Hospital universitario de Galdakao-Usansolo or EUSTAT and researchers from other national and international universities such as Universidad Politécnic de Catalunya, Universidad Carlos III de Madrid, Universidad de Vigo and University of Auckland, among others.

For more information look at the following web page: <https://www.mathmode.science/home>

# Research Group of Queueing Systems Analysis

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KEY WORDS: Queueing theory; Performance evaluation; Resource-sharing problems.

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The Internet is today the fundamental component of worldwide communications infrastructure. In recent years, the use of both the Internet and wireless services has experienced an explosive growth and has had a striking impact in the world-wide economy. Network operators and service providers anticipate further expansion, boosted by the emergence of all-optical networking as well as the convergence of wireless and Internet access, along with a fundamental trend towards service integration. It is expected that future information and communication systems will accommodate a variety of new applications with a diverse range of Quality-of-Service (QoS) requirements. These research group focuses on the modeling and performance evaluation of large-scale distributed systems. More precisely, we aim to model the communication system, analyze the performance of this model, and propose algorithms/mechanisms that improve the performance of end users.

The main challenges are the need to cope with the management of heterogeneous resources in both data and services, due to the fact that arrival times of queries and their service requirements are unknown; and the need to cope with little or no knowledge of the explicit dynamics of the system. Hence, queueing theory and stochastic processes are a fundamental tool to analyze these systems. In fact, they provide a wide set of mathematical tools to define models that allow us to predict the performance of queues or waiting lines. Once the evaluation of the performance of a system has been done, one can think of the design of efficient algorithms to apply to those systems, i.e., how the system must be designed so as to ensure that its performance is as close as possible to the optimal performance that can be achieved.

Some of the current research topics covered by our group are the following:

- Performance Evaluation and Optimization of Parallel Server Systems
- Analysis of Queueing Games
- Optimization using the Age of Information Metric
- Learning in Queueing Systems

The main tools we use in our research are:

- The theory of Markov chains and its approximations
- Markov decision processes in discrete and continuous time
- Non-cooperative Game Theory
- Reinforcement Learning

# Mathematical Analysis and Applications

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

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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 linear and nonlinear partial differential equations (Dirac equation, Schrödinger equation, and the vortex filament Equation, among others) and related problems, in connection with some physical phenomena; unique continuation, control theory and inverse problems; 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 sub-Laplacian 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 following ones:

- Funded by the Basque Government:
  - IT1615-22, Fourier Analysis and Partial Differential Equations. Principal Investigator: Carlos Pérez.
- Funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe”:
  - PID2021-122156NB-I00, Harmonic analysis meets inverse problems. Principal Investigators: Pedro Caro and Ioannis Parissis.
  - PID2021-126813NB-I00, Análisis matemático y numérico de ecuaciones en derivadas parciales. Principal Investigators: Francisco de la Hoz and Luis Vega.
  - PID2021-123034NB-I00, Spectral theory and PDE: Real and Fourier Analysis. Principal Investigators: Renato Lucà and Luca Fanelli.
- Excellence Accreditation "Severo Ochoa":
  - Centre of Excellence "Severo Ochoa" CEX2021-001142-S. Host institution: BCAM. Principal Investigator: Luis Vega.



GEOLOGIA

GEOLOGÍA

# HAREA-Coastal Geology Research Group

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KEY WORDS: environmental transformation, natural processes, anthropogenic impact, sea-level rise.

The HAREA-Coastal Geology research group ([www.ehu.eus/harea-geologicalitoral](http://www.ehu.eus/harea-geologicalitoral)) 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, based on scientific criteria, 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., Gardoki, J. and Fernández Martín-Consuegra, A. 2020. Recent coastal anthropogenic impact recorded in the Basque Mud Patch (southern Bay of Biscay shelf). *Quaternary International* 566-567: 357-367. <https://doi.org/10.1016/j.quaint.2020.03.042>).
2. **Holocene relative sea-level (RSL) change.** An increase in the rate of RSL rise 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., Cearreta, A., Monge-Ganuzas, M., Nikitina, D., Li, T. and Horton, B.P. 2023. Holocene environmental evolution and relative sea-level change in the Oka estuary (Urdaibai Biosphere Reserve, northern Spain). *Estuarine, Coastal and Shelf Science*. <https://doi.org/10.1016/j.ecss.2023.108310>).
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 reconstructing the past features, to understand the present conditions and to deduce the future environmental variability (Pascual, A., Rodríguez-Lázaro, J., Martínez-García, B. and Varela, Z. 2020. Palaeoceanographic and palaeoclimatic changes during the last 37,000 years detected in the SE Bay of Biscay based on benthic foraminifera. *Quaternary International* 566-567: 323-336. <https://doi.org/10.1016/j.quaint.2020.03.043>; Sainz de Murieta, E., Cunha, P.P., Cearreta, A., Murray, A.S. and Buylaert, J.-P. 2021. The Oyambre coastal terrace: A detailed sedimentary record of the Last Interglacial Stage in northern Iberia (Cantabrian coast, Spain). *Journal of Quaternary Science* 36: 570-585. <https://doi.org/10.1002/jqs.3317>).
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. Geological studies contribute to understand the role of the anthropogenic influence and to establish suitable strategies for a sustainable development and harnessing (Cearreta, A., Irabien, M.J., Gómez Arozamena, J., El bani Altuna, N. and Goffard, A. 2021. Environmental evolution of the Basque Coast Geopark estuaries (southern Bay of Biscay) during the last 10,000 years. *Journal of Marine Systems* 219 (103557): 1-21. <https://doi.org/10.1016/j.jmarsys.2021.103557>).
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., Williams, M., Zalasiewicz, J., Turner, S., ..., Cearreta, A., et al. 2022. Epochs, events and episodes: Marking the geological impact of humans. *Earth-Science Reviews* 234 (104171): 1-28. <https://doi.org/10.1016/j.earscirev.2022.104171>).

This research group has a leading role in the UPV/EHU Doctorate Programme on Quaternary: Environmental Changes and Human Footprint (<https://www.ehu.eus/es/web/doktoregoa/doctorado-cuaternalario-cambios-ambientales-huella-humana>). **Acknowledgements:** IT1616-22 (Basque Government).



# Hydro-Environmental Processes research group (HGI)

(Faculty of Science and Technology, Department of Geology)

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KEY WORDS: water, soil, climate, rock

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The consolidated HGI research group (IT-1678/22) is structured along four axes: water, soil, rock and climate. The Territory-Landscape-Heritage action scenario is marked by climate change.

**Water** is the geological regulating and modelling agent of the environment and the one that links the group's research: surface water, groundwater, mine acidic water, seawater, salty water, hydrothermal water,...

**Soil**, an essential and practically non-renewable resource, performs important ecosystemic functions that are threatened due to high environmental pressure and degradation. Understanding and characterising soils is essential for predicting their response to different climate and land-use scenarios.

The past is the most important key to the future. Therefore the knowledge of the responses recorded in the rocks of previous climatic events allows us to predict future scenarios: soil erosion and cave filling, variations in temperature and precipitation recorded in speleothems, past acidification of the seas and proliferation of unique biota, variations in sea level and formation of scrapes, alteration of cultural heritage, ...

The use of geological resources throughout human history has modified the landscape and the territory. The evolution of landscapes, the cultural elements built and the **rocks** used are often the link between natural and cultural heritage and Geology.

## RESEARCH LINES

The Research Group is structured in four research lines. These lines are interrelated with each other:

- **Hydro-geo-environmental processes at river basin scale:** Monitoring and understanding of hydrological, surface and subsurface, processes; geo-environmental implications and their modelling; enhancing the value of hydrology, in its broadest sense, as a fundamental pillar of territorial management on a river basin scale.
- **Soil characterisation and functionality:** Physico-chemical-biological-petrological characterisation, age, erosion, geomorphology-connectivity: soil characterisation and evolution; soil dynamics: erosion, landslides, accumulation (caves, sinkholes, flood plains...); ecosystem value: hydrological soil function.
- **Impacts of Global Change on the Territory:** Retrospective on geological systems: hydrology, speleothems, fluvial terraces and terraces, soils; environmental impact of mining; current impacts of Global Change on land instabilities; hydrological forecasting from changes in climate and land use for adaptive land management.
- **Integrative approach in Landscape-Heritage-Territory studies:** Characterisation and recovery of degraded spaces and multidisciplinary analysis: characterisation and enhancement of geological heritage; integration of geological and geo-environmental studies in cultural heritage in a transdisciplinary way; understanding the origin and evolution of the landscape from a geo-environmental point of view; monitoring, study and valorisation of singular spaces; monitoring, consolidation and valorisation of built heritage; recovery of industrial areas.

## DISSEMINATION

One of the objectives of HGI is to disseminate Geology to people in society in a simple and clear format. The Group members organise numerous activities in this respect: guided field trips, conferences, practical activities for students, collaborations with the media (press, radio, television and social networks), "Geology Days for myopic and absent-minded poets" (now in its fourth edition), international cooperation activities and dissemination activities that are repeated annually (geolodía, zientzia azoka, mendifilm, zientzia astea...).

# Applying geology to cultural heritage materials

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*Graciela Ponce-Antón<sup>1</sup> M<sup>a</sup> Cruz Zuluaga<sup>1</sup>, Luis Ángel Ortega<sup>1</sup> and Ainhoa Alonso-Olazabal<sup>1</sup>*  
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KEY WORDS: geological approach, mineralogical and petrological characterization, mortars, plasters, bricks and tiles, technological inputs.

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Socio-economic development of historical periods is analysed by a multidisciplinary research group formed by mineralogists and petrologists in collaboration with archaeologists and architects. The research team has been working for the last fifteen years on different lines of research related to building materials in the historical and archaeological fields.

The characterisation of archaeological materials provides clues to human technological evolution, technological skills, and cultural and trade relationships.

## **MORTARS AND PLASTERS**

Mortar and plaster studies allow the assessment of their durability over time, the evaluation of building deterioration and the formulation of compatible repair mortars and plaster for use in historic buildings. Mineralogical, chemical and physical characterisation and hydric behaviour studies allow the durability of historic building materials to be determined. Archaeometric features also reveal repair work carried out during the life of the historic building and its effects.

## **BRICKS AND TILES**

The study of bricks and tiles makes it possible to identify raw material sources and to characterise production technology and trade. Ancient workshops and production methods can be identified through petrological study. In our group, this line of research is just beginning to develop. However, initial results indicate that the different processing techniques observed are linked to the regional origins of the craftsmen and the working methods used.

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# Palaeontology, Geology and Heritage from the Mesozoic and Cenozoic of the western Pyrenees

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

This group includes researchers from different fields (palaeontology, sedimentary geology and biology) from the Universidad del País Vasco/Euskal Herriko Unibertsitatea, in collaboration with researchers from other centres and institutions, both national and foreign. Research group IT1485-22 from the Basque Government / EJ.

The main goal of our research is to contribute to the better understanding of the palaeobiodiversity of western Pyrenees throughout the study of sedimentary rocks and fossils of invertebrates, vertebrates and associated biota from the Mesozoic and Cenozoic deposits of the Basque-Cantabrian region and nearby sedimentary basins. Besides, studies on living faunas are used as an actualistic approach to the understanding on fossil vertebrate communities. The obtained knowledge is of utmost importance to understand the geological processes that occurred during the history of these Pyrenean basins and the Earth and to decipher how these processes affected the once living communities. 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 in an ancient changing Earth, as well as to better understand the today's changing biosphere.

For this purpose, our main lines of research are:

1. Palaeobiology and biochronology of vertebrate faunas and related biota from the Mesozoic and Cenozoic deposits of the western Pyrenees.
2. Evolutionary palaeoecology and palaeobiogeography: environmental and biotic changes.
3. Geological context, environmental analysis and taphonomy of the Mesozoic and Cenozoic biota.
4. Geological heritage and geoconservation of palaeontological sites and fossil associations from the western Pyrenees, and their social projection.

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

Recent publications:

-Díaz-Martínez, I., López-Horgue, M. A., Agirrezabala, L. M., Cónsole-Gonella, C. & Pereda-Suberbiola, X. (2022). Dinosaur tracks in a Cretaceous (lower Albian) braid delta system (Basque-Cantabrian Basin, western Pyrenees: linking trace fossil suites and short-term preservation windows. *GSL Special Publications* 522.

<https://doi.org/10.1144/SP522-2021-197>

-Isasmendi, E., Torices, A., Canudo, J. I., Currie, P. J., & Pereda-Suberbiola, X. (2022). Upper Cretaceous European theropod palaeobiodiversity, palaeobiogeography and the intra-Maastrichtian faunal turnover: new contributions from the Iberian fossil site of Laño. *Papers in Palaeontology*, 8(1), e1419.

-Badiola, A., Perales-Gogenola, L., Astibia, H. & Pereda-Suberbiola, X. (2022): A synthesis of Eocene equoids (*Perissodactyla*, *Mammalia*) from the Iberian Peninsula: new signs of endemism, *Historical Biology*. DOI: 10.1080/08912963.2022.2060098

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KIMIKA

QUÍMICA

# Integrative strategies to assess global issues in human and environmental health

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KEY WORDS: environment pollutants, emerging contaminants, xenobiotics, antibiotics, contamination, analytical chemistry, food safety, climate change, aquatic environment, metabolomics, cannabinoids, bioaccumulation, toxicity, wastewater, Alzheimer, microplastics.

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The use of a large number of compounds -some of them pollutants - in our daily life inevitably leads to their release into the human and 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 multidisciplinary 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 human and environmental health analytical issues, and we collaborate actively with many national and European research groups.

Within the framework of the OneHealth concept, we develop high-throughput analytical methods for innovative sample treatments and bioassays, and to validate target and nontarget analytical methods for efficient (bio)monitoring of surface waters and biofluids (plasma, urine, and breast milk). AQUASOMIC project is focused on the assessment of the occurrence of emerging contaminants in surface waters and the strategies to mitigate their effects in drinking water, or on the assessment of exposure to contaminants by analysing biofluids and wastewater. This will allow exposomic studies to shed some light on the impact of environmental contaminants on human and environmental health. AMMONTOX project focuses on the issue of oils spills and aims at exploring the suitability of the Adverse-Outcomes driven Whole-Mixture Toxicity Assessment approach as a better alternative to the commonly used Chemically oriented Mixture Toxicity Assessment that pursues identifying chemicals responsible of the mixture toxicity. PLASTEmer is a project that aims to determine the presence and impact of microplastics (MPs) in the environment and to study the interactions of these materials with other pollutants (metals and organic chemicals pollutants). Given the urgent need to standardise studies on MPs, the main objective of the Elkartek 2021 is to develop a robust technology based on analytical methods to identify MPs in biological tissues, classify them by size and quantify them.

One of society's major concerns is health and IBeA is increasingly active in this area. Elkartek 2022 addresses new avenues in the early detection and classification of Alzheimer's disease, through developments based on spectroscopic and metabolomic methods combined with artificial intelligence. Medicinal use of cannabis is also a new broad research line included among our priorities. Cannabis sativa L is the most widely used illegal drug over world. However, it is known that it can be also used for medicinal purposes to combat problems, such as asthma, cough, insomnia, migraines, and throat infections. The full characterization of the plant's components and the isolation of compounds with medicinal properties is, nowadays, an outstanding research field.

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.

# Studies in Cultural Heritage and Landscape by means of Analytical Chemistry - IBeA Research Group

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KEY WORDS: Cultural Heritage, Landscape, transdisciplinary.

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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. Our research group develops innovative analytical strategies to evaluate the impact of chemical contaminants, microorganisms and the environmental conditions on the Cultural Heritage and Landscape scenarios. The most relevant ongoing projects are:

1. **NanoCult** (Advanced Nano-solutions for consolidation and multifunctional protection in cultural heritage): The main objective of this project is to guarantee the conservation of cultural heritage materials, stone and mural paintings, through innovative diagnostic techniques, the development of non-invasive cleaning methodologies, the formulation of consolidating and protecting products based on nanotechnology and their following application on real cases, innovative processes of solutions.
2. **Demora** (Development of mortar resistant to environmental pollution and biodegradation and of innovative sustainable systems for the cleaning and restoration of Built Heritage): This project tries to solve several problems related to the built heritage, as preparation of cements resistant for restoration or development of non-invasive methods for metals runoff cleaning on Built Heritage among others.
3. **Herculano**: A diagnostic study is being carried out on the degradations of the tuff of the archaeological park of Herculaneum (Italy), and possible materials for its restoration.
4. **Enclosure** (Eco-design of nanocelulose-based solutions for cultural heritage conservation: materials development, validation and life cycle assessment): This project will provide holistic solutions for respectful cultural heritage conservation through the eco-design, testing and validation of environmentally sustainable nature-based materials.
5. **Mars2020 and ExoMars missions**: Official members of Nasa's Mars2020 mission through the SuperCam instrument science group. Part of the team of the future ESA Rosalind Franklin Mission, through the RLS (Raman Laser Spectrometer) instrument; and the national SIGUEMars Network, where meteorites and Martian analogs were characterized.
6. **Analysis of meteorites and analogs**: Thanks to an agreement with NASA (Johnson Space Center), meteorites found in Antarctica for analysis using non-destructive techniques are received. Furthermore, we have an extensive study of the east coast of Bizkaia, as Martian analog.

# What impact has the research of the FARMARTEM group on the society?

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KEY WORDS: health, environmental protection, dating, art heritage,

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The research carried out by the FARMARTEM group tries to give response to the current challenges of our society. In this sense, the group are involved in four research lines: Metabolomics and Drug Analysis, Environmental Analysis, Forensic Analysis and Conservation of Art Heritage. Results of these research lines have an important impact on the health, the environment, the dating and the art heritage.

## HEALTH

- Smart nutraceuticals for the prevention of childhood obesity.
- Antibody drug conjugates (ADCs) as new strategy to fight against cancer.
- Drug dose in paediatric population. Metabolomics as a tool for biomarkers search of organ maturation involved in the drug metabolism.
- Resistance to antifungal drugs.

## ENVIRONMENT

- Dielectric gas mixture of medium voltage electrical distribution cells. Alternative to SF<sub>6</sub> use
- Protein baits applied to control the invasive species *Vespa Velutina* (Asian hornet).
- Monitoring of hydrogen and methane produced by green algae.
- Quality control of waters from drinking water treatment plant.
- UV filters analysis in environmental waters by using low toxicity deep eutectic solvent (DES).

## DATING

- Pen inks and papers dating in questioned documents.
- Acrylic paints dating in contemporary artworks.
- Post-mortem interval of human skeletal remains.

## ART HERITAGE

- Characterization and conservation of contemporary artworks.
- Catalogue of the art heritage of the University of the Basque Country (UPV/EHU).
- Catalogue of Faustino Orbegozo Eizaguirre Foundation artworks.
- Polychromatic coatings on concrete.

Chromatographic techniques coupled to mass spectrometry together with sample treatment procedures such as solid phase microextraction or head-space procedures are being mainly applied for tackling the health and environment challenges. Non-invasive analytical techniques (Visible microspectrophotometry, Raman spectroscopy and Infrared spectroscopy-Attenuated transmission reflectance) are also used especially to face with the dating and the art heritage demands.

# Microfluidics Cluster UPV/EHU

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KEY WORDS: Microfluidics, Lab-on-a-chip, cell culture, surface engineering, sensors and actuators.

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Microfluidics investigates and develops miniature devices which can sense, pump, mix, monitor and control small volumes of fluids. In recent years, the so-called Lab-on-a-Chip concept has gained great importance in the area of microfluidics, due to its diverse applications in the field of research, especially in diagnostics and basic research. It consists in the integration of several laboratory functions in a single device. The dimensions of these devices range from millimeters to a few centimeters and it functions with volumes between microliters and milliliters. In this way, all the functions of a laboratory, such as sample collection, differentiation, transport or analysis, among others, are combined in a small device. Lab-on-a-Chip usually combines microfluidics, sensors and actuators and surface engineering. The principal advantages of Lab-on-a-Chip devices are its low cost, portability, automation and minimal user intervention.

Therefore, the main focus of our group, the Microfluidic Cluster UPV/EHU, is the development of simple to use devices, able to provide accurate analytical measurements of biological systems under controlled microenvironment or chemical measurements at the point of need/care. For this purpose, we combine knowledge of chemistry, physics, biology and engineering to develop devices and platforms for the following applications:

1. **Alginate beads:** hydrogels as biosensors and actuators. They are used as a biosystems for biomarkers detection such as glucose, lactate or cholesterol and as an actuator when they are combined with magnetic nanoparticles.
2. **Ionogel pillar arrays:** pH colorimetric measurements using ionogel micropillars.
3. **Integrated sensors for root plants exudation:** development of paper-based microfluidic devices for the investigation of root exudates and root microinteractions.
4. **Ionogel-based sensors for water analysis at the point-of-need:** development of devices that combine paper microfluidics and ionogels for the detection of nitrite and nitrate in water.
5. **SCADA platform:** generation of single cell arrays for biology studies such as cell adhesion and cytotoxicity measurements.
6. **Functional intelligent electrode:** development of devices which are able to capture and release cells while monitoring their performance in a continuous mode.
7. **Autonomous microfluidics devices:** development of autonomous devices for the sequential addition of samples by integration of a PDMS pump.
8. **Paper-based microfluidics:** development of a paper-based devices for the determination of sexual chromosomes in a sample for forensic analysis.
9. **Glass fiber optics:** measurement and analysis of the concentration of different compounds in an optical fiber device.
10. **CellStudio:** a combination of cell and microspheres patterns for the detection of secreted molecules by fluorescence.
11. **Magnetic manipulation:** handling of substances with a superparamagnetic ring made by ferrofluids.



# Quantum Computing & Quantum Sensing

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KEY WORDS: qubit, quantum algorithms, superconducting circuits, NV-centers, sensing

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The field of quantum technologies has shown immense potential in both computing and sensing. This scientific poster session will be divided into two separate parts to focus on these distinct but promising areas.

The first part of the quantum computing side will explore the fundamental concepts of superposition and entanglement in quantum computing. The concept and physical system of the qubit will also be introduced and compared to its classical counterpart. The poster will highlight the potential of quantum computing through a section called "The bright side of quantum computing" and showcase its ability to accelerate certain tasks. A final section will highlight the ongoing research and investigation of software and hardware problems in the field. This section will address the types of problems currently being investigated, such as information coding and noise correction, as well as highlight different hardware platforms with a focus on superconducting circuits.

The quantum sensing side will be focused on NV centers. The structure of NV centers will be visually presented along with an explanation of its promising potential and key characteristics. The significance of sensing, particularly for medical applications, will also be discussed. Additionally, the protocols utilized to determine physical quantities of interest through these structures will be outlined.

# Advanced spectroscopic and magnetic techniques in molecular and nanoscale research

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KEY WORDS: laser spectroscopy, microwave spectroscopy, ultrafast processes, nanomagnetism, nanostructures, lipidomics, cancer, metabolites, vaccines, nanomedicine, biosensors.

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The Spectroscopy Group works on 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 interaction 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 anesthetic-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 diagnosis, regenerative medicine and neurostimulation.

# Innovative macromolecular materials: new perspectives for new challenges

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KEY WORDS: natural polymers, hydrogels, nanogels, printable materials, surface modification, bioremediation, click chemistry, piezoelectric materials, polymer fibers, polymeric coatings

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LABQUIMAC is a research group of the Physical Chemistry Department of UPV/EHU that carries out investigations in the field of polymeric materials. Founded in the 70s by Luis M. León and currently lead by José Luis Vilas, the group explores the possibilities of macromolecular compounds and their role in material processing for a broad range of applications in an attempt to provide innovative solutions for the challenges of daily life and industry.

The versatility of polymeric compounds allows for a wide variety of possible modifications, morphologies, synthetic routes and manufacture techniques in order to obtain the desired properties for each application. With a heavy focus on natural, renewable and biofriendly materials for a sustainable development, the modern approaches in polymer chemistry respond to the growing concern of society about the use of petroleum derivatives and the environmental impact of some chemical processes.

This poster communication summarizes the main research lines and areas of investigation currently being developed by the LABQUIMAC macromolecular chemistry research group. These include, polymeric coatings from natural oils and resins with improved mechanical and anti-corrosive properties, surface modification and “click-chemistry” based approach for biocompatible materials for biomedicine, polymeric fibers and piezoelectric hydrogels for sensors, polymeric nanoparticles for controlled release and bioremediation, photopolymerizable and self-healable hydrogels, and advanced manufacturing techniques such as 3D bioprinting and electrospinning.

# Device engineering and quantum operations

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KEY WORDS: quantum devices, quantum operations, adiabatic processes, shortcuts to adiabaticity, machine learning.

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Quantum devices are inherently fragile and require precise control for reliable quantum operations. The use of adiabatic processes can mitigate the effects of decoherence, but traditional adiabatic methods can be time-consuming and impractical for large-scale quantum systems.

In recent years, shortcuts to adiabaticity (STA) have emerged as a promising approach to speed up adiabatic processes [1]. STA are fast routes to the final results of slow, adiabatic changes of the controlling parameters of a system. They have become instrumental in designing all kinds of operations and devices for quantum technologies since they help to mitigate decoherence while improving robustness with respect to different perturbations and imperfect driving. Moreover, because they are designed by a set of analytical and numerical methods, they combine well with other concepts and control methods.

However, shortcuts designs may not be optimal and their implementation can be complicated when dealing with complex quantum systems. Therefore, machine learning (ML) can be a good alternative to deal with these problems [2,3]. ML refers to the use of algorithms that can automatically learn from data and improve their performance over time without being explicitly programmed. ML algorithms can be broadly classified into two categories: supervised learning and reinforcement learning and can be seen as optimal STA protocols.

One example of an application where both ML and STA are used is the optimization of quantum gates. Quantum gates are fundamental building blocks for quantum circuits and are used to implement quantum algorithms and protocols. The design of efficient and accurate quantum gates is a key challenge in the development of practical quantum technologies. Another application where both ML and STA are used is in the preparation of highly entangled quantum states. Entangled states are a key resource in quantum information processing and are used for tasks such as quantum teleportation, quantum cryptography, and quantum error correction.

However, preparing highly entangled states is a challenging task, as it requires precise control over the interaction between multiple qubits. STA techniques can be used to speed up the preparation of entangled states by designing fast and accurate protocols that are robust to decoherence and noise in the quantum hardware. ML algorithms can then be used to optimize the control parameters for these protocols, resulting in faster and more accurate entanglement generation. Of course, ML can be also applicable to other scenarios, for instance, atomic cooling in harmonic trap with random noise.

Overall, the combination of ML and STA techniques has the potential to significantly enhance the performance and scalability of quantum technologies, enabling the development of more powerful quantum computers, simulators, and sensors.

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# Molecular tools for tunable photonics of multifunctional dyes and materials

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KEY WORDS: organic dyes, hybrid materials, nanoparticles, fluorescence, photosensitizers, quirkality.

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The staff of the Molecular Spectroscopy group comprises researchers and professors holding advanced skills in molecular spectroscopy and computational chemistry. Our laboratory is equipped with high-resolution techniques, which allow measuring the absorption and emission signatures of these photoactive systems in diverse states (liquid, solid, films) and with time resolution (picoseconds or nanoseconds) along the whole ultraviolet, visible and near infrared region of the electromagnetic spectrum. We apply such dual and complementary experimental-theoretical knowledge and resources in the design, synthesis, characterization and testing of multifunctional dyes and materials with tailored photophysical properties, by means of dye and materials chemistry, for light-driven applications. To accomplish our goals, the research activity is structured in three transversal research lines:

1. **Design and characterization of multifunctional dye as smart probes for diagnosis and photodynamic therapy in bioimaging.** The aim is to take as starting point a chemically versatile molecular scaffold, where, after suitable chemical modifications, we can promote the sought after photophysical processes and recognition properties. That is, rationally design a single molecular probe endowed with fluorescence response, stability, chirality and ability to generate singlet oxygen for targetable and photoactivatable theragnostic performance.
2. **Functionalized nanosystems as drugs carriers for phototherapy and theragnosis.** Nanomaterials, such as nanoparticles, nanocellulose or nanoclays, are appealing for controlled drug delivery in target cells or microorganism. The aim is to use these nanocarriers, chemically functionalized at the surface to improve their stability and biorecognition, to selectively unleash the encapsulated or anchored photoactivatable drugs specifically designed for the bioimaging-guided treatment or cancer of microbial diseases.
3. **Photoactive materials for applied photonics.** Solid-state materials have inherent advantages for practical applications owing to their low size and supramolecular organization. The aim is to design materials suitable for lasers, energy conversion and non-linear optics by the rational selection of host (zeolitic porous materials) and guest (photoactive dyes) or via self-assembly of organic molecules.

The successful achievement of these research scopes requires a multidisciplinary and intensive collaboration with research groups specialized in complementary fields, such as organic (dye synthesis) and inorganic (solid hosts synthesis) chemistry, physics (laser, circularly polarized luminescence and non-linear optics measurements) or biology (bioimaging and cyto- and photo-toxicity assays). Such coordinated work provide us the necessary feedback to improve and redesign the next generation of modern dyes and materials with tailored and improved photonic properties for optics and bioapplications.

# MOF-POM Research Team

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KEY WORDS: MOFs, POMs, MOGs, MOAs, Photocatalysis, CO<sub>2</sub> valorization, Pollutant capture, Sensors, Drug delivery.

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Below you can find an insight into the main lines of our research group, altogether with their applications fields:

**Polyoxometalates (POMs).** Polyoxometalates (POMs) constitute a wide family of anionic clusters formed by oxygen and transition metals from the first groups (mainly V, Mo and W) usually in their highest oxidation states. POMs exhibit great structural diversity, ranging from small and simple species such as dimetalate anions, to large and complex protein-sized clusters. 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 last few years, we have synthesized dual magneto-luminescent compounds, as well as extended systems with catalytic and sorption properties able to respond to the application of a given external stimulus.

**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 applications in catalysis, gas storage, chemical separations, sensing, ion exchange, drug delivery, and optics.

**Supramolecular Metal-Organic Frameworks (SMOFs).** Considering 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 architecture displaying potentially accessible voids. Although such kind 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. We have recently proved the sensing capacity of this new family of materials.

**Metal-organic gels (MOGs) and Metal-organic aerogels (MOAs).** 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 the solvent within. Gel drying by evaporation of the solvent induces a severe shrinkage of the microstructure and leads to materials 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 hundreds of times lighter than MOFs. They have been successfully employed for the electro- and photocatalytic reduction of CO<sub>2</sub> into valuable chemicals.

**Hybrid MOP-POMs.** This new family of materials developed by us consists of cationic discrete metal-organic clusters and anionic polyoxometalates which are combined to provide a chemically and photochemically stable material. The synergistic effect between both discrete entities allows to markedly overpass the photochemical activity of the single ionic components. It is envisaged a fruitful future for this kind of material in photocatalysis.

# Materials and Solid State Chemistry Group: Unravelling Materials for a Better World

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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<sub>2</sub> batteries, electrochemistry.

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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 fluorescent and bio-functionalized polymeric coatings.
- Fabrication of micrometric platforms (microdisks and microspheres) loaded with MNPs, biomolecules and drugs.

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

Our research aims at contributing to the development of innovative electrochemical storage technologies by targeting low-cost and environmentally friendly energy storage systems. Specifically, we explore the potential of three main technologies: lithium/sodium-ion batteries, lithium/sodium-ion hybrid capacitors and lithium/sodium-O<sub>2</sub> batteries that have the ability to meet the energy demand and revolutionize the energy storage industry. Our work focuses on the development of new materials to be integrated 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

# Group of Asymmetric Synthesis, Sustainable Chemistry and Biomimetic Processes

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KEY WORDS: Organocatalysis, Sustainable Chemistry, Green Chemistry, Biomimetic Processes.

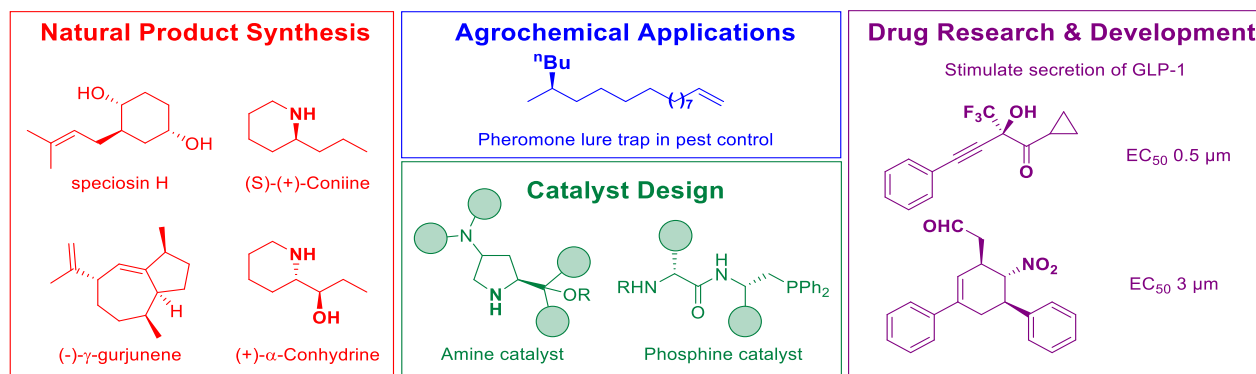
Observing how Mother Nature solves complex problems in an easy way, the human being has been trying to imitate it for many centuries. Thus, the high catalytic efficiency of several enzymes in many natural processes has inspired many researchers to imitate and even improve its action, creating new protein-based biocatalysts, and more recently, using small molecules as simple catalysts. Different types of catalysis exist being the so-called ORGANOCatalysis the one reducing the use of low abundant but expensive metals



In asymmetric synthesis, not only should the catalyst accelerate the reaction but it also should be very stereoselective and flexible, in order to allow its use for the synthesis of different target molecules such as 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. Moreover, catalysis is meant to play an important role in the Sustainable Development GOALS (SDGs).

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 as 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>).



# Development of more sustainable synthetic methods

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KEY WORDS: sustainable chemistry, new catalysts, renewable sources.

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Our research group (NEWSYNMETH) works actively on the development of environmentally more benign synthetic protocols for the access to compounds of interest. In order to achieve this goal, our projects are designed taking into account the following two strategies:

1. The development of efficient chemical processes that minimize the production of by-products, thus promoting catalysis, prioritizing the use of renewable reagents and benign solvents, as well as minimizing the energy cost. Therefore, our research projects focus on:
  - The creation of molecular complexity and diversity from simple substrates through cascade reactions, advantageous processes that avoid several purification steps associated with traditional stepwise synthesis. Energy saving and minimization of waste are also achieved.
  - Catalysis. Our catalytic systems allow us to minimize the amount of catalyst to be used, reaching infinitesimal values in some cases so that reactions become cheaper and purification of the final products is simplified. In addition, the catalytic activity of more abundant and less toxic metals such as iron, nickel, copper, etc. is also explored.
  - Use of safer, non-flammable and more sustainable reaction media. Solventless reactions are also explored.
  - Reducing the energy consumption is also one of our major concerns. In this regard, microwave irradiation often results in better performances and reaction rates.
2. Waste reuse. The massive use of plastics in today's society has turned the prevention, reuse and recycling of waste into key objectives of both the action plan and the waste management legislation. Accordingly, new methods for the "upcycling" of polymer waste based on its degradation and subsequent use as substrate are currently under research.

# Organometallics in Synthesis

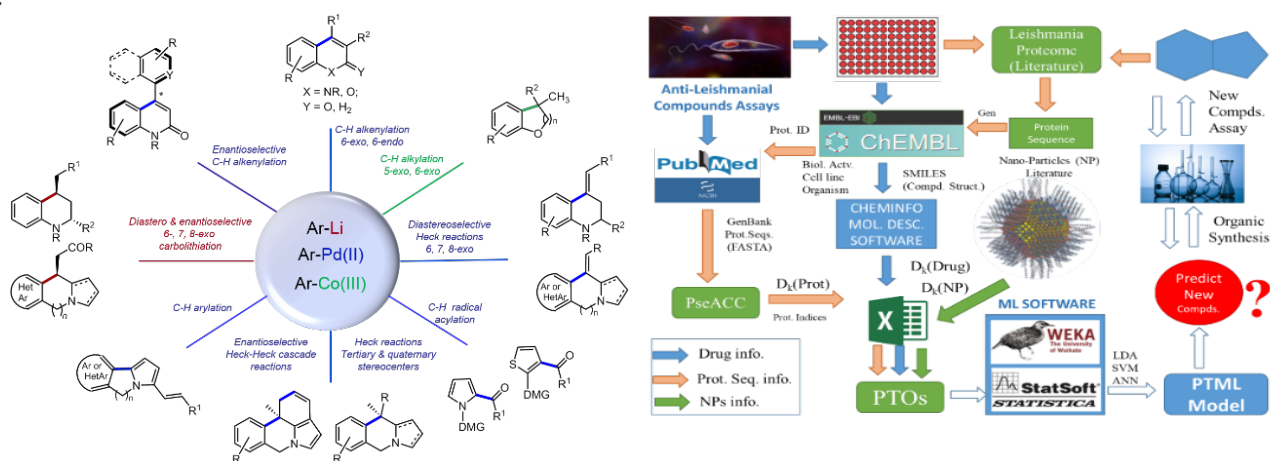
B. Fundora, Y. Velásquez, E. Vásquez, M. Baltasar, S. He, S. Brown, F. Chávez, D. Peñuela, B. Taboada, U. Calderón, E. Sustatxa, I. Barbola, C. Santiago, S. Arrasate, H. González-Díaz, N. Sotomayor, E. Lete  
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KEY WORDS: synthesis, catalysis, chemoinformatics.

The development of innovative synthetic methodology is crucial for the discovery of new active molecules in the pharmaceutical industry. New synthetic methods and reactivity patterns capable of allowing the preparation of complex molecules in a safe and environmentally compatible manner are required. 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. We also carry out interdisciplinary projects that involve computational chemistry and development of Perturbation-Theory Machine Learning Predictive Algorithms (PT-ML) for reactivity prediction and for the design of biologically active molecules to help in the drug-discovery process. Our research interests are summarized in the following topics

**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 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 C-H alkenylation for the generation of axial chirality, as well as C-H radical acylation are also being studied. On the other hand, the use in catalysis of cheaper, earth-abundant and less toxic metals, such as Co(III), offers opportunities for the development of new reactivity and synthetic applications.

**Computational chemistry. Machine learning algorithms for prediction of chemical reactivity and 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, PTML 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 and discovery of more effective and safer drugs



For recent reviews, see: *Trends Chem.* **2022**, *4*, 495; *Catal. Sci. Technol.* **2020**, *10*, 5345; *ACS Omega* **2020**, *5*, 24974; *Molecules* **2020**, *25*, 3247. For some recent publications, see: *Org. Biomol. Chem.* **2022**, *20*, 852; *J. Chem. Inf. Model.* **2022**, *62*, 3928; *Eur. J. Med. Chem.* **2021**, 113458; *J. Org. Chem.* **2020**, *85*, 10261; *J. Org. Chem.* **2020**, *85*, *4*, 2486; *Eur. J. Org. Chem.* **2020**, 4284; *Curr. Top. Med. Chem.* **2020**, *20*, 305

More detailed information can be found in our web page: [www.ehu.es/es/web/oms/home](http://www.ehu.es/es/web/oms/home)



INGENIARITZA  
KIMIKOA

INGENIERÍA  
QUÍMICA

# Environmental sustainability: purification of industrial off-gases and CO<sub>2</sub> capture and conversion to fuels and high-added value chemicals

A. Aranzabal, J.L. Ayastuy, A. Bermejo, Z. Boukha, A. Choya, J.A. De Diego, U. De La Torre, B. De Rivas, D. Gallego, A. Gil, E. Gómez, J.A. González-Marcos, M.P. González-Marcos, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, M.A. Gutiérrez-Ortiz, J. Ibáñez, U. Iriarte, G. Llorente, R. López-Fonseca, J.A. Onrubia-Calvo, G. Penche, B. Pereda-Ayo, A. Reynoso, N. Vera  
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KEY WORDS: environmental catalysis, NSR, SCR, NO<sub>x</sub> removal, CO<sub>2</sub> methanation, P2G

## CATALYTIC TECHNOLOGIES FOR POLLUTANT ABATEMENT FROM AUTOMOBILES AND INDUSTRIAL EFFLUENTS

**Mobile sources.** TQSA does research on two technologies for NO<sub>x</sub> removal from diesel engine exhaust gases: NO<sub>x</sub> storage and reduction (NSR) and selective catalytic reduction (SCR). The NSR technology requires a catalyst combining NO<sub>x</sub> adsorption sites and metallic sites to enhance oxidation and reduction reactions, what is achieved on a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> formulation washcoated over cordierite monolith. On the other hand, the SCR technology feeds continuously a reducing agent (NH<sub>3</sub> or hydrocarbon) which is adsorbed on Cu-zeolite catalyst and subsequently reacts with NO<sub>x</sub> to selectively form N<sub>2</sub>. Both technologies can be combined in two consecutive bed reactors achieving potential zero emission levels of pollutants (CO, HC and NO<sub>x</sub>).

**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 NO<sub>x</sub> (solid wastes incineration plants). Under this frame, TQSA develops: i) Catalysts for individual pollutant removal, such as chlorinated volatile organic compounds, or methane from its own combustion in small engines; ii) Catalysts for simultaneous elimination of dioxins (PCCD)/furanes(F) together with NO<sub>x</sub> from municipal waste incineration plants.

## CO<sub>2</sub> VALORIZATION: OPPORTUNITIES FOR INDUSTRY

**Fuels: valorizing CO<sub>2</sub> in a low-carbon circular consumption approach.** 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 SNG, which is also injected into the mentioned network. Wind, solar or any other renewable energy can be used in the P2G process. At TQSA, we are designing catalysts for the production of methane, methanol, gasoline and kerosene. Recently, we are also interested in valorizing the CO<sub>2</sub> directly captured from the atmosphere.

**Plastics: CO<sub>2</sub> as a substitute for fossil resources.** CO<sub>2</sub> can replace fossil resources as a source of carbon for the production of plastic polymers, in particular polypropylene carbonates (PPC), polycarbonates and polyurethane. The copolymerization of CO<sub>2</sub> and propylene oxide (PO) is especially relevant, since PPCs thus obtained, exhibit excellent biodegradable/biocompatible properties. The catalytic copolymerization of CO<sub>2</sub> and epoxides constitutes a technology that combines numerous economic and environmental advantages. Several catalysts, including Zn-Co double metal cyanide (DMC) and two-dimensional (2D) layered double metal cyanides (Ni-Ni, Co-Ni, Fe-Ni, Mn-Ni) with valuable and advanced structures are developed in TQSA for this technology.

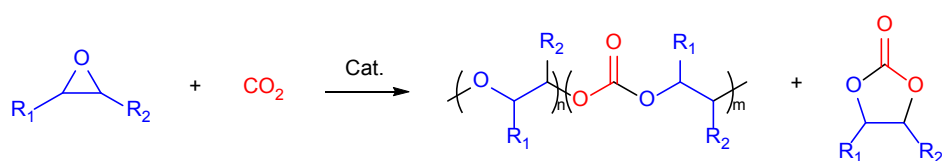


Figure 1. Reaction scheme of the copolymerization of CO<sub>2</sub> and polypropylene oxide (PO).

# Challenges in decarbonising our energy and raw materials supply: valorisation of biogas and biomass-derived wastes

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A. Aranzabal, J.L. Ayastuy, A. Bermejo, Z. Boukha, A. Choya, J.A. De Diego, U. De La Torre, B. De Rivas, D. Gallego, A. Gil, E. Gómez, J.A. González-Marcos, M.P. González-Marcos, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, M.A. Gutiérrez-Ortiz, J. Ibáñez, U. Iriarte, G. Llorente, R. López-Fonseca, J.A. Onrubia, G. Penche, B. Pereda-Ayo, A. Reynoso, N. Vera  
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KEY WORDS: Biomass, waste valorisation, reforming processes, hydrogen production, syngas

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One of the main causes of climate change on the planet is the emission of gases such as CO<sub>2</sub>, derived from the use of fossil fuels for the production of chemicals and energy. For example, the synthesis of polymer materials consume up to roughly 80% of the carbon resources in the chemical industry. The most straightforward option to address the global warning challenge and the transition to circular economy, aiming to Clean Energy Transition and Climate Change, is the use of biomass (organic wastes and biogas) as a raw material, since it is the only sustainable source of organic carbon. Our groups develop two catalytic approaches to accomplish this ambitious goal focused on the decarbonisation of the economy to mitigate the climate challenge.

On one hand, we transform non-edible biomass-derived polyols into high value-added products by partial hydrodeoxygenation (HDO), in aqueous phase. In this reaction, oxygen molecules from the polyol are removed with the use of hydrogen. For this target we use in-situ generated hydrogen by aqueous-phase reforming (APR) of the polyol, which then is used for the HDO. This strategy avoid the use of external hydrogen making the process greener and safer. To convert the biomass-derived feedstock into high value-added fuels and chemicals, its oxygen content must be reduced. This can be achieved by either decarboxylation/decarbonylation reactions or hydrodeoxygenation. Decarboxylation/decarbonylation reactions imply cleavage of C-C bonds, and therefore give a shorter carbon chains (undesirable for fuels and chemicals). HDO is a combination of C-O bond cleavages by H<sub>2</sub> and C-O bond cleavages through the removal of H<sub>2</sub>O. By HDO reaction, selective cleavage of C-O over C-C bonds occurs, and products with the same carbon number of the original feedstock are obtained. In order to favour HDO a proper catalyst should properly balance its hydrogenation/dehydrogenation activity (metal sites) and dehydration function (acid sites). We use three biomass-derived representative platform molecules, glycerol, xylitol and sorbitol, the three included in top-12 building block chemicals that can be upgraded to high value-added products. We start from nickel- or cobalt-based catalysts, which are active for hydrogen production. Doping these base catalysts with other metals (Cu, W, Mo) we can tune both the metal sites and the surface acid properties that can change the obtained products distribution. In addition, the operation conditions such as temperature, pressure or residence time have a notable impact on the selectivity of the process.

On the other hand, we are actively involved in the design of an innovative intensified chemical process for the valorisation of raw biogas (mixture of CO<sub>2</sub>+CH<sub>4</sub>), an increasingly abundant resource from landfills and digestion of organic wastes, into high-quality syngas (CO+H<sub>2</sub>) by combined dry reforming (with controlled amounts of O<sub>2</sub>/H<sub>2</sub>O) over advanced nickel catalysts supported on open cell foams operating under industrially relevant conditions. In the context of development of carbon utilisation technologies for the synthesis of biochemicals and biofuels from syngas as an intermediate, this strategy will significantly contribute for the simultaneous recycling of the two most important greenhouse gases. The obtained results will be valuable for advancing the industrial maturity of this catalytic reforming technology, which is penalised by high energy requirements, limited catalyst durability and the required tuning of the composition of the product stream to be efficiently used for renewable gas-to-liquid processes, and for improving its competitiveness in terms of economic aspects and carbon efficiency. Particularly, we are interested in lowering the reaction temperature while operating with high flow rates of CH<sub>4</sub>-rich streams (CH<sub>4</sub>/CO<sub>2</sub> > 1) by optimising the design of advanced spinel-derived nickel/cobalt foam catalysts; increasing the resistance to coking and poisoning by present bioimpurities; and adjusting the H<sub>2</sub>/CO molar ratio of the product stream. All these aspects are challenging pitfalls that need to be addressed to bridge the gap between lab-scale and pilot plant prototype. In sum, our research activities will open the way to significant breakthroughs resulting in a step ahead towards robust, mature intensified technologies that could play vital role in a low-carbon modern society.

# Reactions and technologies for a circular economy

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*R. Aguado, H. Altzibar, J. Álvarez, S. Álvarez, M. Amutio, M. Arabiourrutia, J.M. Arandes, A. Arregi, M. Artetxe, M.J. Azkoiti, M. Bolaños, I. Crespo, I. Estiati, I. García, A. Gutiérrez, P.K. Mollick, G. López, M. Olazar, S. Orozco, R. Palos, S. Rodríguez, M.J. San José, X. Sukunza, M.A. Suárez, M. Tellabide, J.D. Trueba*  
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KEY WORDS: Waste-refinery, recycling, plastics, hydrogen, fuels, chemicals.

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The excellent properties of plastic materials, such as lightweight, resistance to corrosion, colour, transparency, versatility, or low cost, have led to their massive use worldwide, which is causing serious health and environmental problems due to their short usage time, low biodegradability, and/or the microplastics and nanoplastics generated by their degradation. Over the last few years, around 40% of the waste plastic collected in Europe is recycled, another 40% is used for energy recovery, and around 20% is sent to landfills. Hence, the European Commission established an action plan based on a circular economy, which pursues a transformation from the old linear model to the circular model in which the waste is reintroduced into the production cycle. A specific strategic plan for plastics was set in 2018 with the aim of recycling all plastic packaging by 2030.

The Catalytic Processes and Waste (CPWW) valorization research group focuses on the thermochemical conversion technologies for plastics waste recycling, as they allow for producing fuels and high value added chemicals, and therefore boosting the circular economy by reintroducing these wastes into the production cycle. The research group offers different technological solutions (subject to UPV/EHU patents) that overcome the outstanding difficulties related to the handling, heat transfer, etc. of these wastes from the consumer society. The group addresses plastics valorization with three strategies: i) the recovery of monomers and/or the production of fuels by means of fast pyrolysis; ii) the incorporation of plastics or pyrolysis waxes into refinery units; and iii) the production of H<sub>2</sub> through in line fast pyrolysis and steam catalytic reforming. Moreover, special attention is paid to the design and improvement of the reactors required for these processes.

Most plastics are suitable for the recovery of their monomers and raw materials. High performance is achieved with the fast pyrolysis technology in conical spouted beds. The use of acid catalysts in situ allows for lowering the temperature and selectively directing the production either towards the original monomers (light olefins), around 60% with HZSM-5 based catalyst or gasoline and diesel fuels, up to 80% (60% +20%, respectively) with HY based or spent FCC catalysts. 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 also noteworthy.

Besides, the implication of the oil industry that generates these materials seems necessary for the recycling of such a large number of plastics. The refineries have the means to convert them into fuels and raw materials, and the capacity to commercialize the products complying with the usual quality requirements. The hydrocracking unit is a key component in refineries for the conversion of heavy oil fractions into lower molecular weight streams, at the same time that undesirable molecules are removed, in particular S, N and metals. After subsequent reforming and conditioning stages, hydrocracked streams are suitable for being used in the blending of commercial naphtha and medium distillate pools. The results of the group have shown that this co-feeding leads to the production of a less aromatic and more paraffinic naphtha fraction, an advantage for complying with fuel market requirements. Hence, in the hydrocracking of High Density Polyethylene (HDPE)/Vacuum Gas Oil (VGO) with a Pt-Pd/HY catalyst at 420 °C, we can achieve a conversion of 94% for the VGO and of 79% for the HDPE, with a high naphtha yield, 53%, and low Light Cycle Oil yield, 7%.

The production of H<sub>2</sub> from plastics is studied in pilot plant units with an original technology consisting of two reactors connected inline (conical spouted bed-fluidized bed), leading to a high H<sub>2</sub> production (≈40 wt%) and energy efficiency. The study of the units is subject to continuous innovations in catalysts and reactors. Advanced studies on fluid dynamics are carried out in order to develop design models suitable for scaling up.

The group devotes a great deal of attention to the scaling up of the originally proposed processes by collaborating with spin offs, such as Spouted Bed Solutions. Likewise, society's current interest in recycling supports the collaboration with companies (e.g. Petronor), technology centers (e.g. Gaiker and Ikerlan), and other universities, such as: Ilam, Tehran, Hamedan, (Iran) Clakson (USA), UNAM (Mexico), Sao Carlos, Sao Paulo (Brazil), Hamburg, Stuttgart (Germany), Queen's, Liverpool (UK), Xi'an (China), El Manar (Tunisia), etc.

# Catalytic processes for decarbonization

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A.T. Aguayo, A. Ateka, P.L. Benito, J. Bilbao, P. Comendador, M. Cortazar, G. Elordi, E. Epelde, J. Ereña, E. Fernández, A.G. Gayubo, S. Iglesias, L. Landa, L. Olazar, O. Parra, A. Portillo, A. Remiro, A. Saiz, J.F. Saldarriaga, L. Santamaría, I. Sierra, Z. Tabernilla, J. Valecillos, B. Valle, H. Vicente  
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KEY WORDS: decarbonization, Biorefinery, hydrogen, biomass.

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The global surface temperature has already increased by 1.1 °C since pre-industrial times according to the Intergovernmental Panel on Climate Change (IPCC), and almost every year a new high temperature record is set, leading to disturbing scenarios in the near future. This increase cannot be explained without the human influence and the CO<sub>2</sub> emissions associated with the use of fossil fuels. Hence, we confront a paramount challenge to shift the established uses and habits to a carbon neutral model. Although electrification and the production of electricity via more sustainable ways is the prevalent route, it cannot cover all situations.

The Catalytic Processes and Waste Valorization research group focuses on the sustainable production of fuels and raw materials from non-fossil sources (biomass and its derivatives) and CO<sub>2</sub> to aid the replacement of the current energy model. On the one hand, the valorization of lignocellulosic biomass (which does not interfere with human and animal food chains) to improve the management of forestry and agricultural waste is vital. On the other hand, the carbon dioxide capture and utilization is required to ensure a neutral CO<sub>2</sub> balance.

The production of H<sub>2</sub> via the reforming of biomass derived oxygenates is studied by two routes, direct and indirect. The direct route consists of two stages in line: fast pyrolysis and volatile catalytic reforming. The group has developed technologies for the fast pyrolysis of lignocellulosic biomass, attaining a bio-oil (condensable product) yield above 65 wt%. 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<sub>2</sub> yield that is close to the stoichiometric one. In the indirect route, the steam reforming of the bio-oil produced by fast pyrolysis is carried out, with the additional advantage of avoiding the costly dehydration processes required for the valorization of these oxygenates as fuels and other treatments (hydrodeoxygenation, esterification, etc.) required for its feeding to refinery units (cracking or hydroprocessing). As CO<sub>2</sub> is produced in the steam reforming of biomass derived oxygenates, an alternative combined steam and CO<sub>2</sub> reforming process (CSDR) is analyzed as well in, with the objective of producing a useful syngas (H<sub>2</sub>+ CO) for chemical synthesis (either for the production of fuels or chemicals) and, in addition, as a green and effective method for CO<sub>2</sub> valorization.

Besides, for the replacement of fossil sources by CO<sub>2</sub> as a carbon source to promote the circular carbon economy, the catalytic hydrogenation of CO<sub>2</sub> for the production of liquid fuels and bulk chemicals is also studied. In a first stage, using metallic catalysts typically based on Cu-ZnO, methanol is formed by CO<sub>2</sub> hydrogenation, and subsequently, converted into target chemicals (higher alcohols), building blocks (olefins), and fuels (gasoline, aromatics, etc.) using appropriate acid catalysts in a second stage. Moreover, both stages can be integrated in a single reactor. The direct synthesis of hydrocarbons from CO<sub>2</sub> has several thermodynamic advantages as opposed to the indirect routes (in two stages), and lower capital investment and operating costs are required. Two main routes can be distinguished for the direct conversion of CO<sub>2</sub> into hydrocarbons: 1) In the Modified Fischer Tropsch (MFT) synthesis, CO<sub>2</sub> reacts according to the Anderson-Schulz-Flory (ASF) mechanism using Fe- or Co-based catalysts. The products are *in situ* transformed over a zeo-type providing the adequate acidity and shape selectivity for the selective production of the desired hydrocarbon fraction; 2) In the route with oxygenates (methanol/dimethyl ether (DME)) as intermediates, OX/ZEO (metallic oxide/zeotype) catalysts are employed, in which the metallic oxide is responsible for the formation of the oxygenates, and the zeotype is used for the selective conversion of these into hydrocarbons.

The study of these catalytic processes is part of the Biorefinery R&D platform, and addresses different features: catalyst design and deepening on the reaction mechanism, kinetic modeling, proposals and design of new reactors, and simulation and scaling up of industrial processes. The most outstanding innovation consists of the proposal of membrane reactors to enhance the yield and energy efficiency of the processes. Finally, the collaboration with companies (such as Total Energies) and other universities is also noteworthy, as reflected in the publications: Málaga, UAM, UPV, INCAPE (Argentina), King Abdullah (Saudi Arabia), Western Ontario (Canada), IPPI (Iran), Los Andes (Colombia), and so on.

The background is a light orange gradient. It features several abstract geometric elements: a large, dark orange, rounded shape in the upper right corner; three thin white lines in the upper left quadrant; and two thin white lines in the lower right quadrant.

SGIKER



# Advanced research facilities of the UPV/EHU

## SGIker

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KEY WORDS: Advanced, research, facility.

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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
- 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 first 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.



ABSTRACTS

AHOZKO  
KOMUNIKAZIOAK

COMUNICACIONES  
ORALES



BIOZIENTZIAK

BIOCIENCIAS

# SAGUZARREN DIETA ETA EKOLOGIA: Zer izan hura jan

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*Miren Aldasoro<sup>1</sup>, Joxerra Aihartza<sup>1</sup>, Lander Olasagasti<sup>1</sup>, Nere Vallejo<sup>1</sup>,*  
<sup>1</sup>Jokabide Ekologia eta Eboluzioa Saila, EHU.

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HITZ-GAKOAK: saguzarrak, dieta, ekologia, biologia molekularra.

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Munduan 1400 saguzar espezie daude. Saguzarrak hegan egiteko gaitasuna duten ugaztun bakarrak dira, beraien zentzumen nagusia ekokopapena da eta izaera koloniala dute. Euskal Herrian 26 bat espezie ditugu, eta habitat galera eta beste hainbat arrisku faktorerengatik guztiak legez babestuta daude. Gure espezie guztiak intsektu jaleak dira, eta haien dieta aztertzeak beraien bizimodu eta beharren inguruko informazio asko eman diezaguke. Saguzarren gorotzetan dagoen DNA teknika molekularren bitartez aztertzen dugu, eta horrek zer jan duten esaten digu. Horrekin galdera ezberdinei erantzuna eman diezaiekegu, hala nola, espezieen arteko dieten ezberdintasunak, harrapakin eskuragarritasunaren eta hautespenaren arteko erlazioak, espezie baten dieta denbora eta lekuaren arabera nola aldatzen den, helduen dieta espezializatuak izatera nola iristen diren, edota gizakiontzako kaltegarriak diren izurriteen gainean saguzarrek izan dezaketen eragina.

Esaterako, Euskal Herriko hiru ferra-saguzarren garapena aztertu dugu. Horretarako, hegan hasi berritako saguzarren eta saguzar helduen dietak alderatu ditugu. Kolonietan bertan harrapatutako banakoek datuak eta gorotzak hartu eta gero, lanketa molekularra eta estatistikoa egin ditugu. Hortatik saguzarren garapen eta ikasketa prozesuen inguruko informazioa lortu dugu. Emaitzek erakusten duten arabera, nahiz eta saguzar espezie bakoitzak oso dieta ezberdinak izan, antzeko garapen ereduak erakusten dituzte.

Bestetik, lanketa molekularra beste norantz ere egin daiteke: Guk izurrite espezie konkretu bat analizatu nahi dugu (adb. pinu-beldarra edo "prozesionaria"). Laborategiko protokolo espezifiko bat garatzen dugu lehenengo eta, ondoren, gorotzetan aplikatzen dugu guk aztertu ditugun saguzarrek izurrite hori jan ote duten eta zenbat jan duten jakiteko.

# Testing the effectiveness and toxicity of different antifouling compounds to target and non-target marine species

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KEY WORDS: antifouling paints, biofouling, non-target species.

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Biofouling, known as the unwanted settlement and growth of organisms on wetted surfaces, is one of the major challenges faced by the boating sector, since it can compromise the navigation efficiency and hydrodynamics of boats, while contributing to the introduction and spread of non-indigenous species (NIS). In order to prevent or minimize the development of these communities, antifouling (AF) coatings are commonly applied, being biocide-based (BC) ones the most commonly used coating typology. However, there is some uncertainty regarding their actual effectiveness or their potential indirect environmental impact. Therefore, new commercially available alternatives, such as foul-release (FR) coatings, are emerging. This study aims to test the effects of the two antifouling typologies:

1. From an ecotoxicological approach, exposing selected target and non-target marine species to the coatings and their individual components in a controlled environment;
2. From an ecological approach, testing in field conditions the performance of the selected coatings and analysing the impact on target biofouling communities.

## OVERVIEW OF PRELIMINARY RESULTS

### *Effects on non-target planktonic species (laboratory experiments)*

When exposed to different paint lixiviates at diverse concentrations, the growth patterns of phytoplankton change, evidencing species-specific responses. As regards zooplankton, results from toxicological tests highlight the role of booster biocides in increasing the toxicity of the main active biocide, explaining, at least partially, the high toxicity of the BC coating lixiviate.

### *Effects on target biofouling species (field experiments)*

Significant differences emerged among treatments in terms of total surface coverage, fouling biomass and community structure, as well as significant decrease in BC coatings' efficiency with time. Interestingly, crustacean NIS/native ratio was higher for BC treatment, suggesting biocide resistance.

The integration of the results from both methodological approaches will enable to suggest best practices for boat maintenance and point out priorities for biofouling management.

Work funded by the Basque Government (grant to consolidated research group IT1743-22 and pre-doctoral grant to MS).

# Effects of amphibian loss on periphyton

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KEY WORDS: Common midwife toad, marbled newt, algae

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Amphibians are declining worldwide due to a combination of environmental stressors and infectious diseases. However, despite being one of the most endangered groups, the effects of their loss on ecosystem functioning have been scarcely studied.

In a field experiment in montane streams, we compared the biomass and community structure of primary producers (periphyton) in the presence and absence of common midwife toad tadpoles (*Alytes obstetricans*) and macroinvertebrate larvae (*Allogamus laureatus*). We observed that tadpole presence caused lower periphyton biomass accrual, altered algal community composition, and induced higher macroinvertebrate growth.

In a mesocosm experiment, we studied the effects of amphibian species loss on the ecosystem, simulating the reduction and loss of common midwife toad and marbled newt, two of the species most affected by emergent diseases. The original community, composed of four species, was compared with several scenarios of reduction and loss of common midwife toad and/or marbled newt, thus modifying species composition but maintaining total tadpole abundance. Common midwife toad loss caused a strong reduction in biomass and changed algal community, whereas marbled newt loss presented similar but weaker and not statistically significant effects.

Both studies show the importance of amphibian presence in aquatic ecosystems whose main resource are primary producers, due to the control that amphibian larvae induce on periphyton growth and community composition. Therefore, it is expected that amphibian loss have fundamental consequences on the functioning of these ecosystems.

# Study of the environmental factors effect on the resistance mechanisms and virulence of *Candida auris*

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KEY WORDS: *Candida auris*, environmental factors, Genomics, Proteomics, CRISPR-Cas9.

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*Candida auris* is an emerging pathogenic yeast that was first described in 2009 and that is causing serious problems in global healthcare. In recent years, infections caused by *C. auris* have increased, creating such concern that the CDC (Centers for Disease Control and Prevention, USA) made this species the first fungus to cause a global health alert. Recently, the World Health Organization has published the fungal priority pathogens list, in which *C. auris* is in the Critical Priority Group. To begin with, it presents a significant multidrug resistance to antifungals, with some strains being resistant to all the available antifungals. It is normally misidentified in laboratories, leading to a late detection of cases. In addition, it is related to high mortality rate, which can reach 60 %. Finally, due to its ability to survive on abiotic and biotic surfaces, this fungus often creates outbreaks in hospitals, spreading among patients. This ability has been related to the high resistance that it shows to environmental factors. In fact, it has been proposed that its sudden appearance is due to the increase in temperatures produced by global warming. Consequently, our research group objective is to assess the effect of environmental factors in the resistance mechanisms and virulence of *C. auris*.

The sensitivity of 5 clinical strains of *C. auris* isolated from the Hospital Universitario y Politécnico La Fe (Valencia) was characterized in different stresses, such as cell wall, membrane, osmotic, pH and H<sub>2</sub>O<sub>2</sub> stresses. Although *C. auris* shows more resistance to all those stresses compared to the other *Candida* species tested, *C. albicans* and *C. haemolunii*, the resistance to H<sub>2</sub>O<sub>2</sub> was one of the highest and more interesting, as it could be associated with a higher virulence and ability to evade the host immune response. In consequence, genes that are overexpressed in presence of H<sub>2</sub>O<sub>2</sub> were detected using RT-qPCR at 8, 16 and 24 hours, as well as proteins that are expressed specifically or overexpressed using 2 Dimensional Electrophoresis technique. One of those genes was selected and a knock-out strain was generated using CRISPR-Cas9 technique. In preliminary studies, the deletion strain has shown a lower resistance to H<sub>2</sub>O<sub>2</sub> *in vitro* and lower survival percentage in RAW 264.7 macrophages line, which could be related to the lower resistance to Reactive Oxygen Species (ROS) in the phagosomes.

We are currently studying the virulence of the mutant strain compared to the wild type in *Galleria mellonella* invertebrate animal model. In case that promising results are obtained, we will proceed to test the virulence of the mutant in a murine model.

In conclusion, the study of environmental factors, such as oxidative stress, can help us understanding the resistance mechanism and virulence of *C. auris*, as well as identifying new molecular therapeutic and/or diagnostic targets.

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# Exploring functional features of the gut microbiota to improve chicken broiler health and production

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KEY WORDS: hologenomics, microbiota, chicken.

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Despite poultry being one of the most optimised production systems, a pressing need exists to shift towards a more robust and sustainable agricultural model that enhances production efficiency, decreases the use of antibiotics, and ensures animal welfare. Understanding the functional dynamics of host-associated microbial communities is essential for developing more sustainable microbe-based solutions. We applied multi-omics to 610 broiler chicken caecal samples to characterise and model the functional dynamics of 825 caecal bacteria. We then studied the link between microbial functional attributes and host body weight in chickens with a regular gut microbiota and chickens with *Campylobacter* infection. Chickens with a regular gut microbiota revealed higher microbial community diversity metrics with chicken age, but the overall metabolic capacity and activity of the microbiota exhibited an unexpected decrease. The intensity of this decrease was associated with animal growth, whereby chickens with higher abundances of low-capacity bacteria exhibited higher body weights. Chickens with *Campylobacter* infection diverged from non-infected chickens early in the experiment, presenting a microbial community dominated by members of the Bacteroidota phylum. The Bacteroidota-dominated microbiota had a higher metabolic capacity than the regular microbiota, and this increase could explain the loss of chicken body weight seen at the end of the experiment, as there was no evidence of host energy expenditure in an immune response. This previously unreported link between metabolic capacity of microbes and animal body weight opens new avenues in the search for microbe-based solutions to improve sustainability of animal production.



# Proximity proteomics as a strategy for studying interactors of the E2F7 transcription factor

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KEY WORDS: Cancer, Cell Cycle, Proximity Biotinylation, Proteomics.

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E2F transcription factors (E2F1-8) play a key role in the regulation of cell cycle progression and cell fate, and their dysregulation can result in several pathologies, including cancer and autoimmune diseases. For some E2Fs (E2F1-6) the mechanism by which they regulate their target genes has been thoroughly studied. By contrast, E2F7-8 have been investigated less extensively, and little is known on the protein networks that cooperate with these E2F factors to regulate transcriptional activity. In our lab, we have developed a proximity biotinylation-based proteomics approach using the TurboID biotin ligase in order to study the proteins with which E2F7 interacts to achieve its transcriptional function. With this aim, we generated stable cell lines that express TurboID-E2F7 in response to the addition of doxycycline. Our data confirm that TurboID-E2F7 localizes mainly in the nucleus, similarly to the wild-type E2F7. Importantly, mass spectrometry analysis of the biotinylated proteins identified both known and novel E2F7 interactors. Our data reveal that the TurboID system is a powerful approach for analyzing E2F7-dependent protein interactions and for studying mechanisms of cell cycle-dependent transcriptional regulation.

# P. aeruginosa patogenoaren efektoreen ikerketa: biofisika eta biologia estrukturala

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KEY WORDS: *P. aeruginosa* · T6SS · bakterio-efektorea · Tse5 biofisika · biologia estrukturala

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Gaixotasun kutsakorren artean munduan heriotza gehien eragiten dutenak arnasbideetako infekzioak dira eta horren adibide izan daiteke SARS-CoV-2 birusa. Hala ere, badira gizakiak kaltetzen dituzten beste patogeno batzuk ere: *Pseudomonas aeruginosa* bakterioak, esaterako, pneumonia eragiten du. Bakterio honek ostalaria infektatzeko T6SS (*Type VI Secretion System*) xiringa formako jariapen-sistemaren jariapen bidez burutzen du. T6SS jariapen-sistemak efektoreak (toxinak) zelula ostalariaren zitoplasman injektatzen ditu zuzenean. Efektore hauen artean funtzio anitzeko proteinak aurkitzen dira: mintzeko lipidoak degradatzetik hasi eta proteinen sintesia inhibitzen duten entzimetaraino. Azken urteotan gure taldeak Tse5 (*Type VI secretion system exported effector 5*) efektorearen gainean ikerketa zentratu du. Tse5 efektorea 2014. urtean aurkitu zen, baina bere funtzio biologikoa eta itu zelularra ezagutu gabe gelditu zen. Biofisika Institutua diziplina anitzeko zentro bat da, teknika biofisikoak eta biologia estrukturalako teknikak aplikatzeko tresnak eta langileak dituena. Horri esker, azken urteotan Tse5 efektorearen domeinu toxikoa, C-muturrean kokatzen dena (Tse5-CT), zelula ostariaren mintzean txertatzeko eta ioiak garraiatzeko poroak sortzen duela bermatu dugu.

# Co-translational folding and calmodulin

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KEY WORDS: co-translational folding, calmodulin, potassium channel Kv7.2.

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Several diseases, such as Alzheimer and Parkinson, are related to protein co-translational miss-folding. While in vivo folding is a vectorial process, due to technical limitations it has been traditionally analyzed following in vitro unfolding and refolding approaches, in which interactions with more residues occur, changing the available folding pathways. Thus, little is known about co-translational folding of ion channels and other proteins. In a previous report, we found that an epilepsy-causing mutation located in the calmodulin (CaM) binding IQ motif of the neuronal voltage-gated Kv7.2 channel, affected co-translational folding of Calcium Responsive Domain (CRD) of this channel. This domain, is located intracellularly and binds CaM, the most important calcium modulator in eukaryotic cells. Although it is known that CaM presents different roles in complex with Kv7.2, such as, calcium signaling and traffic through the membrane, this is the first time where CaM has been suggested to affect also co-translational folding. Herein, we present a Force Profile Analysis (FPA) of the Kv7.2 CRD. By using an arresting peptide (AP) that interrupts protein synthesis at the ribosomal tunnel, it is possible to detect forces exerted during co-translational folding because they may lead to synthesis restoration and production of the full-length protein. To test the effect of CaM in CDR folding, we have employed a reporter consisting of Kv7.2 CRD fused to SecM AP flanked by two fluorophores of different color. By changing the length of the CDR-AP linker, the relative emission of constructs with two fluorophores (i.e. full length) to that of truncated proteins with one fluorophore (i.e. arrested at the ribosome) was readily quantified. The proteins were produced in bacteria (that do not produce CaM) in both control condition or after co-expressing CaM. The fraction of full-length protein dramatically increased at certain regions of the CRD profile when CaM was co-expressed. Three such regions were identified, that appeared to correspond to the exit from the ribosomal tunnel of the three CRD helices (A, TW and B), consistent with the hypothesis that CaM plays a role in co-translational folding of the Kv7.2 CRD.

# Metagenomic analysis of pulmonary microbiome in Cystic Fibrosis patients

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KEY WORDS: Cystic Fibrosis, metagenomics, Nanopore Sequencing

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It is estimated that in the Basque Country approximately 1 in 3,500 births suffer from Cystic Fibrosis (CF). This is an autosomal recessive inherited disease which is considered the most frequent and severe rare disease in Caucasian, and which causes early death (life expectancy estimated at about 50 years). The defective gene is the Cystic Fibrosis Transmembrane Conductance Regulator (CFTR). The main cause of morbidity and mortality in CF is lung disease, due to very thick secretions that obstruct the bronchi, and favor bronchial infection and inflammation. This infection leads to chronic respiratory insufficiency and respiratory failure, resulting in the need for lung transplantation, or even death of the patient.

Our working hypothesis and motivations are that improved detection of infections in people with CF, and the development of personalized treatments against these infections will improve and extend the lives of people with CF. To this end, the aim of this work is to perform a targeted metagenomic analysis of CF patient's microbiome by next generation sequencing (Oxford Nanopore). Here, we show that the microbiome analysis allows to identify pathogens that are not detected by traditional clinical microbiology, providing better quantification, and early diagnosis.

# Analysis of intragenomic 16S and 23S rRNA gene variability to improve differentiation of *Vibrio* species

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KEY WORDS: ribosomal operon, phylogenetic marker, *Vibrio* spp.

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## BACKGROUND AND AIM

The growing incidence of *Vibrio*-associated diseases, presumably the result of climate-driven increases in surface water temperature, suggests the need to regularly monitor assemblage composition and abundance of marine *Vibrio* pathogens. Although the 16S rRNA gene is frequently used as a phylogenetic marker in analysis of microbial diversity in marine and aquatic systems, in analysis of environmental DNA this marker often fails to reveal closely related species, including those in *Vibrio*. Here, we investigate whether inclusion and analysis of 23S rRNA sequence can help overcome the intrinsic weaknesses of 16S rRNA analyses for the differentiation of *Vibrio* species.

## MATERIALS AND METHODS

We created a data repository of ribosomal operon genes by retrieving all copies of 16S rRNA and 23S rRNA sequences from 40 fully-sequenced *Vibrio* genomes. After sequence alignment with MAFFT (Version 7.490), we corrected sequence length variation that arose from errors in annotation, and manually trimmed some aligned sequences in MEGA-X to produce an alignment with uniform 5'- and 3' extremities. This alignment was used for phylogeny estimation with IQTREE (Version 2.1.3).

## RESULTS AND CONCLUSIONS

First, we construct a maximum likelihood 16S rRNA gene tree using all available operons to assess the use of this gene to identify clades of *Vibrio* species. Within the 16S rRNA tree, we identify informative bases responsible for polyphyly, and demonstrate the role of these positions in determining tree topology. We demonstrate that concatenation of 16S and 23S rRNA genes increases the number of informative nucleotide positions, thereby overcoming ambiguities in 16S rRNA-based phylogenetic reconstructions and improving the differentiation of *Vibrio* species. These findings highlight alternative approaches that considerably advance the differentiation of *Vibrio* species, and facilitate species identification in environmental samples.



FISIKA ETA  
INGENIARITZA  
ELEKTRONIKOA

FÍSICA E  
INGENIERÍA  
ELECTRÓNICA

# Simulating the early universe: axion inflation

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KEY WORDS: Early Universe, Cosmological Simulations, Axion Inflation.

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The early universe is an exciting period in the history and evolution of the universe. However, due to the severe physical conditions of that time, it is very difficult to perform experiments that try to mimic the peculiarities of that epoch. That is why in our group, we specialize in performing computational simulations, which provide us with relevant information to better understand the physics that happened at that time in the universe. One of the phenomena that we analyze is the cosmological inflation, which describes the accelerated expansion that the universe underwent in its first moments of existence. More specifically, we are currently studying an inflationary model called axion inflation, whose interest lies in the rich phenomenology to which it gives rise: primordial black holes and gravitational waves. In this short talk, I will try to bring computational cosmology closer to the audience, and in particular to explain in an informative way the details of how we study the axion inflation model.

# Gravitation and quantum mechanics: quantum BKL conjecture

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*Sara Fernández Uria*

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The Belinski-Khalatnikov-Lifshitz conjecture (1970) postulates that singularities are inherent phenomena of general relativity, and, in particular, describes how the spacetime behaves close to a generic spacelike singularity: the dynamics is oscillatory, local, and chaotic. Although a formal proof is not yet available, it is supported by many numerical studies. However, it is developed in a purely classical framework, and close to the singularity, quantum effects must be considered; thus, it cannot be complete. Therefore, if done correctly, its quantum version can be a very convenient starting point to try to quantize general relativity, since it predicts a simplification of the general dynamics near these regions—where quantum effects become relevant—. That is, a quantum BKL conjecture may give some clues on how to combine gravitation and quantum mechanics.



# How Computational Methods Unveil the Complexities of Strong Electron Correlation and Relativistic Effects in Condensed Matter Systems

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KEY WORDS: strong correlation, Kondo effect, Numerical Renormalization Group, relativistic effects, electron-phonon interaction, spin-phonon interaction, Rashba model

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The physical properties of materials arising from many-body interactions are the main research subject of the computational condensed matter physics group. In particular, we work on problems where electrons, vibrations (phonons) and magnetism (spins) are coupled. Computational methods permit us to simulate condensed matter systems and to understand the properties that arise from many-body interactions. As a starting point, we use Density Functional Theory (DFT) [1] to compute the electronic structure of solids; this provides an accurate description of many of their properties. On top of DFT, we introduce new methodological developments to tackle different scenarios of many-body interactions such as strongly correlated systems and relativistic effects.

In metallic systems with magnetic impurities, the electrostatic repulsion between electrons favors the formation of localized magnetic moments. These magnetic moments are screened by the conduction electrons at low temperature, leading to what is known as the Kondo effect [2]. K.G. Wilson and co-workers developed the Numerical Renormalization Group (NRG) technique, which provided the first rigorous, non-perturbative calculation of the low-temperature screened ground state [3]. One of our lines of research focuses on the implementation of discrete point-group symmetries in the NRG procedure, which allows us to perform calculations for complex systems of impurities in crystalline environments.

We are also interested in relativistic effects arising from spin-orbit coupling. Particularly, we focus on the interplay between spin and lattice vibrations (spin-phonon coupling), and we aim to investigate the magnetic properties of adsorbed atoms (adatoms). Here, phonons are believed to be relevant to the stability of the magnetic moment of the adatoms [4], but it is unclear how the whole mechanism works, and hence further research is needed. To that end, we work with a simple model of the spin-orbit interaction and we simulate the impurity with time-periodic potential. For an efficient calculation of the time evolution, we are developing a new technique based on Green's functions and Floquet theory.

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# Experimental research on the thermo-optical behaviour of materials: emissometry, thermography and spectroscopy

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KEY WORDS: infrared emissometry, thermography, spectroscopy.

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Experimental research on the thermo-optical behaviour of materials involves studying the interaction between electromagnetic radiation, matter and heat. Since its foundation, the Group of Thermophysical Properties of Materials (GPTM), of the University of the Basque Country (UPV/EHU), has studied the aforementioned properties from a theoretical and experimental point of view; and has also worked with industrial partners to implement specific solutions based on experimental results or simulations. Nowadays, infrared emissometry, thermography and spectroscopy are three of the main research lines developed by the Group.

Regarding infrared emissivity, it is a property that determines the capacity of the surface of a body to emit thermal radiation. It changes with the temperature of the body, and depends on the wavelength and on the direction in which the surface is observed. Quantitatively, it is defined as the ratio of the radiance emitted by the surface to the radiation of a perfect emitter, a black body that follows Stefan-Boltzmann law. Thus, it varies from 0 to 1. The HAIRL emissometer was designed and build, at the UPV/EHU, by former members of the GPTM in order to perform direct emissivity measurements. The instrument is an international reference that can measure high accuracy directional and spectral emissivity in the mid-infrared range under controlled atmospheric conditions, and in a wide range of temperatures (from 373 K to 1273 K). The emissometer has been used to study materials with high scientific and industrial interest: from pure metals to aeronautical and high-entropy alloys, multilayer and patterned surfaces for concentrated solar power systems, and ceramic materials for high-temperature applications.

Apart from those use cases, infrared thermography also relies on precise emissivity data in order to estimate the temperature of a surface. That kind of techniques are widely used in industrial applications to monitor and even to control processes such as additive manufacturing or metallurgical processes, where temperature can only be measured by means of non-contact procedures. The Group can provide accurate spectral and directional data, as well as integrated values, like total directional or hemispherical emissivities, which are crucial for the proper calibration of thermal imaging cameras.

Finally, infrared spectroscopy is one of the most common and widespread spectroscopic techniques, and it is used to study the interaction between the electromagnetic radiation and matter, by means of reflectivity, absorptivity and transmittance experiments. It is usually applied to identify functional groups and chemical substances in solids, liquids and gases. However, in our case, we use infrared spectroscopy to study the effect on the optical properties of the nanoscale morphology and the structure of heterogeneous materials, in order to tailor their optical behaviour by altering the nanostructure.

# New generation of Shape Memory and High-Entropy Alloys developed by Additive Manufacturing

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KEY WORDS: Shape Memory Alloys, High Entropy Alloys, Additive Manufacturing, Electron Microscopy, Superelasticity.

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Materials science opens the third millennium with the challenges of two new paradigms: The breaking conception of the new metallic alloys called High Entropy Alloys (HEA) and the new emerging technologies of materials processing by Additive Manufacturing (AM).

High Entropy alloys are a combination of five or more principal elements in equal (or nearly) proportions. This new approach of alloying brings with it a radical departure from the usual alloys, developed up to now, based on a main element. Furthermore, HEA exhibit properties exceeding those of conventional alloys, such as superior ductility and fracture toughness at cryogenic temperatures.

Additive manufacturing is a production technique which consists of adding material layer upon layer, based on a computer aided design; previously atomized metallic powders are melted by a laser or electron beam, and then added to the growing sample in order to produce complex 3D components. Due to its versatility, AM use has reached several sectors including aerospace, automotive industry, civil engineering, etc.

## ADVANCED SHAPE MEMORY MATERIALS

In addition, the main activity of our Research Group is focused on Shape Memory Alloys (SMA) and at present we are affording the following challenges: (1) To develop new HEA with shape memory and superelastic properties, (2) produce both SMA and HEA by Additive Manufacturing and (3) improving and optimizing the mechanical properties of SMA and HEA not only at macro scale but even at micro and nano scale.

To approach these objectives we are collaborating with International Excellence Research Centres as well as with several Technologic Centres from the CAV, such as CEIT, TEKNIKER and LORTEK.

Our research activity covers all aspects of the Materials Science, starting from the production of the alloys, followed by a powerful characterization of the microstructure. Then the phase transformations and the control of the microstructure are studied to master the physical and mechanical properties, particularly the functional properties of shape memory and superelasticity. This is being possible thanks to the scientific expertise of the Research Group on Physical Metallurgy and the involvement of many advanced experimental techniques covering, among other, the following aspects:

- Design and production of SMA and HEA by induction melting and growing of single crystals.
- Atomization, HIP and hot rolling in collaboration with the technologic centre CEIT and the CENIM.
- Additive Manufacturing, in collaboration with the technologic centres TEKNIKER y LORTEK.
- Scanning and Transmission electron microscopy down to the atomic resolution and with in-situ tests.
- Internal Friction and Mechanical Spectroscopy for studying the atomic defects mobility.
- Differential scanning calorimetry and electrical resistivity to study the phase transformations.
- Mechanical properties characterization from macro to nano scale through nano-compression.
- Computer assisted design, properties analysis and simulation of the material behaviour.

Along this talk, an overview of the last achievements obtained on the described topics will be shortly presented, with particular emphasis on the new challenges that are being afforded in the present projects.

# Using Quantum Computers to Study the Subatomic World

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KEY WORDS: Quantum Simulation, Lattice gauge theories, Quantum algorithms

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Quantum computers are presented to the general public as tools which can be used to solve certain computational tasks while requiring an exponentially lower amount of resources compared to their classical counterpart. While this is certainly the main motivation supporting the development of quantum computers, too much focus is often put over the advantage that these devices provide for very mathematically oriented tasks, such that factorization of primes, database search or optimization problems. However, the best suited tasks for quantum computers are those concerning the simulation of quantum mechanical phenomena. Quantum computers offer an exponential advantage in memory when it comes to store quantum states and, in many cases, the dynamical evolution of the system to be simulated can be realized in a very natural way. Additionally, since we are always interested in the expectation value of observables when simulating quantum systems, the presence of noise is less detrimental than in other applications. Because these are quantities obtained by taking the average after many simulations and measurements. The research in our group is focused on this direction. We are developing algorithms that take advantage of the qualities of quantum computers in order to simulate gauge theories. Gauge theories are the mathematical formalism used in the description of many relevant phenomena in modern physics, the most famous example being the Standard Model. Solving these models is not a trivial task at all, neither analytically nor numerically. Using quantum computers for this task could help scientists to gain new insights about the most fundamental aspects of modern physics.

# Quantum Computing (Talk)

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KEY WORDS: qubit, quantum algorithms

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The main objective of this talk is to introduce quantum computing to students. For this purpose, the most basic and important concepts such as qubit, entanglement and superposition will be briefly introduced. It will be explained why these elements are able to generate a computing paradigm that can overcome the classical paradigm known so far. The explanation of these concepts will serve to motivate the need for research in this field. Finally, some of the problems that must be addressed for quantum computing to become a reality in industry and not just a utopia will be presented. Noise, decoherence, the problem of information loading and the need to design implementable algorithms, among others, will be discussed.

# Applications of Artificial Intelligence: dialogue modelling, ride comfort in autonomous vehicles, and emotion recognition

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KEY WORDS: machine learning, dialogue modelling, autonomous vehicles, emotion recognition.

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Artificial intelligence (AI) and machine learning (ML) are powerful tools that are increasingly being used in various fields of science and technology. In this presentation, we analyze three specific applications of these models: dialogue systems, detection of motion sickness in autonomous cars, and emotion recognition.

Regarding dialogue systems, their usefulness in virtual assistance, and improving human-machine interaction is highlighted. We describe some of the applications of dialogue systems and discuss future research lines. More specifically, we explore the impact of Virtual Coaching in elderly and how it might help to improve their healthy life years. Also, several machine learning methodologies such as Generative Adversarial Networks, Transfer Learning, Modular Systems and Reinforcement learning are compared depending on the use-case.

Autonomous vehicles represent the leading change in research in the automotive industry, with many Advanced Driving Assistance Systems (ADAS) being developed accordingly. With drivers becoming mere passengers, factors like ride comfort gain importance. Acquiring car signals that can be processed into comfort and motion sickness measurements by using signal filters and data augmentation algorithms is key to objectively assess ride comfort. Clustering algorithms allow the comparison of driving styles and driver performance. Moreover, the use of Neural Networks and tree-based algorithms like XGBoost can be used as Regression tools to help validate the obtained results. By studying the influence of different road types, drivers and cars we can assess the different origins of motion sickness and obtain methods to reduce it.

Finally, we address the topic of emotion recognition through AI and ML models. Emotion recognition is a very subjective and therefore challenging research area. Text- and speech-based models are introduced. Text-based emotion recognition can be approached in many ways. For instance, key word dictionaries can be helpful, but also end-to-end methodologies such as pretrained transformers can be employed to obtain state-of-the-art results. Similarly, emotions can be detected from speech using ad hock features such as the pitch or the speech rate, or using end-to-end audio processing transformer neural networks.

# Research on Magnetism and Magnetic Materials at the UPV/EHU

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KEY WORDS: magnetic materials, magnetic sensors, magnetotactic bacteria, microfluidics, magnetostriction.

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Magnetic materials have been investigated for centuries due to their unique properties, that allow them to be used in countless applications, such as motors, generators, sensors, and data storage devices, among others. The Magnetism and Magnetic Materials Group (GMMM) focuses on the study and development of new magnetic materials and their applicability in different fields. Nowadays we are working on two main topics: Magnetic materials for biomedical applications and Magnetoelastic sensors.

## **MAGNETIC MATERIALS FOR BIOMEDICAL APPLICATIONS**

A promising candidate for their use in biomedical applications are magnetotactic bacteria, aquatic microorganisms able to align and navigate along geomagnetic field lines thanks to the presence of a chain of single-domain magnetic nanoparticles. To develop this ability, magnetotactic bacteria biomineralize magnetic nanoparticles, which have genetically controlled sizes and shapes and are surrounded by a biocompatible membrane, making them ideal for biomedical applications. Due to their characteristics, such as self-propulsion by flagellas, magnetotaxis, aerotaxis, and their capability to grow and proliferate in hypoxic regions, these microorganisms show a potential use in biomedical applications as nanobiorobots for localized hyperthermia or drug delivery, for example.

To fully exploit the potential of these bacteria, we also study their movement under applied external magnetic fields by guiding them through different microfluidic devices. In order to quantify their concentration and/or provide feedback for their guidance, we are developing magnetic sensors (based on the magnetoresistance effect) integrated in the microfluidic channels to detect the presence and movement of the bacteria. The fabrication of these sensors requires techniques such as thin-film deposition, photolithography and soft lithography. Various simulation tools are used to create models and optimize the performance of the devices before their fabrication.

## **MAGNETOELASTIC SENSORS**

Magnetoelastic sensors are made of amorphous ferromagnetic alloys, usually in the shape of ribbons. In these materials the property called magnetostriction provides a strong coupling between their magnetic and mechanical properties, so that they can be mechanically excited by the application of alternating magnetic fields and vice versa. They can be driven to resonance, and this resonant behaviour is highly sensitive to changes on different external factors, which has been used to develop several sensor applications.

In particular, we focus on their performance and applicability as mass sensors. In this research line we study the sensor performance and different approaches to improve their sensitivity, as well as their functionalization with other materials to design specific sensing applications. The applications developed include the use of these sensors to follow the evolution of precipitation reactions and to detect the presence of different gases like CO<sub>2</sub> and H<sub>2</sub>O.

# Basic concepts on particle accelerators and microphonies control

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KEY WORDS: Particle accelerators, Automatic control, microphonies.

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The main purpose of this talk is to explain in a simple way the basic concepts for the acceleration of charged particles in particle accelerators, as well as to make known the work we are carrying out in the field of microphonies control.

In this way, through this divulgative work, we intend to make more accessible to the non-scientific public the knowledge about these machines that are undoubtedly a scientific milestone of humanity. First of all, a brief explanation of the uses and importance of particle accelerators in today's society is given. Then, the theoretical basis for understanding the operation of these machines is presented, explaining basic concepts such as Lorentz forces and resonances. Finally, special emphasis is placed on the so-called resonant cavities, which are the devices in which particles are accelerated.

Our work deals with a current problem suffered by superconducting radio frequency cavities (SRF) called microphonic detuning [1]. This detuning derives from mechanical perturbations suffered by the cavity and results in the loss of efficiency in transferring energy to the particles. This type of perturbation is especially problematic in the last generation of linear accelerators (Linacs), since the cavities are operated with a very high loaded quality factor (QL). This allows them to reach extremely high acceleration gradients, but at the same time makes them very sensitive to mechanical perturbations [2].

The basic principles of microphonies control are also mentioned and our proposed solution (Modified Active Disturbance Rejection Algorithm or MADRC [3]) is briefly described. This is a control algorithm that provides excellent disturbance suppression, but suffers greatly from delay. Our work is based on modifying this algorithm in order to make it more resistant to delay without compromising too much the disturbance suppression.

Lastly, the results obtained by implementing our controller on a real SRF cavity on the HobiCat test bench of the Helmholtz-Zentrum Berlin (HZB) are presented.

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MATEMATIKA

MATEMÁTICAS

# New advances in the development of prediction models for complex survey data

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KEY WORDS: prediction models, complex survey data, sampling weights.

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Complex survey data are becoming increasingly relevant among researchers in different fields, such as social and health sciences among others, which have to deal with this type of data on a daily basis. Complex survey data are data collected by sampling the finite population of interest for the survey, by means of some complex sampling design, which may include techniques such as stratification and/or clustering in different stages of the sampling scheme. One of the particularities of complex survey data is the sampling weights, which 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 and needs to be checked before any implementation.

In particular, complex survey data are commonly used to develop prediction models. The aim of this doctoral thesis focuses on logistic regression models for binary outcomes. Specifically, our goal is to analyze the impact of complex designs throughout the process of development of these models and to make new proposals when necessary. The aim of the talk is to summarize the advances we have achieved so far.

One of the most discussed topics in this area is the estimation of logistic regression model parameters. In the context of logistic regression models for dichotomous response variables, in particular, the pseudo-likelihood function 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, researchers are still debating whether it is indeed necessary to take sampling weights into account when estimating parameters. 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. The results suggest the convenience of considering sampling weights for this purpose (Iparragirre et al., 2023).

Nevertheless, in addition to the estimation of model parameters, model and variable selection is another aspect that should be taken into account in the development of prediction models in order to end up with a valid model. LASSO regression models are one of the most commonly used methods for this purpose for which cross-validation is the most widely applied validation technique to choose the tuning parameter. We propose a new design-based cross-validation method which considers complex sampling designs. The results of the simulation study that has been conducted suggest a considerable improvement when the new proposal design-based cross-validation is used instead of the traditional cross-validation.

Finally, before implementing logistic regression models in practice, we need to analyze their ability to discriminate between individuals with and without the event of interest. The discrimination ability of logistic regression models is usually analyzed by means of the receiver operating characteristic (ROC) curve and the area under the curve (AUC). For this reason, we propose new estimators for the ROC curve and AUC that consider sampling weights in order to obtain unbiased estimates. Along the same line, we also propose new optimal cut-off points' estimators for the optimal classification of individuals as units with and without the event of interest (Iparragirre et al., 2022).

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# Cohomological uniqueness of finite groups

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KEY WORDS: group, cohomology.

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Given a finite group, we can define its cohomology groups. Group cohomology provides a framework to analyse intrinsic algebraic properties of a given group or to study automorphisms of groups, and it also has applications in algebra and number theory.

It is natural to ask how well the structure of a group is encoded in its cohomology, and whether the cohomology is unique when restricting to certain families of groups. Nevertheless, computing cohomology is extremely complicated and thus, there are few examples in the literature.

In this talk, we will introduce the concept of group cohomology and study some easy examples.

# Numerical methods for fractional calculus

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KEY WORDS: hypergeometric function, pseudo-spectral method, fractional Laplacian

At the moment, we develop a fast and spectrally accurate pseudo-spectral method to approximate numerically the fractional Laplacian  $(-\Delta)^{\alpha/2}$  on  $\mathbb{R}$ . More precisely, the change of variable  $x = L \cot(s)$ , with  $L > 0$  and  $s \in (0, \pi)$ , we allow us to map  $\mathbb{R}$  into a finite interval where spectral or pseudo-spectral methods might be performed. Indeed, we have obtained the following representation for the fractional Laplacian with  $\alpha = 1$  in this new variable applied to elementary trigonometric functions:

$$\begin{aligned} (-\Delta)_x^{1/2} e^{ik \cot^{-1}(x/L)} &= (-\Delta)_s^{1/2} e^{iks} = \frac{-2i}{L\pi(k+2)} - \frac{k}{L} \sin^2(s) e^{iks} + \frac{8i}{L\pi(4-k^2)} {}_2F_1 \left[ 1, -\frac{k}{2} - 1; -\frac{k}{2} + 2; e^{i2s} \right] \\ &= \frac{-2i}{L\pi(k+2)} - \frac{2ik}{L\pi} e^{iks} \left( \cos(s) + \sin^2(s) \ln \left( \cot \left( \frac{s}{2} \right) \right) + \sum_{n=0}^{\frac{k-1}{2}} \frac{4e^{-i(2n+1)s}}{(2n-1)(2n+1)(2n+3)} \right), \end{aligned}$$

for an odd negative number  $k$ . Using the fact that  $(-\Delta)_s^{1/2} e^{iks} = \overline{(-\Delta)_s^{1/2} e^{-iks}}$ , we get it for odd negative numbers.

Note that, in general, the numerical computation of  ${}_2F_1$  is extremely complex and even commercial implementations exhibit limitations. Therefore, being able to express the Gauss hypergeometric function  ${}_2F_1$  as a finite sum is very important.

Moreover, the other crucial point of this paper, is the use of a fast convolution algorithm to compute simultaneously  $(-\Delta)_s^{1/2} e^{iks}$  for extremely large sets of odd values of  $n$ . This allows us to compute by means of a fast convolution in  $O(P \log(P))$  operations, whereas if we do a direct calculation we need  $O(P^2)$  operations. Because of this, we are capable of developing an efficient pseudo-spectral method for the computation of  $(-\Delta)_x^{1/2} u(x)$ .

The next step is to extend the results to the odd case for all  $\alpha \neq 1$  and then generalise them to several dimensions.



GEOLOGIA

GEOLOGÍA

# Geomicrobiological interactions and mineral neof ormation in Acid Mine Drainage-affected environments

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KEY WORDS: acid pit lakes (APLs), acid mine drainage (AMD), mineral neof ormation, metal-microbe interaction.

## BACKGROUND

Spain has an extensive history of mining. Particularly in the Iberian Pyrite Belt (Devonian-Carboniferous, SW Spain) and La Unión-Sierra de Cartagena (late-Tertiary, SE Spain) districts, it was primarily focused on mineral exploitation of ore deposits rich in metallic sulfides and sulfosalts (e.g. pyrite, sphalerite, galena). Open-pit exploitation exposed these minerals to oxidation, causing long-term pollution by Acid Mine Drainage (AMD), especially after abandonment and flooding, releasing toxic elements like Fe, Al, Zn, Cu, As, Pb, and Cd into environment. While the microbial ecology of bacterial communities in Acidic Pit Lakes (APL) and chemical neutralization processes are well known, the existing knowledge on biomineralization at moderate temperatures (direct and indirect) is rather limited, particularly in terms of mineralogy and geochemistry of sulfide neof ormation related to Metal + H<sub>2</sub>S reaction, with the latter arising from sulfate-reducing microbial metabolism.

## OBJECTIVES

The primary objective of my PhD project is to identify and characterize newly formed mineral phases resulting from direct (biomineralization) or indirect (bio-induced mineralization) microbial-metal-mineral interactions, as well as to investigate metal mobility during neof ormation and early diagenesis. The results might contribute to the improvement of biotechnological and bioremediation strategies, enabling more effective mitigation of environmental contamination and promoting sustainable resource recovery.

## MATERIALS AND METHODS

Numerous limnological, mineralogical, geochemical, and ecological techniques were employed to characterize natural macrocosms (i.e. APLs)<sup>[1,2]</sup>. Incubation columns, constructed using original APLs' water and sediments, facilitated laboratory investigation of these systems<sup>[3]</sup>. This approach enabled the assessment of geochemical conditions' evolution (e.g. pH, ORP, metal mobility), mineralogical and microbiological response to the variation of specific environmental conditions (e.g. change in light and nutrient availability, microbial activity rate), identifying key controlling factors. The microbial community was characterized by 16S rRNA gene sequencing. The use of classical mineralogical techniques, such as optical microscopy or XRD, were found to be limited by the (sub)micrometric size and low crystallinity of neof ormed minerals, especially sulfides. Consequently, for qualitative identification of the neof ormed minerals electron microscopy (scanning and/or transmission) was required. Additionally, the mineral precipitation kinetics under similar geochemical conditions was contrasted using applied mineralogy techniques<sup>[4]</sup>. The synchrotron-based X-ray Absorption on the Fe, Cu, Zn and As K-edges allowed the semiquantitative determination of the main sulfide minerals, based on the interatomic distance between the closest neighbors (e.g. Cu-S), while sequential extraction method provided quantitative distribution of elements among different phases (e.g. carbonate, oxides, sulfides), allowing the estimation of the microbial impact. Finally, synchrotron-based cryo-Transmission soft X-ray microscopy allowed the image acquisition of unstained and intact biological samples in its' almost native state, establishing the microbe-mineral interaction.

## CURRENT RESULTS

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# Theropod dinosaurs of the Iberian Peninsula: Cretaceous predators of the Basque-Cantabrian, Cameros and Pyrenean basins

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KEY WORDS: Theropoda, Dinosauria, Cretaceous.

Together with Sauropoda, theropods are considered to be members of clade Saurischia. Theropoda comprises the carnivorous dinosaurs, if not all, many of which became secondarily adapted to herbivory, omnivory, insectivory or even filter feeding strategies. Theropods are known for being exclusively bipedal with elongated necks, and long and horizontally projecting tails in most of the subclades. Once they first appeared in the fossil record, Theropoda rapidly evolved to become a highly diverse clade filling a wide array of ecological niches. All non-avian dinosaurs went extinct after the K-Pg event 66 million years ago, but birds survived and thrived throughout the Cenozoic.

Theropod dinosaurs are well known in many localities of the Jurassic and Cretaceous deposits of the Iberian Peninsula. In the northern part of Iberia, theropod remains have been up to date recovered the deposits of the Basque-Cantabrian, Cameros and South Pyrenean basins.

The Early Cretaceous Cameros Basin theropods are known from the upper Hauterivian-lower Barremian Golmayo and Pinilla de los Moros formations (DS 6), and the upper Barremian-lower Aptian Castrillo de la Reina Formation and Enciso Group (DS 7) (Burgos and La Rioja). Most of the remains consist of isolated teeth, but cranial and postcranial remains have also been recovered. These remains have been attributed to Allosauroidea, Baryonychinae (Spinosauridae), Carcharodontosauria, Dromaeosauridae and other coelurosaurians. Baryonychines are by far the dominant medium- to large-sized theropods of the area. They are abundant in the lacustrine-palustrine deposits of Eastern Cameros and the fluvio-lacustrine environments of Western Cameros. Further research includes the description of a new genus and species close to *Baryonyx* on the basis of a partial skeleton found in Igea (La Rioja). Other spinosaurid partial skeletons of Igea are also in the process of being studied and published.

In the Basque-Cantabrian Basin many uppermost Cretaceous dinosaur-bearing sites have been documented, but the upper Campanian Laño site (Sedano Formation) is the one with the best and most abundant theropod record. This mostly consists of isolated theropod teeth that belong to an abelisaurid and several small coelurosaurians. The abelisaurid belongs to the genus *Arcovenator*, whereas the coelurosaurian teeth have been regarded as cf. *Paronychodon*, cf. *Richardoestesia*, Paraves indet. and Dromaeosauridae indet. In addition, a possible ornithomimosaur and the giant bird *Gargantuavis* also identified in Laño make this site the most important uppermost Cretaceous site of Iberia regarding theropod dinosaurs.

The South Pyrenean Basin is also an excellent window to understand the uppermost Cretaceous theropod faunas, just before the K-Pg extinction event. In the late Maastrichtian dinosaur-bearing localities of the Arén and Tremp formations, theropods are represented by an indeterminate abelisaurid different from *Arcovenator*, cf. *Richardoestesia*, cf. *Paronychodon*, as well as indeterminate Paraves and Dromaeosauridae. This theropod assemblage slightly differs from the upper Campanian one from Laño, suggesting this association may have been affected by the intra-Maastrichtian faunal turnover event.

## Main publications:

Isasmendi et al. (2020). *Cretaceous Research*, 116: 104600. DOI: 10.1016/j.cretres.2020.104600.

Isasmendi et al. (2022). *Ekaia*. DOI: 10.1387/ekaia.22806.

Isasmendi et al. (2022). *Historical Biology*, online. DOI: 10.1080/08912963.2022.2069019.

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# La exploración y apropiación del medio subterráneo en el paleolítico: una aproximación desde la geología y el arte parietal

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KEY WORDS: Geomorfología del Karst, Cuevas Decoradas, Paleolítico, Sistemas de Información Geográfica.

Las cuevas representan un ambiente hostil para la vida humana, dada la completa oscuridad, la humedad y la topografía generalmente irregular. Sin embargo, las poblaciones humanas han frecuentado estos paisajes subterráneos desde al menos el Pleistoceno medio, y particularmente durante las fases finales del Pleistoceno y Holocenos posteriores. De hecho, los estadios isotópicos marinos (MIS) 3-2 destacan por la expansión exponencial de las visitas humanas a las zonas profundas de las cavernas, al parecer estrechamente ligados a la realización de la actividad gráfica. Por lo tanto, los estudios de las características espaciales del contexto antrópico antiguo en las cuevas son de gran interés, ya que ayudan a decodificar el comportamiento y las capacidades de los grupos humanos del pasado.

El objetivo de este proyecto es analizar de manera objetiva, precisa y cuantitativa la apropiación y la exploración del endokarst por parte de los grupos humanos paleolíticos, a partir del estudio geomorfológico detallado de varias cuevas decoradas en el Paleolítico superior y del uso de herramientas digitales, como los Sistemas de Información Geográfica (SIG). Para ello nuestro proyecto contará con cuatro ejes principales:

1. Por un lado, se estudiará la geomorfología y la evolución kárstica de varias cuevas decoradas en el Pleistoceno superior final, identificando y señalando los procesos y modificaciones acaecidos, así como su estratigrafía relativa, y en la medida que se pueda, cronológica (mediante la técnica de datación de espeleotemas a partir de las series del Uranio). Se tendrá especial interés en conocer con la mayor exactitud posible la disposición y la morfología que tenía la cavidad en el periodo de su uso en el pasado, para evitar sacar conclusiones sesgadas a partir de una visión actual del contexto.
2. Por otro lado, a partir de las conclusiones extraídas del estudio geomorfológico, y valiéndose de la tecnología de documentación 3D (láser escáner y fotogrametría) y los softwares de edición tridimensional (mayormente, CloudCompare®, Meshlab® y Blender®), se tratará de reconstruir el aspecto que tendría la cueva en el momento de las visitas de los grupos humanos al final del Pleistoceno.
3. Acto seguido, emplearemos los resultados de distintos programas de arqueología experimental, para poder realizar estimaciones precisas sobre el uso humano que tuvieron las cuevas de nuestro estudio (principalmente enfocados en la accesibilidad, la visibilidad y el aforo de los sectores decorados). Para ello utilizaremos los 3D modificados de las cavernas decoradas, que muestran el aspecto que tendrían originalmente, a partir de los SIG, valiéndose de numerosos scripts en lenguaje Python diseñados *ad hoc* para este tipo de estudios.
4. Finalmente, los resultados serán analizados estadísticamente mediante unos análisis de estudio multivariable a partir del software R. El objetivo será tratar de identificar patrones comunes en la selección de los espacios decorados mediante la estadística analítica, así como ayudar a medir el coste y el esfuerzo invertido en estos entornos. Estos resultados ayudarán a inferir el nivel de inversión que realizaron estas sociedades antiguas del Pleistoceno superior para poder visitar, “explorar” y antropizar, mediante la realización de arte parietal, estos recónditos espacios del mundo subterráneo. Los resultados se compararán con la dispersión actual del registro arqueológico, teniendo en cuenta los procesos tafonómicos identificados, para poder validar los resultados.



# Tecto-termo-sedimentary evolution in an hyper-extensive context: the oriental margin of the Basque-Cantabrian Basin

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KEY WORDS: hydrothermalism, Cretaceous, hyperextension.

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Multidisciplinary investigation is imperative when it comes to geology. The combination of different fields of knowledge enables the characterisation of geological processes from micro- to macro-scale. Thus, correlation of sedimentological, structural, petrological and geochemical data is a must for a solid basin evolution understanding. Based on field and analytical methods, the milestone of this study is the interpretation of the geological evolution and related hydrothermalism of the southern and northern margins of the Bortziriak massif, in the eastern Basque-Cantabrian Basin (BCB), in a Cretaceous hyper-extensive context.

Hyperextension involves an extreme stretching and thinning of the continental crust and a subsequent asthenospheric mantle exhumation. This geodynamic setting is suitable for the development of synsedimentary hydrothermal systems. Such systems transfer heat and elements towards the surface. In that a permeable scenario, deep radiogenic fluids and seawater interact with rocks, sediments and biota giving rise to mineralisations and complex ecosystems. Furthermore, depending on regional and local tectonics, that interaction would vary in space and in time.

## HOW TO TRACE PAST HYDROTHERMAL PROCESSES

Characterised by field and microscopic observations, mineral replacement, neomorphism, recrystallisation, dissolution, cementation (diagenetic processes, in general) evidences are detailed. Mineral cross-cutting relationships and texture interpretation allows ordering relatively diagenetic processes in time and space.

Furthermore, geochemical approaches function as precise palaeothermometers and clocks. On the one hand,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  stable isotopes, clumped-isotopes and fluid-inclusion microthermometry provide information concerning past hydrothermal fluid temperature. On the other, U-Pb dating allows to date precisely million years old carbonate minerals. But not only that, elemental analysis of mayor, trace and REE combined with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios gives provenance information of the fluids.

The gathering and correlation of all these geological data has already made it possible to constrain certain hydrothermal processes and related events, although all the pieces have yet to be put together for the creation of a more regional model of the eastern BCB.

# Mineralogy, petrography and petrogenesis of the aplopegmatites of Belvís de Monroy (Cáceres)

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KEY WORDS: Pegmatites, Central Iberian Zone, Mineral Resources.

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Pegmatites are rocks whose economic interest is growing; they are enriched in elements used in the most advanced electronic technologies, such as Li, Ta or Nb, as well as different industrial minerals, such as quartz, feldspar or spodumene. To this economic interest, we must add the high scientific interest that their study presents. Pegmatites are important showcase that allows us to know the last stages of crystallization of extremely fractionated granitic systems. In this sense, it should be noted that the genesis of pegmatitic rocks has been a highly controversial issue for some time. The coexistence of very common minerals in granitic rocks with “exotic” minerals, rich in rare elements, has given rise to numerous genetic models.

The Belvís de Monroy pluton is the westernmost and the most fractionated granitic intrusion of the Montes de Toledo Batholith. This inversely zoned pluton shares geochemical characteristics with granites associated with pegmatitic mineralized fields of the ZCI. This intrusion of peraluminic composition stands out for its character perphosphoric, in addition to containing peculiar accessory mineral phases such as gahnite, chrysoberyl and beryl. In the field of Belvís de Monroy (Cáceres) numerous aplopegmatitic bodies are located and some of them have been described as bodies enriched in Li, Sn, P and B. They show great textural, mineralogical, petrographical and structural variety. This makes its detailed mineralogical-petrological study of great interest, either to understand the processes of differentiation and emplacement of the different magmas granitic-pegmatitic, or to glimpse the potential that the pegmatitic field could hold in relation to the exploration of Li mineralizations.

In this project, a petrographic and mineralogical study of the pegmatites and granite rocks of this area is proposed, as well as a geochemical and geochronological characterization. In this way, field and laboratory work will be carried out using different techniques, for example: X-ray diffraction (XRD), X-ray fluorescence (XRF), electron microprobe (EMP), LA-ICP-MS, geochronology of Ar-Ar or U/Pb...

All of this, together with geochemical modelling, will make it possible to establish a petrogenetic model in which the genetic relationships between the pegmatites, the outcropping granites in the area and the host rock are determined, as well as the internal evolution of the pegmatitic dykes. Likewise, the geochemical behavior of some elements (e.g. P, B, F, Li, Nb and Ta) during pegmatitic crystallization will be established. The quantitative determination of the metasomatic processes on the host rock of the pegmatitic bodies will serve to determine mineral exploration indicators.

The study of this mineralization will help to understand the distribution and behavior of Li and other elements (e.g. B and P), in the ZCI during the Variscan orogeny, which will allow to advance in the knowledge of the regional and historical geology of this region and in the genesis of the rocks carriers of these elements. This research presents a clear economic interest, since its results will facilitate the characterization of these deposits and the discovery of new mineralized bodies, helping to establish new exploration patterns for this type of rock.

# Cyclostratigraphic, paleoclimatic and paleoenvironmental analysis of middle/upper Eocene hemipelagic deposits from the Northern Iberian continental margin (Pamplona Marl Formation, Western Pyrenees)

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KEY WORDS: Eocene (Bartonian/Priabonian), chronostratigraphy, Milankovitch cycles, magnetostratigraphy, calcareous nanofossils.

A common goal of the Intergovernmental Panel for Climate Change (IPCC) and the International Union of Geological Sciences (IUGS) is the study of sedimentary records that were influenced by astronomically paced periodic climate-change cycles (Milankovitch cycles) in ancient times of intense greenhouse effect, as this information may provide insights into the future consequences of the ongoing global warming. Most studies are carried out using ocean drilling cores, but these cores commonly present low sedimentation rates and hiatuses, hence the information must be complemented with the study of expanded terrestrial outcrops.

During the Mesozoic and Cenozoic the northern continental margin of the Iberian peninsula was characterized by the accumulation of thick deep marine sedimentary successions which are now exposed in accessible outcrops of both the Basque-Cantabrian and South Pyrenean regions. Given their former location at a paleolatitude of 25°-35°N, these sedimentary successions registered reliably the climate changes of the time. This doctoral thesis aims to determine the influence of orbitally forced climate-change episodes (Milankovitch cycles) on the middle/upper Eocene (Bartonian/Priabonian) Pamplona Marls Formation throughout several outcrops of the western Pyrenees.

To this end, a high-resolution study of several paleoclimatic proxies has been conducted on the Pamplona Marls outcrops located in the Jaca-Pamplona basin, more precisely in the area of the Yesa water reservoir (province of Zaragoza) to the south of the overthrusting belt of the Leyre mountain range. The succession consists of a conspicuous alternation of marl and marly limestone metric layers. The magnetostratigraphy and calcareous nanofossil biostratigraphy of most of the layers, combined with the spectral analysis of the magnetic susceptibility of more than 500 rock samples, yielded a detailed astrochronological and cyclostratigraphic framework which can be correlated with other geological sections of the same age and compared with global astronomical solutions. This has shown that the lithological alternation was caused by seasonality variations driven by precession cycles of 21,000 years, and these were modulated by climate-change episodes driven by eccentricity cycles of 100,000 years. Thus, the precise age model obtained in the studied succession substantially exceeds the resolution of the astronomical solutions calculated by mathematical models for the same time interval. This will allow the improvement of the astrochronological time scale following the guidelines of the IUGS and the International Commission on Stratigraphy (ICS).

Following the astrochronological analysis, a detailed paleoenvironmental analysis of the most characteristic cycles will be conducted in order to understand the relationship between variations in the intensity/frequency of different paleoclimatic parameters (e.g., temperature, rainfall, runoff, etc.) and hemipelagic sedimentary processes (e.g., variations in biological productivity, carbonate dissolution due to lysocline rises, or terrigenous dilution produced by increased rates of continental weathering). The assessment of climatic and environmental feedback (both positive and negative) will increase our understanding of climate change processes in greenhouse conditions, which is one of the main research lines promoted by the IPCC. Consequently, although this doctoral thesis is focused in the middle/upper Eocene of the Basque-Cantabrian Basin, the results will have global applications in the development of both the astronomical time scale and models of marine sedimentation under changing climates.



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# Design of new theranostic platforms: Multifunctional microdiscs with enhances magneto-thermal effect

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KEY WORDS: magnetite nanoparticles, photolithography, hybrid microdiscs, magnetic hyperthermia.

In the past few years, the research on magnetic nanoparticles (MNPs) in biomedicine has increased due to their potential as anti-cancer agents through the minimally-invasive magnetic hyperthermia therapy. However, the incorporation of MNPs into a biological environment has two significant limitations: MNPs tend to agglomerate, reducing their magneto-thermal capacity, and they are prematurely eliminated by endocytic mechanisms, limiting the efficacy of the therapy. For overcoming these two drawbacks, the fabrication of hybrid microdiscs (MDs) (polymeric-inorganic) as platforms to support the MNPs is presented. These MDs are formed by depositing an inorganic film (Au or SiO<sub>2</sub>), a polymeric multilayer and a monolayer of magnetite (Fe<sub>3</sub>O<sub>4</sub>) NPs onto a sacrificial photolithographic template. In order to obtain an efficient lift-off of the microdisc, it is crucial to manufacture a mushroom-shaped template using a bilayer process.

In the present work we describe the optimisation of the fabrication of the mushroom-shaped photolithographic templates in three different sizes (40, 20 and 10 μm) and on the assembly of the polymeric and MNP layers by means of the Layer-by-Layer (LbL) deposition process. To achieve an appropriate assembly of the MNPs, different parameters of the deposition process (NPs concentration, sputtering/flushing times...) have been optimised. Furthermore, we have assembled different Fe<sub>3</sub>O<sub>4</sub> NPs (with sizes between 20-25 nm and several morphologies) on top of the MDs and have their heating capacity. Finally, in order to demonstrate the suitability of these microplatforms for biomedical applications, *in vitro* experiments in colon cancer derived cell line (HCT116) were carried out, being demonstrated the large resistance of the MDs to endocytosis and their good biocompatibility in cellular environment.

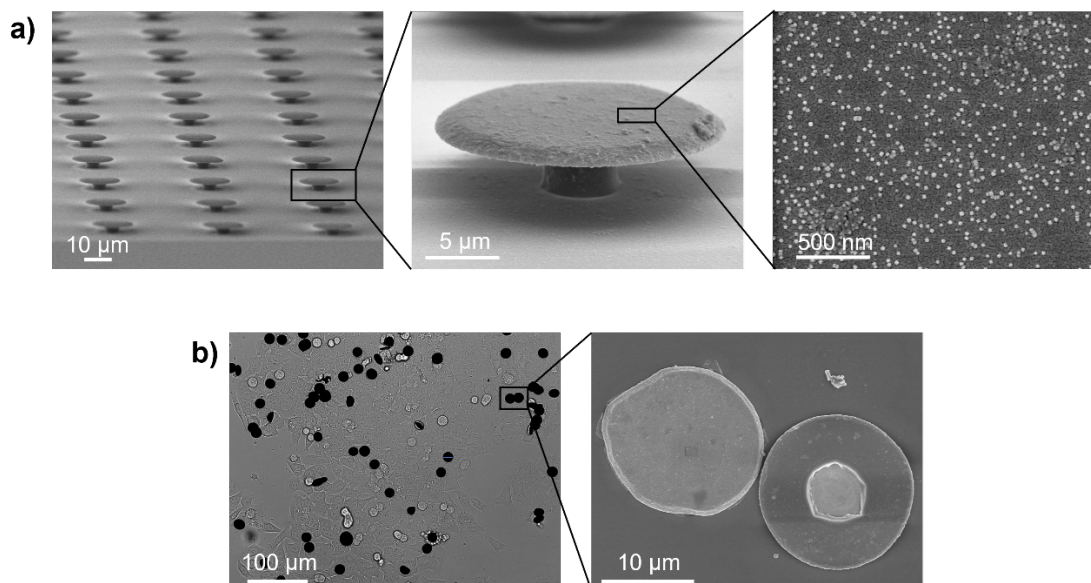


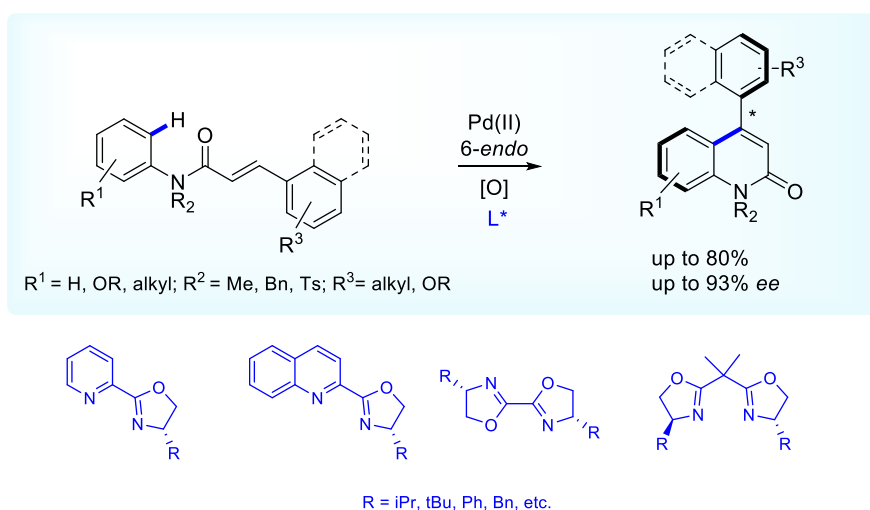
Figure 1. a) SEM images of a mushroom-shaped template after SiO<sub>2</sub> deposition and LbL process with MNPs deposited and b) HCT116 cells incubated with MDs.

# Synthesis of Axially Chiral 4-Aryl-quinolin-2(1H)-ones *via* intramolecular C-H Alkenylation

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KEY WORDS: C-H activation, palladium, axial chirality,

Axially chiral biaryl scaffolds are privileged structures used in organic synthesis as ligands or chiral catalysts, but also present in natural and synthetic compounds with relevant biological properties. Significant progress has been achieved in the atroposelective synthesis of biaryls over the past decade, and different methodologies have been developed for the atroposelective synthesis of enantioenriched biaryls, based on palladium chemistry [1]. However, the enantioselective synthesis of atropoisomers through enantioselective C-H activation reactions remains a challenge. In this context, Pd(II) catalyzed dehydrogenative Heck reactions (DHR) have been described in which the stereoselectivity is controlled by a chiral directing group [2] and by the use of transient chiral auxiliaries or chiral ligands [3]. Related intramolecular approaches have received much less attention. To our knowledge, there are no examples in which the chiral axis is generated through an intramolecular DHR. We have reported that 4-substituted quinolones are efficiently obtained via a selective 6-endo intramolecular C-H alkenylation of *N*-phenylacrylamides [4]. Therefore, our present goal is the application of this strategy for the atroposelective synthesis of axially chiral 4-arylquinolin-2(1H)-ones (Scheme 1). For enantioselectivity control, different types of chiral ligands for palladium (II) have been studied, such as bis(oxazoline), pyridine-oxazoline and quinoline-oxazoline ligands. We have also studied different catalysts, oxidants and experimental conditions. It has been observed that the solvent plays a fundamental role, and 4-arylquinolin-2(1H)-ones can be obtained in an enantiodivergent manner just by selecting the appropriate solvent. The protecting group on nitrogen is also fundamental to obtain high enantiomeric purities, up to 93 % ee. Details of these transformations will be given



**Scheme 1.** Atroposelective synthesis of 4-arylquinolin-2(1H)-ones

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# Zirconium MOFs for their application in CO<sub>2</sub> valorization

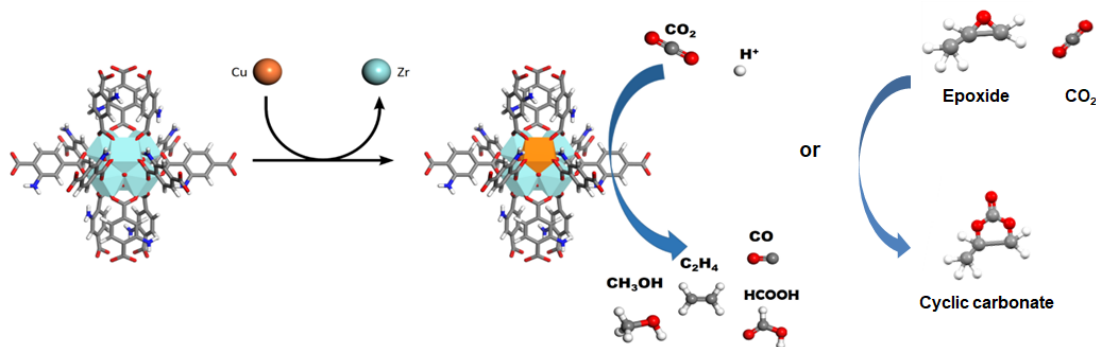
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KEY WORDS: metal-organic framework, catalyst, CO<sub>2</sub> valorization, electroreduction

The increase in the human industrial activity in recent decades has led to a significant rise in CO<sub>2</sub> emissions into the atmosphere, causing serious problems such as global warming and climate change. To promote sustainable growth, reducing these emissions or converting them into useful molecules is crucial. Different approaches, such as CO<sub>2</sub> capture and sequestration, storage, or conversion into valuable chemicals can be used to achieve this goal. Recently, MOFs have emerged as a promising alternative to conventional materials in all these technologies. Zirconium MOFs are promising materials due to their stability, tunability, and high surface area. They are particularly useful in catalysis, gas separation, and gas and liquid storage applications. However, the difficulty of obtaining new topologies is a challenge due to the strength of the bonds and hardness of the building blocks. In 2019, a new polymorph of UiO-66, named EHU-30, was reported by our research group, overcoming this challenge. Recently, the family was expanded to include EHU-30-NH<sub>2</sub>, which is an isorecticular amino-functionalised counterpart. Considering all the aforementioned, this work focuses on the applications of EHU-30 family MOFs in chemical transformation by the CO<sub>2</sub> electroreduction to valuable chemicals and fuels and CO<sub>2</sub> fixation using epoxides to form cyclic carbonates (Figure 1).

The results of the CO<sub>2</sub> electroreduction reaction demonstrated that MOFs containing the amino functional group performed better than their non-functionalised counterparts due to superior CO<sub>2</sub> adsorption. The introduction of copper(II) improved their performance, product selectivity towards more reduced species, and doubled the total reaction rates and Faradaic efficiencies (FE). Additionally, copper doping prevented the rapid deactivation commonly observed in Cu-based MOFs, ensuring stable and continuous transformation of CO<sub>2</sub> into valuable products. The mechanism of CO<sub>2</sub> fixation reaction into epoxides proceeds in such a way that the MOF coordinates with the epoxide and activates it, so that the cocatalyst attacks it nucleophilically. The resulting intermediate compound reacts with CO<sub>2</sub>, producing the cyclic carbonate. The study reveals that a reduction in the size of the organic substrate and the presence of amino functional groups in the framework lead to an increase in the reaction yield. The introduction of Cu-doped compounds also improves the yield compared to the starting MOF. Furthermore, the Zr metal-organic network enhances the stability of the material during the CO<sub>2</sub> fixation process on epoxides.



**Figure 1.** Scheme depicting the copper doping process of EHU-30-NH<sub>2</sub>, showing how a Zr atom is displaced by the introduced Cu atom, and how this material can be used to catalyze the CO<sub>2</sub> conversion to alcohols and hydrocarbons and to fix CO<sub>2</sub> into epoxides.

# Natural polymers as biocompatible nanocarriers for encapsulation and controlled release of nutrients

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KEY WORDS: biopolymer, nanocarrier, nanogel, encapsulation, controlled-release

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Natural polymers have emerged as promising candidates for the sustainable development of materials in areas such as biomedicine, agriculture, food industry or ecosystem bioremediation. In the last years, there is a growing interest in designing advanced materials using naturally abundant and renewable feedstocks. On top of that, due to some inherent properties of these polymers, such as gel formation capacity, biocompatibility, biodegradability and non-toxicity, they have a promising role in applications such as targeted delivery and nutrient, enzyme, and cell encapsulation.

In this research, these materials of natural origin are brought into the field of nanotechnology in order to take advantage of the unique properties that come with the reduced particle size. Used as so called “nanocarriers”, biopolymers can provide a controlled sustained release of nutrients and active compounds and protect the cargo from external effects that could negatively affect their performance. In the search for a cost-efficient and biofriendly synthesis method, this study focuses on nanogel formation by self-assembly and polycomplex formation at room temperature, using different combinations of polyanions and polycations of natural origin, namely, sodium alginate (SA), chitosan (CS), k-carrageenan (k-CA) and modified starch (MS). Nanogel suspensions are characterized in terms of particle size and surface zeta potential, using techniques such as Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM). So far, stable colloids of both positively ( $> +30$  mV) and negatively ( $< -30$  mV) charged nanometric particles ( $d_{dry} < 100$  nm) have been obtained for the study of their encapsulation and controlled release capacity for urea and other nutrients.



# Gas-phase structural elucidation of multi-conformational systems: a further step in rotational spectroscopy

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KEY WORDS: microwave spectroscopy, supersonic expansion, multi-conformational systems.

Exploring the conformational landscape of multi-conformational systems, such as macrolactones, can be challenging, as their great flexibility leads to small structural changes that result in a large number of energy minima. High-resolution gas-phase microwave spectroscopy in combination with supersonic expansion has proven to be a unique technique, being able to isolate and discern conformers or clusters unambiguously without masking effects. Macrolactones, cyclic structures with one or more ester linkages consisting of an alkyl ring architecture of 12 or more atoms, are a good example of structural complexity because of the rich conformational panorama they present. These compounds are considered “privileged scaffolds” within the medicinal chemistry community, because their study led to the discovery of bioactive compounds. However, gas-phase studies on the changes in structure and intra/intermolecular interactions after solvation of these biomolecules are very scarce.

Based on the previous rotational study of oxacyclotridecan-2-one (C12) and 16-hexadecanolide (C15), where, uncommonly, 22 conformers for C12 and 20 for C15 were observed,<sup>1</sup> in this work we have studied the structural behaviour of these molecular systems after the addition of individual water (W) molecules. This was possible thanks to the development of the chirp-pulsed (CP) technology, which has made affordable molecular targets previously out of reach in terms of size and conformational complexity.<sup>2</sup> These two case studies push the limits of the CP technique and quantum chemistry calculations, due to their virtually strain-free cyclic structures. This rotational study fills the gap in the understanding of the relationship between shape and physicochemical properties of molecules.

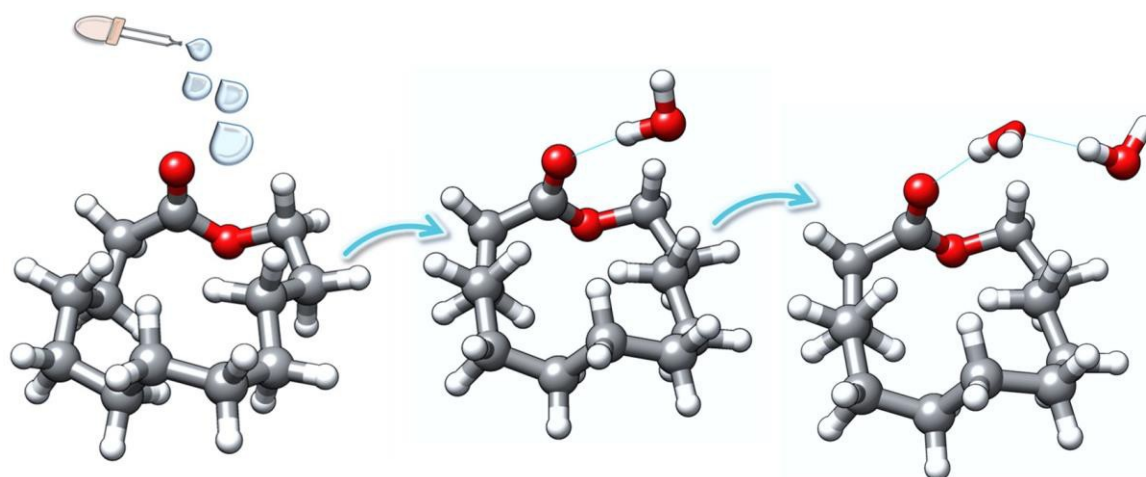


Figure 1. Addition of water molecules to the C12 macrolactone.

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# High density microcapsules composed of marine oils and probiotics for the prevention of childhood obesity

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KEY WORDS: childhood obesity; microcapsules; oils; probiotics.

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Childhood obesity is one of the most serious public health problems of the 21st century. In children, obesity is associated with an increased likelihood of premature death and disability in adulthood, as well as a greater probability of cardiovascular disease, diabetes, musculoskeletal disorders, and an increased risk of certain cancers.

It has been shown that an increase of physical activity and of intake of foods rich in anti-inflammatory and antioxidant compounds, such as omega fatty acids, can reduce obesity. Medical nutritionists and clinical trials had also indicated the benefit of the use of microorganisms (probiotics) for the improvement of some metabolic parameters, which are related to obesity.

A great number of studies in animal model have revealed that gut microbiota and their metabolites, in particular short-chain fatty acids (SCFA), play an important role in obesity. SCFAs are produced in the colon as a result of a complex interaction between diet, gut microbiota, and the host. They are the final products of anaerobic fermentation of dietary fibres and proteins in the small intestine. Micronutrients and SCFAs may regulate host energy metabolism in the development of diet-induced obesity.

For this reason, dietary supplementation with foods containing SCFA-producing gut microorganisms (probiotics) could help to reduce childhood obesity by adding foods containing these microorganisms to their diets.

However, it remains to be demonstrated that a combination of microorganisms together with omega fatty acids and in the presence of nutrient substrates can provide benefits in reducing the risk of fat accumulation by improving the hepatic metabolic pathway. So that, the main objective of this work is to study the efficacy of microcapsules containing marine oils and probiotics to prevent the childhood obesity.

For this purpose, firstly, a study of the oxidative stability of high-density microcapsules containing marine oils rich in omega fatty acids has been performed. It was concluded that encapsulated oils were stable until at least 3 months in accelerated and long-term conditions (40 °C at 75% of RH for 6 months and 25 °C at 60% of RH for 1 year, respectively); and that omega 6 and 9 fatty acids remained stable during the 6 months of the study while omega 3 fatty acids showed a small decrease in the 3<sup>rd</sup> month in both studied conditions.

Secondly, the selection of the most adequate microorganisms upon the basis of their production of SCFAs in the presence of a variety of substrates is being carried out. Once the microorganisms are chosen, their microencapsulation with oils rich in omega fatty acids will be done in order to determine the effect of the intake of these high density microcapsules in obese rats.

# Eco-design of nanocellulose-based solutions for cultural heritage conservation: materials development, validation and life cycle assessment

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KEY WORDS: cultural heritage conservation, nanocellulose-based solutions, green materials

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Over the past two decades, the need for effective technologies, tailored materials, and innovative solutions for conserving cultural heritage has increased substantially. New conservation technologies should ideally employ environmentally-friendly materials and procedures, minimizing those that can be hazardous to the end-user or present ecotoxicity. Unfortunately, very few technologies/materials in this field can be considered entirely sustainable.

To address this issue, the **ENCLOSURE** project aims to provide holistic solutions for respectful cultural heritage conservation through the **eco-design, testing, and validation** of environmentally sustainable nature-based materials that adhere to Circular Economy paradigm and European Green Deal. Nanocelluloses obtained from green routes will be used as platform materials to develop hydrogels, aerogels, and coatings, among other alternatives. Cellulose nanofibers (CNFs) and bacterial cellulose (BC) obtained from biomass wastes will be mainly used to generate the desired materials. These materials will be tuned to absorb salts, clean soiling and degraded organics, and protect the painting layers in wall and canvas paintings. Although the effectiveness of ENCLOSURE materials will be tested in wall/canvas paintings, this project aims to pave the way for the future use of nanocelluloses in other heritage materials, positioning these new technologies as a family of environmentally sustainable solutions.

To test the effectiveness and harmlessness of the developed materials, the preparation of mock-ups that realistically reproduce the artworks will be crucial. Non-invasive methodologies based on spectroscopic imaging will be developed to validate the use of the developed conservation solutions. These methodologies will be transferred from benchtop to portable instrumentation capable of conducting in situ imaging, allowing quick decisions while conservation protocols are being applied or detecting conservation necessities.

This proposal goes beyond the Safe-by-Design concept recently applied in cultural heritage conservation, quantifying and analyzing additional impact metrics, such as Life Cycle Assessment (LCA), offering transparent and comparable sustainable opportunities.

The ENCLOSURE project brings together a multi/interdisciplinary network of researchers with background in natural sciences (chemistry and geology), materials engineering and soft sciences (conservation) to achieve all the mentioned objectives.

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QUÍMICA

# Conical Spouted Beds Equipped with Internal Devices

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KEY WORDS: Conical spouted bed, hydrodynamics, draft tubes, fountain confiner.

## INTRODUCTION AND OBJECTIVES

The conical spouted bed is an alternative gas-solid contact method to the well-established fixed and fluidized beds. It consists of a conical base contactor with a single air inlet nozzle at the center of the base. The air is introduced through the nozzle, which drags the solid particles up, and a central spout zone is therefore created. Accordingly, both the air and the particles ascend and enter to the fountain core. Subsequently, the particles descend by gravity in the fountain periphery and annular zone, and incorporate into the spout along the bed height. The cyclic movement of the particles leads to a much better contact than in fluidized beds. Moreover, the spouted bed regime allows operating with a wide range of particle sizes, as well as sticky and coarse (greater than 1 mm) particles. However, the main limitation of this technology lies in its scaling up. Accordingly, the ratio of the gas inlet diameter to particle diameter,  $D_0/d_p$ , cannot be higher than 20-30 in order to guarantee stable operation. The use of internal devices, such as draft tubes and fountain confiner, allows increasing the  $D_0/d_p$  ratio to 1000, and therefore ensures stable operation even with ultrafine particles (well below 1 mm).

The characteristics of the spouted bed make it suitable for a wide range of applications, such as drying, combustion, pyrolysis, gasification or coating. Industrial operations require estimating the heat and mass transfer rates, which are significantly conditioned by the cross-flow of solid particles from the annulus into the spout. Although the cross-flow depends on the air velocity, it also depends on the spout geometry. Thus, when no draft tube or nonporous draft tubes are used, the spout geometry is assumed to be axisymmetric. However, operating with open-sided draft tubes, this assumption cannot be longer made, as the spout geometry depends on the configuration used. Therefore, the aim of this work is to assess the effect of the air inlet diameter and the draft tube aperture ratio (opened fraction of the tube) on the spout geometry in a fountain confined conical spouted bed.

## METHODOLOGY

Particles show negative and lower velocities in the annulus than in the spout. Thus, there is a radial position in which the velocity of the particles is null, which is commonly known as the spout-annulus interface. An optical system fitted with a borescope has been used to track particles in the annulus and spout. A sophisticated algorithm developed by our research group has been used, which allows detecting, tracking and calculating the velocity of a particle in consecutive frames of both dense and diluted zones. Accordingly, the spout geometry was obtained by measuring the velocity of the particles in different bed heights and radial positions on a pilot scale plant. This procedure has been repeated in different configurations varying the air inlet diameter (3, 4, 5 cm) and the draft tube aperture ratio (42, 57, 78%).

## RESULTS

The results show that the spout geometry depends on the air inlet diameter and draft tube aperture ratio used. Small air inlet diameters lead to narrow spouts in the lower section of the bed and a pronounced expansion in the upper section of the bed. However, great air inlet diameters lead to straight spout geometries. Regarding the effect of the aperture ratio, narrower spouts are observed as the aperture ratio is decreased. Furthermore, the geometry of the spout also depends on the bed height. Thus, many spout geometries have been characterized, such as three pointed star, clover-like or circular, especially in the upper section of the bed. These results obtained allow a better understanding of fine particle spouting hydrodynamics in conical beds, which is essential information for the scaling up.

# Thermochemical processes for waste valorization.

## Pyrolysis of plastics

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KEY WORDS: Waste valorization, Conical spouted bed reactor, Pyrolysis, Plastics, Catalyst.

The suitable properties and flexibilities of plastic materials are promoting their leading role in several market sectors, such as packaging, automotive, building, or electronics. Thus, plastic production has monotonously increased in the last decades, reaching a global value of 36 million tons in 2020. Moreover, a substantial fraction of these plastics has a short life cycle and immediately ends in waste plastic streams. The unsuitable management of waste plastics and their nonbiodegradable natures cause several environmental problems associated with their accumulation in terrestrial and marine environments.

In order to minimize plastic wastes landfill, several valorization alternatives have been proposed, which range from primary routes of direct recycling to quaternary routes of energy valorization. In this scenario, tertiary valorization, such as thermochemical conversion technologies for plastics waste recycling, represent promising alternatives, as they allow producing fuel and high value-added chemicals, and therefore boosting circular economy by reintroducing these wastes into the production cycle. The production of fuels and chemicals has been addressed following two main strategies; the development of specific pyrolysis processes and the integration of waste plastics or plastic-derived products in refinery units. Another relevant tertiary valorization route of waste plastics lies in the gasification aimed at the production of a gaseous stream for energy or synthesis purposes. And, in addition, another process based on pyrolysis and reforming strategies has been proposed for H<sub>2</sub> production [1].

This research addresses the pyrolysis of plastics in a bench scale unit provided with a fountain confined conical spouted bed reactor (CSBR) operating in continuous mode, whose aim is to analyze the performance of this novel reactor configuration in the catalytic pyrolysis of high-density polyethylene (HDPE) over a spent fluid catalytic cracking (FCC) catalyst.

HDPE has been pyrolyzed at 550 °C and to analyze the effect of the catalyst, experiments have been carried out with different amounts of catalyst (7, 15, 30 and 45 g of FCC spent catalyst). The experiments have been undertaken in continuous regime by feeding 1 g min<sup>-1</sup> of HDPE and 7 L min<sup>-1</sup> of nitrogen, which corresponds to the flow rate necessary to obtain 4 times the minimum spouting velocity [2]. The products were quantified on-line by an Agilent 7890 chromatograph, and the non-condensable gases were analyzed by G.A.S. Compact GC<sup>4.0</sup> chromatograph. To compare the results obtained in the catalytic pyrolysis of HDPE, the products have been grouped into four lumps: C<sub>1</sub>-C<sub>4</sub> gas fraction; C<sub>5</sub>-C<sub>11</sub> hydrocarbons; C<sub>12</sub>-C<sub>18</sub> hydrocarbons; and C<sub>19+</sub> or waxes.

The results obtained for the space time of 7 g<sub>cat</sub> min g<sub>HDPE</sub><sup>-1</sup> showed that the main products were waxes, while in the experiments carried out with space-time above 15 g<sub>cat</sub> min g<sub>HDPE</sub><sup>-1</sup> C<sub>5</sub>-C<sub>11</sub> fraction was the main one. That showed a limited cracking activity when 7 g<sub>cat</sub> min g<sub>HDPE</sub><sup>-1</sup> is using because the yield of waxes was reduced from 66 wt% to zero when the space-time was increased to 15 g<sub>cat</sub> min g<sub>HDPE</sub><sup>-1</sup>. On the other hand, the yield of C<sub>1</sub>-C<sub>4</sub> gas fraction, C<sub>5</sub>-C<sub>11</sub> hydrocarbons, and C<sub>12</sub>-C<sub>18</sub> hydrocarbons increases considerably from 9.6, 17.9 and 6.4 wt% to 25.5, 56.4 and 18.1 wt%, respectively.

It can be concluded that the conical spouted bed reactor has shown good performance in the continuous catalytic pyrolysis of HDPE using spent FCC catalyst, since it has obtained a high yield of C<sub>1</sub>-C<sub>4</sub> gas fraction rich in light olefins and gasoline fraction (C<sub>5</sub>-C<sub>11</sub>).

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# Valorization of plastics waste through catalytic cracking and hydroprocessing

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KEY WORDS: catalysis, Waste Refinery, plastics, catalytic cracking, hydroprocessing

Plastics are a product derived from petroleum whose excellent physical and chemical properties have earned them a place at the top of the consumer pyramid, making use of them in various industries such as food, energy and technology. However, of the 391 million tons of plastics produced in 2021, the recycling rate is between 30 and 35 %, while the rest goes to landfills (around 50 %) and incinerators.

In a broader context, refineries are demanding an urgent change in their conventional operating practices since the demand for fuels and commodities in the short term is growing while the quality of the crude oil obtained is deteriorating. For this reason, refineries are increasingly open to the intensification of their usual processes by, for example, the introduction of waste materials such as plastics, tires or biomass derivatives.

Among the conventional refinery units capable of absorbing these alternative materials, catalytic cracking and hydroprocessing units are the optimal options because of their already existence in actual plants, their versatility and their potential to perform integrated recycling focused on the production of high-value compounds such as light olefins, monomers and BTX aromatics.

Catalytic cracking is one of the most relevant processes in the petroleum industry, involving passing the feed through a low-density bed and cracking it to lower boiling point compounds. Hydroprocessing is a very versatile refinery process that consists of the application of high temperature and hydrogen pressures in the presence of a catalyst, which allows not only to obtain fractions of high interest as fuel or other materials (such as monomers), but also to adjust the quality of these products.

## ACHIEVEMENTS TO DATE

Our laboratory covers both processes for waste valorization and the intensification of both refinery operations to maximize the production of automotive-like fuels, highlighting some of the following contributions:

- The intensification of midstream hydroprocessing to obtain high-quality gasoline using catalysts that contribute to a more sustainable refinery.
- Through catalytic cracking, waste plastics and tire pyrolysis oil have been converted into gasoline with high commercial value due to their olefin and aromatics content, adjusting conversion and yields to maximize the highest value products.
- The use of hydrocracking for the joint valorization of heavy streams and plastics to obtain commercial fuels, analyzing in detail the mechanisms of the process and the minimization of catalyst deactivation.

## IN THE SPOTLIGHT

With a solid foundation, we are now focused on moving forward with the following studies:

- To establish the feasibility of plastics recycling in continuous hydrocrackers by reducing the cost of catalysts and maximizing the quality of the fuels obtained.
- To obtain high-quality fuels from the chemical recycling of blends of refinery streams with liquids obtained from the pyrolysis of plastics from real electrical and electronic waste.
- To exploit the potential of hydroprocessing of bio-oil to produce fuels and chemicals

With all this, we intend to contribute to the Waste Refinery through a viable proposal for these processes' application to actual plants.

# Production of C<sub>2+</sub> hydrocarbons from CO<sub>2</sub> hydrogenation and oligomerization of light olefins

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KEY WORDS: CO<sub>2</sub>, catalysis, olefins, gasoline, membrane, oligomerization

The increase in greenhouse gas emissions and the fuel scarcity have become one of the major problems of recent decades. Primary energy consumption has grown steadily since the beginning of the 20<sup>th</sup> century and, although renewable energies are increasingly occupying a larger place in the energy mix, energy generated from fossil fuels is still predominant. Dependence on fossil fuels has a direct impact on greenhouse gas emissions, CO<sub>2</sub> being the most abundant. For this reason, there is an increasing effort to promote carbon capture and utilization technologies. Within these technologies, great importance is being given to the conversion of CO<sub>2</sub> to higher value-added products, especially by the catalytic hydrogenation of CO<sub>2</sub> [1]. In our research line, the focus is on the production of light olefins and of gasoline. Light olefins (ethylene, propylene, butene...) are the main petrochemical building block, and they are among the most important chemicals and raw materials to produce polymers such as polyethylene or polypropylene [2]. The direct production of light olefins from CO<sub>2</sub> is therefore an interesting route to help to mitigate climate change. The operating conditions used in this process are high temperature and pressure (400 °C and 30 bar), in order to thermodynamically favor the reactions. On the other hand, because of the increasingly scarce raw material for gasoline production, we have focused our efforts on the synthesis of gasoline from CO<sub>2</sub> hydrogenation. The gasoline obtained is an isoparaffinic gasoline, this is, adequate for its implementation in the gasoline pool of refineries. For this process, higher temperature and pressure are required (420 °C and 50 bar). For both the production of light olefins and gasoline from CO<sub>2</sub>, the so-called tandem catalysts are used, composed by a metallic oxide and a zeolite. For example, we have tested In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> or ZnO-ZrO<sub>2</sub> oxides and SAPO-34 and HZSM-5 zeolites.

Another technique to improve the process is the implementation of water permselective membranes, zeolite membranes in our case. The zeolite membranes are a type of inorganic membranes, and they can separate liquid and gas species with very similar size and shape, thanks to their defined pore size and adsorption capacity [3]. Up to date, we have synthesized several zeolite membranes, such as LTA (Linde Type A) or sodalite.

Alternatively to the direct synthesis of gasoline from CO<sub>2</sub>, the obtained light olefins can be also use for fuel production. These olefins, in addition to being used as raw materials in petrochemicals, also serve as feed for other processes in our research line, for instance, the oligomerization of ethylene. In the oligomerization process, two olefins (identical or different) combine to give a higher olefin. With this process, we have produced clean liquid fuels such as gasoline or jet fuel. For this process, we use medium temperature (275 - 350 °C) and low pressure (1.5 bar). The zeolite employed in this case is HZSM-5.

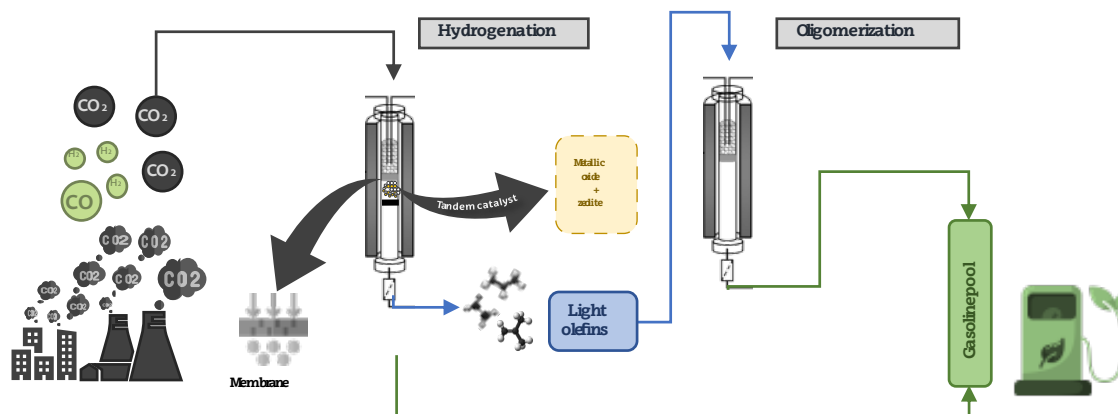


Figure 1. Scheme of the processes carried out in our line.

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# Design of catalysts for the simultaneous removal of NO<sub>x</sub> and dioxins in gaseous effluents of Waste Energy Recovery plants

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KEY WORDS: modified MnO<sub>x</sub>-CeO<sub>2</sub> catalysis, SCR, NO<sub>x</sub> removal, PCDD/F removal, waste energy recovery plants.

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Waste management is one of the biggest challenges in developed societies. Thermal incineration of municipal solid waste before disposal allows for a huge reduction in the volume of waste, while its energy is recovered to produce heat and/or electricity. However, all incineration processes generate, to a certain extent, pollutants such as NO<sub>x</sub> and PCDD/Fs (dioxins and furans), that must be removed from the exhaust gases in the gas cleaning lines.

In Waste Energy Recovery plants, the gas cleaning line is the most important part of the plant. There, destruction of NO<sub>x</sub> is typically carried out through non-catalytic reduction with NH<sub>3</sub>, while PCDD/Fs are separated from the gases by adsorption, where a polluted new solid phase requiring further treatment is generated. However, we have shown that both kind of pollutants (NO<sub>x</sub> and PCDD/Fs) can be simultaneously removed from the gas stream through destruction with the use of an adequate catalyst, complying not only with actual regulations, but also with those in the future, which are expected to be much more tightening, while preventing additional treatments.

Commercial VO<sub>x</sub>/TiO<sub>2</sub>-based catalysts, used in SCR to remove NO<sub>x</sub>, have proved to be adequate catalysts for this process, with good selectivity, although they require a relatively big reactor size to be effective in the removal of both pollutants in a wide range of temperatures: NO<sub>x</sub> removal efficiency decreases at high temperature, where oxidation of PCDD/Fs is favoured, because of parallel reactions. Besides, vanadium compounds are known to be toxic. Thus, new, non-toxic, more active catalytic formulations are currently under research.

In this line, we have prepared and tested a wide variety of catalytic formulations for this process. Among them, some catalytic MnO<sub>x</sub>-CeO<sub>2</sub> formulations have proved to present a high activity in a wide range of temperatures. Catalytic activity in a process depends not only on catalytic composition, but also on catalyst preparation procedure, which defines catalytic properties. In the simultaneous removal of NO<sub>x</sub> and PCDD/Fs, MnO<sub>x</sub>-CeO<sub>2</sub> formulations with high Mn content and prepared by co-precipitation have shown to be particularly active. Preparation variables such as precipitating agent, stirring rate and maturation time have shown to be key factors. The excellent performance of these catalysts, mainly at low temperature, has been associated with the formation of a Mn-Ce mixed oxide phase, in which a high interaction between Mn and Ce occurs, together with a phase of Mn<sub>2</sub>O<sub>3</sub>. Other manganese oxides, which have been obtained with other preparation procedures, have been found not to present so good behaviour.

Our research is focused also on reaction mechanism. FTIR studies indicate that reaction mechanism on these catalyst formulations changes with temperature and is associated with the different phases of the catalyst. Because of the presence of chlorine species (associated mostly with the reactants, PCDD/Fs), which adsorb on the catalytic surface during reaction, the catalysts lose activity with time on stream. This loss occurs mostly in the low temperature range and can be reverted above 300 °C. However, it affects the low temperature performance of the catalysts in actual operation.

Because of this, we are at present directing the research to modifying MnO<sub>x</sub>-CeO<sub>2</sub> catalytic formulations for preventing deactivation while increasing selectivity (to N<sub>2</sub> and the products of total oxidation of PCDD/Fs). We are following two strategies: either the addition of a third metal to the catalyst formulation, or the use of a support with high acidity where the MnO<sub>x</sub>-CeO<sub>2</sub> formulation can be deposited.

# Catalytic valorisation of biomass-derived organic waste: a contribution to the circular economy

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KEY WORDS: Hydrogen production, catalytic processes, aqueous phase reforming, biomass, waste valorization.

One of the main causes of climate change on the planet is the emission of gases such as CO<sub>2</sub>, derived from the use of fossil fuels for the production of chemicals and energy. For example, the synthesis of polymer materials consume up to roughly 80% of the carbon resources in the chemical industry. The most straightforward option to address the global warming challenge and the transition to circular economy is the use of biomass as a raw material, since it is the only sustainable source of organic carbon. The research we carry out represents a step forward in the decarbonisation of the economy to mitigate the climate challenge.

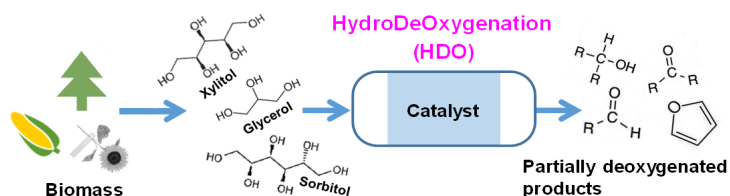


Figure 1. Biomass to high value-added chemicals.

target we use *in-situ* generated hydrogen by aqueous-phase reforming (APR) of the polyol, which then is used for the HDO. This strategy avoid the use of external hydrogen making the process greener and safer.

To convert the biomass-derived feedstock into high value-added fuels and chemicals, its oxygen content must be reduced. This can be done by either decarboxylation/decarbonylation reactions or hydrodeoxygenation. Decarboxylation/decarbonylation reactions imply cleavage of C-C bonds, and therefore give a shorter carbon chains (undesirable for fuels and chemicals). HDO is a combination of C-O bond cleavages by H<sub>2</sub> and C-O bond cleavages through the removal of H<sub>2</sub>O. By HDO reaction, selective cleavage of C-O over C-C bonds occurs, and products with the same carbon number of the original feedstock are obtained. In order to favour HDO a proper catalyst should properly balance its hydrogenation/dehydrogenation activity (metal sites) and dehydration function (acid sites).

We start from nickel- or cobalt-based catalysts, which are active for hydrogen production. Doping these base catalysts with other metals (Cu, W, Mo, etc.) we can tune both the metal sites and the surface acid characteristics that can change the obtained products distribution. In addition, the operation conditions such as temperature, pressure or residence time have huge impact in the product distribution.

In our research we optimize both the catalyst formulation (to be active and durable), and the reaction conditions, to maximize the yield of the targeted partially deoxygenated molecules. We analyse both the gas and the liquid products, which give us the clue to determine the main reaction paths. All the synthesized catalysts are thoroughly characterized in order to gain knowledge on their physical-chemical characteristics, which are used to correlate with their catalytic performance.

In the research, we use three biomass-derived representative platform molecules, glycerol, xylitol and sorbitol, the three included in top-12 building block chemicals that can be upgraded to high value-added products. Glycerol (representative from triglycerides) is typically obtained as a by-product of processes such as transesterification of oils. For example, in biodiesel production, approximately 110 kg of glycerol is produced per ton of biodiesel, usually treated waste product. Xylitol is a representative model molecule from hemicellulosic biomass, and it is manufactured either by hydrogenation of C5-carbohydrates from hemicellulose. Sorbitol is a model compound from cellulosic biomass, and it is manufactured at large scale by catalytic hydrogenation of glucose.

# Strategies for CO<sub>2</sub> capture and valorization to fuels and high-added value chemicals

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KEY WORDS: Climate change, CO<sub>2</sub> capture and utilization, catalytic CO<sub>2</sub> hydrogenation into CH<sub>4</sub>

The fossil fuels consumption has continuously increased since the Industrial Revolution, leading to progressive increase of greenhouse gases (GHGs) emissions to the atmosphere. CO<sub>2</sub> is accepted as the main GHG and its levels in the Earth's atmosphere have exceeded 420 ppm in 2022. In fact, the International Energy Agency (IEA) foresees 35.7 Gt of emitted CO<sub>2</sub> for 2040, a quantity far from enough to avoid severe climate change. In recent decades, many efforts have been made to develop efficient renewable energy sources (wind and solar among others) that reduce the amount of CO<sub>2</sub> emitted. The major drawback of renewable energy is its intermittency. Consequently, large capacity electricity storage and reserve production capacity are required.

Valorization of CO<sub>2</sub> by its hydrogenation to CH<sub>4</sub> with green H<sub>2</sub> is a promising alternative, not only because of buffering the intermittency of renewable energy but also due to its contribution to the reduction of CO<sub>2</sub> anthropogenic emissions. CO<sub>2</sub> adsorbed from the industrial exhaust gases can be combined with green H<sub>2</sub> generated from renewable energies and converted catalytically into methane or synthetic natural gas (SNG), according to the Sabatier reaction ( $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$ ). SNG can be transported and supplied through the current gas grid. Alternatively, ring-opening polymerization (ROP) of epoxides and ring-opening copolymerization (ROCOP) of epoxides and CO<sub>2</sub> represents one of the most successful examples of CO<sub>2</sub> valorization in organic synthesis. It comprises both environmental and economic benefits compared to conventional polymer synthesis processes and contributes to reduce CO<sub>2</sub> emissions.

The Chemical Technologies for Environmental Sustainability research group (TQSA-UPV/EHU) has been actively working on the development of these CO<sub>2</sub> valorization alternatives since 2017. Great efforts have been made in developing different operational strategies, catalytic materials and kinetics models for each approach. The understanding of the reaction mechanism is paramount in modeling, designing, and optimizing industrial operation.

For the CO<sub>2</sub> hydrogenation to CH<sub>4</sub>, the following operation modes have been proposed: carbon capture and utilization in two different stages or, alternatively, integrated operation in a single reaction system. The later approach allows avoiding the previous stages of sequestration, purification and transport of CO<sub>2</sub>, decreasing the global cost and energy consumption of the process. The catalysts developed for the continuous operation consists of Ni or Ru, as active sites, supported on CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or different nature zeolites. Novel formulations based on perovskites or hydroxyapatites have been also developed. In order to carry out integrated CO<sub>2</sub> adsorption and in situ hydrogenation to methane, different adsorbents, such as Ca, Na, Ba or K, have been incorporated over previously described formulations. These new formulations are known as dual function materials (DFMs). On the other hand, very active catalysts are required to turn CO<sub>2</sub> into high value-added polycarbonates under mild reaction conditions at appreciable reaction rates. TQSA group propose the use of transition metal hexacyanoferrate(II) and hexacyanomethylate(III).

Once active, selective and stable formulations were achieved, the knowledge of the reaction scheme and mechanism is useful to develop a kinetic model and design a 2<sup>nd</sup> generation of formulations. Based on spectroscopic (FTIR and NAP-XPS) and modeling techniques, complete reaction pathways have been proposed for the continuous and cycling CO<sub>2</sub> methanation as well as for copolymerization of propylene oxide and CO<sub>2</sub> towards biodegradable aliphatic polycarbonate. This information has been used as a starting point to obtain kinetic models able to describe the kinetic of more promising catalysts developed. Finally, efforts have been focused on modeling CO<sub>2</sub> methanation process able to predict the temperature profile inside the catalytic bed since this reaction is a highly exothermic and the management of the heat generated during the process is critic to avoid thermodynamic limitations. Advantageous results have been obtained, which have resulted useful to propose different reactor designs and operational strategies capable of optimizing the process.

# Decarbonising our energy supply: conversion of biogas by combined dry reforming over advanced nickel catalysts

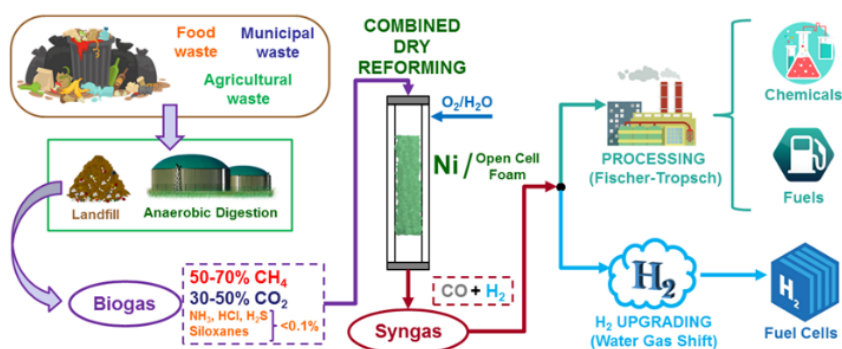
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KEY WORDS: Dry reforming of biogas, Syngas, CO<sub>2</sub> and CH<sub>4</sub> Valorisation, Structured reactors

In view of the current unprecedented global energy crisis the Implementation Plan derived from COP27, recently held in Sharm el Sheikh (Egypt), emphasises the urgent need for rapid and sustained reductions in global GHG emissions across all applicable sectors, by enhancing a clean diversified energy mix, including low-emission and renewable energy, during this critical decade of action. To accomplish this ambitious goal, efficient and integrated approaches based on electrification, sustainable energy resources based on biomass, and CO<sub>2</sub> capture, storage and utilisation are of paramount importance.

Our research is focused on the design of an innovative intensified chemical process for the valorisation of raw biogas (mixture of CO<sub>2</sub>+CH<sub>4</sub>), an increasingly abundant resource, into high-quality syngas (CO+H<sub>2</sub>) by combined dry reforming (with controlled amounts of O<sub>2</sub>/H<sub>2</sub>O) over advanced nickel catalysts supported on open cell foams operating under industrially relevant conditions. In the context of development of carbon utilisation technologies for the synthesis of biochemicals and biofuels from syngas as an intermediate, this strategy will significantly contribute for the simultaneous recycling of the two most important greenhouse gases, with a notable impact on Clean Energy Transition and Climate Change. The obtained results will be valuable for advancing the industrial maturity of this catalytic reforming technology, which is penalised by high energy requirements, limited catalyst durability and the required tuning of the composition of the product stream to be efficiently used for renewable gas-to-liquid processes, and for improving its competitiveness in terms of economic aspects and carbon efficiency.

Thus, our research tasks propose distinct scientific-technological advances devoted to industrial implementation of combined dry reforming of raw biogas focused on (i) lowering the reaction temperature while operating with high flow rates of CH<sub>4</sub>-rich streams (CH<sub>4</sub>/CO<sub>2</sub>>1) by optimising the design of advanced spinel-derived nickel foam catalysts, (ii) increasing the resistance to coking and poisoning by present bioimpurities and (iii) adjusting the H<sub>2</sub>/CO molar ratio of the product stream. All these aspects are challenging pitfalls that need to be addressed to bridge the gap between lab-scale (TRL 1-3) and pilot plant prototype (TRL 4-5). Our research activities will open the way to significant breakthroughs resulting in a step ahead towards a robust, mature intensified technology that could play vital role in a low-carbon modern society.



Combined dry reforming of raw biogas is undoubtedly a very promising process for producing energy carriers, especially considering that GHGs are used as feedstock. However, the role that it will play in the future large-scale production of renewable syngas depends mainly on facing technical and economic issues related to proper catalytic reactor design at the microscopic (nanosized metallic sites) and macroscopic (structured foam catalysts) levels, catalyst deactivation and modulation of H<sub>2</sub>/CO molar ratio of the product stream. Hence, our goal is thus to adequately address key issues related to the integration of renewable technologies into energy systems and the deployment of renewable fuels and bioenergy. Building on these research hypotheses, the overall objective is to design NiAl<sub>2</sub>O<sub>4</sub>-based nickel ceramic foam catalysts and analyse their kinetic performance for combined dry reforming of raw biogas under realistic conditions. These would include the synergistic use of multiple oxidants to obtain syngas with an optimal high H<sub>2</sub>/CO molar ratio, the presence of impurities and the stable operation with short residence times.

## ZABALDUZ

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