ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SPAIN

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

- QUIMA-ULPGC GROUP. Trace Metals (J. Magdalena Santana-Casiano, Melchor González-Dávila, Aridane G. González, D. González-Santana, Verónica Arnone (PhD student))

- Phenolic compounds excreted by marine microalgae, like gentisic acid (GA), influence the Fe marine biogeochemical cycle promoting the formation of the bioavailable Fe in solution. The Fe(III)-GA complex formed in solution produces Fe(II) in a pH-dependent process.
- Transporlar Drift (TDP) is characterized by a higher concentration of trace elements and isotopes (TEIs) than expected for open ocean waters. TDP revealed an important lateral transport that is supplying materials to the central Arctic.
- Fe-binding ligands were determined in cloud waters and these strong organic ligands affect the reactivity, mobility, solubility and speciation of Fe. The complexation of Fe by these ligands is included in cloud models because of the influence on cloud water oxidant capacity.
- In the surface coastal waters of the Macaronesia region (Cape Verde, Canary Islands, and Madeira) both dissolved inorganic and organic complexed Fe and Cu were characterized. 98% of the total dFe was complexed with conditional stability constants between 20.77 and 21.90. More than 99% of dCu was organically complexed with conditional stability constants between 13.40 and 14.42.
- The observed increase in the Fe(II) oxidation rate constant (k') for most of the Macaronesian coastal seawater samples is mainly explained (85%) due to the effect of organic compounds with N in their structures.

- APPLIED PHYSIC DEPARTMENT (Sevilla University) (María Vila Alfageme)

• We have completed a comprehensive compilation on ²³⁴Th measurements through the years. An extensive global oceanic data set, including all the ²³⁴Th data in the published literature, as well as non-published data up to 2019, was compiled by Ceballos-Romero et al. in open access in PANGAEA repository. The compilation include 13 datasets from GEOTRACES cruises and included in GEOTRACES IDP.

https://doi.pangaea.de/10.1594/PANGAEA.918125?format=html#download.

• The use of ²³⁴Th-²³⁸U disequilibrium in the water column is one of the most popular methods to estimate carbon fluxes in the ocean and this technique plays a crucial role in the estimation of carbon export. Thus, it is expected that the compilation serves not only the thorium community, but also modellers and flux evaluation experts, reinforcing the efforts carried out by GEOTRACES to integrate observational and modelling communities. The compilation is presented and discussed in Ceballos-Romero et al. (accepted ESSD, 2022, https://essd.copernicus.org/preprints/essd-2021-259).

- INSTITUTE OF MARINE SCIENCES OF ANDALUSIA (ICMAN-CSIC) (Antonio Tovar Sánchez)

We developed an Automatic Water Autosampler system (AWA) operated from UAVs for sampling surface water sampling. The system significantly helps to the biogeochemical studies of marine systems, especially in extreme or limited access environments. The AWA system has been successfully tested for sampling water for dissolved (<0.22 μ m) trace elements analysis. The AWA is faster, more cost-effective and safer for operators and for the environments than conventional methods. The system has been successfully applied in the Antarctic (i.e. Deception Island) for the chemical (i.e. metals and nutrients) characterization of different water masses (i.e. lake a coastal water) of the island.

GEOTRACES or GEOTRACES relevant cruises

New projects and/or funding

- ATOPFe, Ocean Acidification, temperature and content of organic matter in the persistence of Fe(II) in the Atlantic Ocean. Spanish Project. CTM2017-83476-P. IP: J. Magdalena Santana-Casiano, M. González-Dávila
- COMFORT, Our common future ocean in the Earth system quantifying coupled cycles of carbon, oxygen, and nutrients for determining and achieving safe operating spaces with respect to tipping points. European Union's Horizon 2020 research and innovation programme under grant agreement No 820989. Partner 12. ULPGC responsible: Melchor González-Dávila
- Regional EU FEDER funds. Andalucía. Radioactive tracers and novel modelling techniques for an accurate quantification of the Biological Pump and ocean carbon storage. TRACECARBON. From: 01/09/2021 to: 31/12/2022. 57 200 €
- Novel methodological approach for the study of the sea surf micro-layer based on liquid phase micro-extraction. Department of Knowledge, Research and Universities of the Regional Andalusian Government (Spain), 2021-2023. Role: PI.Budget: 50,000€
- Novel and highly efficient micro-systems for direct determination of trace metals in natural waters. Spanish Ministry of Science and Research. 2019-2022. Role: Researcher. Budget: 90,750€

GEOTRACES workshops and meetings organized (Please include the number of early career researchers involved in each event, when possible)

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Outreach activities conducted (please list any outreach/educational material available that could be shared through the GEOTRACES web site) (We are particularly interested in recordings from webinars from GEOTRACES research)

- Macaronight 2021. La química de metales en un océano cambiante por el cambio climático. https://fpct.ulpgc.es/es/historial-divulgacion-cientifica-fpct/item/572-ya-tenemos-elprograma-de-macaronight-2021.html
- Macaronight 2021. Envenenamiento por metales: ¿Cómo se defienden las microalgas en el medio marino?

https://fpct.ulpgc.es/es/historial-divulgacion-cientifica-fpct/item/572-ya-tenemos-el-programa-de-macaronight-2021.html

• FIMAR 2021. Los metales en el océano: impactos del cambio climático. https://feriainternacionaldelmar.com/programa

Other GEOTRACES activities

- Antonio Tovar-Sánchez, Carolina Gabarró (Coordinators). 2021. *Polar Oceans* (Challenge 6). In: Ocean Science Challenges for 2030. ISBN Vol. 13: 978-84-00-10762-8; e-ISBN Vol. 13: 978-84-00-10763-5. Editorial CSIC: http://editorial.csic.es (correo: publ@csic.es)
- Antonio Tovar-Sánchez (Researche). 2021. Ocean Health (Challenge 4). In: Ocean Science Challenges for 2030. ISBN Vol. 13: 978-84-00-10762-8; e-ISBN Vol. 13: 978-84-00-10763-5. Editorial CSIC: http://editorial.csic.es (correo: publ@csic.es)
- José A. López-López_Guest Editor. Special issue in Frontiers in Marine Science. <u>New</u> <u>Strategies in the Analysis of Marine Pollutants</u>. IF: 4.912, Rank: 6/110 (Mar&Freshwater Biol.)

New GEOTRACES or GEOTRACES-relevant publications (published or in press) (*Please identify those publications acknowledging SCOR funding and for these publications include the number of PhD or postdoc students involved, if possible*)

• Arreguin, M. L., González, A. G., Pérez-Almeida, N., Arnone, V., González-Dávila, M., Santana-Casiano, J. M., 2021. The role of gentisic acid on the Fe(III) redox chemistry in marine environments. Marine Chemistry, 234, 104003.

https://doi.org/10.1016/j.marchem.2021.104003

- Conway, T. M., Homer, T. J., Plancherel, Y., González, A. G., 2021. A decade of progress in understanding cycles of trace elements and their isotopes in the oceans. Chemical Geology, 580, 120381. <u>https://doi.org/10.1016/j.chemgeo.2021.120381</u>
- González González, A., Bianco, A., Boutorh, J., Cheize, M., Mailhot, G., Delort, A. M., Planquette, H., Chaumerliac, N., Deguillaume, L., Sathou, G. 2022. Influence of strong ironbinding ligands on cloud water oxidant capacity.

http://dx.doi.org/10.1016/j.scitotenv.2022.154642

- Arnone, V., González-Santana, D., González-Dávila, M., González, A.G., Santana-Casiano, J. M. 2022. Iron and copper complexation in Macaronesian coastal waters. Mar.Chem. 240, 104087. <u>https://doi.org/10.1016/j.marchem.2022.104087</u>
- Santana Casiano, J. M., González Santana, D., Devresse, Q., Hepach, H., Santana González, C., Quack, B., Engel, A., González Dávila, M. 2022. Exploring the Effects of Organic Matter Characteristics on Fe(II) Oxidation Kinetics in Coastal Seawater https://doi.org/10.1021/acs.est.1c04512
- Abascal, U., Lérida-Toro, V., Lopez-Gutierrez, J. M., & Villa-Alfageme, M. (2022). 137Cs and 129I as dual tracers in the Arctic Ocean. *Ocean Science Meeting*. 2022, 28th February-4th March.
- Villa-Alfageme, M., Muñoz-Nevado, C., & Hurtado-Bermúdez, S. J. (2022). Compilation of sinking velocities in the Atlantic Ocean from 234Th-238U and 210Po-210Pb profiles. *Ocean Science Meeting. 2022*, 28th February-4th March.

- Ceballos-Romero, E., Buesseler, K. O., & Villa-Alfageme, M. (2022). Revisiting five decades of 234Th data: a comprehensive global oceanic compilation. *Ocean Science Meeting*. 2022, 28th February-4th March.
- Herce-Sesa B, <u>López-López JA*</u>, Moreno C (2021) Advances in ionic liquids and deep eutectic solvents-based liquid phase microextraction of metals for sample preparation in Environmental Analytical Chemistry. Trends in Analytical Chemistry.143:116398, IF: 12.296, Rank: 1/87 (Chem. Anal.)
- Belbachir I, López-López JA*, Herce-Sesa B, Moreno C (2022) A liquid micro-extraction based one-step method for the chemical fractionation of copper in seawater. Journal of Hazardous Materials, 430:128505. IF: 10.588, Rank: 10/274 (Environ Sci.)
- Sparaventi E., Araceli Rodríguez-Romero, Andrés Barbosa, Laura Ramajo, Antonio Tovar-Sánchez. Trace elements in Antarctic Penguins and the potential role of guano as source of recycled metals in the Southern Ocean. Chemosphere, 285, 2021, 131423. DOI: <u>https://doi.org/10.1016/j.chemosphere.2021.131423</u>
- Bressac M., Thibaut Wagener, Nathalie Leblond, Antonio Tovar-Sánchez, Céline Ridame, Samuel Albani, Sophie Guasco, Aurélie Dufour, Stéphanie H. M. Jacquet, François Dulac, Karine Desboeufs, and Cécile Guieu.. Subsurface iron accumulation and rapid aluminium removal in the Mediterranean following African dust deposition. Biogeoscience, 18, 6435– 6453, 2021; DOI: <u>https://doi.org/10.5194/bg-18-6435-2021</u>
- Desboeufs K., Franck Fu, Matthieu Bressac, Antonio Tovar-Sánchez, Sylvain Triquet, Jean-François Doussin, Chiara Giorio, Patrick Chazette, Julie Disnaquet, Anaïs Feron, Paola Formenti, Franck Maisonneuve, Araceli Rodríguez-Romero, Pascal Zapf, François Dulac, and Cécile Guieu. Wet deposition in the remote western and central Mediterranean as a source of trace metals to surface seawater. Atmospheric Chemistry and Physics. 22, 2309– 2332, 2022. https://doi.org/10.5194/acp-22-2309-2022.
- Ridame, C., Dinasquet, J., Hallstrøm, S., Bigeard, E., Riemann, L., Van Wambeke, F., Bressac, M., Pulido-Villena, E., Taillandier, V., Gazeau, F., Tovar-Sanchez, A., Baudoux, A.-C., and Guieu, C. N₂ fixation in the Mediterranean Sea related to the composition of the diazotrophic community and impact of dust under present and future environmental conditions, Biogeosciences, 19, 415–435, https://doi.org/10.5194/bg-19-415-2022, 2022.
- Sparaventi E., Rodriíguez-Romero A., Navarro G., Tovar-Sánchez, A. A Novel Automatic Water Autosampler Operated from UAVs for Determining Dissolved Trace Elements. Front. Mar. Sci. 9:879953. doi: 10.3389/fmars.2022.879953

Completed GEOTRACES PhD or Master theses (please include the URL link to the pdf file of the thesis, if available)

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GEOTRACES presentations in international conferences

- González-Santana, D., González-Dávila, M., Lohan, M.C., Artigue, L, Planquette, H., Sarthou, G., Tagliabue, T., and Santana-Casiano, J.M. Iron (II) oxidation kinetics variability in the Atlantic Ocean and development of an improved theoretical equation. Goldschmidt 2021 (4-9 July 2021). Oral communication.
- Arnone, V., González-Dávila, M., González, A.G., Santana-Casiano, J.M. The influence of coastal waters on the organic complexation of iron and copper in the Macaronesia region. ASLO 2021 Aquatic Sciences Meeting (22-27 June 2021). Oral communication.

- Arnone, V., González-Dávila, M., González, A.G., Santana-Casiano, J.M. Iron and copper complexation in the Macaronesian coastal waters. Goldschmidt 2021 (4-9 July 2021). Oral communication.
- González Santana, D. Santana Casiano, J. M., González Dávila, M. 2022. The organic matter effect on Fe(II) oxidation kinetics within coastal seawater. EGU General Assembly 2022 (23-27 May 2022). Oral communication. <u>https://doi.org/10.5194/egusphere-egu22-5936</u>
- José A. López_López, Belén Herce-Sesa, Franz Jirsa, Carlos Moreno. Selective ionic liquid based micro-extraction of Cd: An approach to trace metals speciation in marine waters. IV Pollutant and Toxic Ions and Molecules. Inivited talk. 31 october-04 November 2021. Caparica, Portugal.
- Abascal, U., Lérida-Toro, V., Lopez-Gutierrez, J. M., & Villa-Alfageme, M. (2022). 137Cs and 129I as dual tracers in the Arctic Ocean. Ocean Science Meeting. 2022, 28th February-4th March.
- Villa-Alfageme, M., Muñoz-Nevado, C., & Hurtado-Bermúdez, S. J. (2022). Compilation of sinking velocities in the Atlantic Ocean from 234Th-238U and 210Po-210Pb profiles. Ocean Science Meeting. 2022, 28th February-4th March.
- Ceballos-Romero, E., Buesseler, K. O., & Villa-Alfageme, M. (2022). Revisiting five decades of 234Th data: a comprehensive global oceanic compilation. Ocean Science Meeting. 2022, 28th February-4th March.
- Sparaventi E., Araceli Rodríguez-Romero, Andrés Barbosa, Laura Ramajo, Antonio Tovar-Sánchez. The role of Antarctic penguins recycling trace metals in the Southern Ocean. CICTA. November 29th to December 2nd, 2021, Blumenau, SC, Brazil. Oral Comunication.

Submitted by:

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