GEOTRACES SCIENTIFIC STEERING COMMITTEE Annual report to SCOR 2021/2022

June 2022

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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN ARGENTINA

May 1st, 2021 to April 30th, 2022

GEOTRACES workshops and meetings organized

The first international edition of **Blowing South: Southern Hemisphere Dust Symposium** was held– On line event: November 8-10, 2021.

This symposium focused on bringing together international scientists working on the observation and modeling of the current and paleodust cycle in the southern hemisphere, across temporal and spatial scales, including feedbacks with climate and impact on society.

The participants discussed the latest advances in their work and will share their main scientific questions. This provided an opportunity to discuss recent and ongoing work on these critical issues and to expand on pre-existing collaborations that in certain research areas and in certain regions are still quite limited.

Website: http://dust2021.cima.fcen.uba.ar/

Coordinators:

Nicolás J. Cosentino. Instituto de Geografía (PUC Chile), Núcleo Milenio Paleoclima. Santiago, Chile.

Augusto Crespi Abril. Instituto Patagónico del Mar (IPaM, UNPSJB), Centro para el Estudio de Sistemas Marinos (CESIMAR, CCT CONICET CENPAT). Puerto Madryn, Argentina.

François De Vleeschouwer. Instituto Franco-Argentino para el Estudio del Clima y sus Impactos (IRL3351 IFAECI/CNRS-CONICET-UBA-IRD). Buenos Aires, Argentina

Antonela Iturri. Instituto de Ciencias de la Tierra y Ambientales de La Pampa (INCITAP, CONICET-UNLPam), Universidad Nacional de La Pampa. Santa Rosa, Argentina.

Flavio E. Paparazzo. Instituto Patagónico del Mar (IPaM, UNPSJB), Centro para el Estudio de Sistemas Marinos (CESIMAR, CCT CONICET CENPAT). Puerto Madryn, Argentina.

Other GEOTRACES activities

- Together with Dr. Melisa Daiana Fernandez Severini (IADO-CONICET, Bahía Blanca, Argentina), we are beginning to plan a series of trace metal measurements in the Argentine Sea. Some campaigns have been canceled due to COVID-19. However, we hope that by 2023 some measurements can be made.
- At CENPAT (Technological Scientific Center of which our institute is a part), we submitted a project application to CONICET for the purchase of an IRMS coupled to an Elemental Analyzer. Hopefully next year we will have good news!!

Submitted by Flavio Emiliano Paparazzo (paparazzocnp@gmail.com).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN AUSTRALIA

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

Newly compiled Southern Ocean Ligand (SOLt) Collection of all publicly available Fe complexation datasets for the Southern Ocean including dissolved Fe concentrations, Fe-binding ligand concentrations, and complexation capacities for 25 studies between 1995 – 2019. Link to dataset

GEOTRACES or GEOTRACES relevant cruises

- Southern Ocean Time Series 2021: Process study GIpr08 by Elizabeth Shadwick/Zanna Chase/ Andrew Bowie (Th, Nd isotopes, [REE], TM aerosols)
- *RV Investigator* Jan-Mar 2022 voyage GIpr11 was cancelled due to COVID. Rescheduled for Jan-Mar 2023.

New projects and/or funding

- Successful ARC Infrastructure grant for \$552K: *HydroBox: A containerised hydrochemistry lab for Australian oceanography* led by Chase, Lannuzel et al.
- Australian Research Council Special Research Initiative, Australian Centre for Excellence in Antarctic Research (https://antarctic.org.au/) with two upcoming science voyages on the new Australian Icebreaker RVS Nuyina: Aug-Sep 2023 Marginal Sea Ice Zone (MIZ) voyage around 110°E; Feb-Mar 2025 Denman Ocean voyage on continental shelf adjacent to the Denman Glacier/ Shackleton ice shelf
- A number ACEAS of postdoctoral job vacancies with deadlines on the 26th June: see https://antarctic.org.au/vacancies/

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Genovese, C., Grotti, M., Ardini, F., Wuttig, K., Vivado, D., Cabanes, D., ... Lannuzel, D. (2022). Effect of salinity and temperature on the determination of dissolved iron-binding organic ligands in the polar marine environment. *Marine Chemistry*, 238(August 2021), 104051. (Student-led)
- Seyitmuhammedov, K., Stirling, C. H., Reid, M. R., van Hale, R., Laan, P., Arrigo, K. R., ... Middag, R. (2022). The distribution of Fe across the shelf of the Western Antarctic Peninsula at the start of the phytoplankton growing season. Marine Chemistry, 238, 104066.
- Smith, A. J. R., Ratnarajah, L., Holmes, T. M., Wuttig, K., Townsend, A. T., Westwood, K., ... Lannuzel, D. (2021). Circumpolar Deep Water and Shelf Sediments Support Late Summer Microbial Iron Remineralization. Global Biogeochemical Cycles, 35(11), e2020GB006921. (Student-led; 3 post docs)
- Tagliabue, A., Bowie, A. R., Holmes, T., Latour, P., van der Merwe, P., Gault-Ringold, M., ... Resing, J. A. (2022). Constraining the Contribution of Hydrothermal Iron to Southern Ocean Export Production Using Deep Ocean Iron Observations. *Frontiers in Marine* (1 student; 3 post docs)

Completed GEOTRACES PhD or Master theses

Masters:

• Talitha Nelson: The influence of Antarctic Krill (Euphausia superba) swarms on the iron and carbon cycles in the Southern Ocean, University of Tasmania

PhD:

- Pauline Latour: Manganese biogeochemistry in the Southern Ocean, University of Tasmania
- Abigail Smith: *The distribution and availability of iron in the Antarctic coastal ocean,* University of Tasmania

GEOTRACES presentations in international conferences

• Creac'h et al. 2021 Neodymium isotopes in co-located sediment and seawater samples from the East Antarctic margin

Submitted by Taryn Noble (<u>Taryn.Noble@utas.edu.au</u>).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CANADA

May 1st, 2021 to April 30th, 2022

During the last year Canadian PI's continue to work closely with US and European colleagues on Arctic GEOTRACES synthesis projects and a number of jointly authored manuscripts are planned, in progress or published at this point. The Canadian GEOTRACES community continues to support an ongoing process study making observations of bioactive trace elements and trace element- microbe interactions on time-series cruises completed along Line P in the northeast Pacific. The Canadian community is examining the impact of recent marine heatwaves on chemical and biological fields along Line P. Of note is a new and historic agreement between the Université Laval and the Ifremer to foster collaboration between Canadian and French oceanographers in the Arctic and North Atlantic that should promote GEOTRACES relevant research. The partnership includes ship-time exchange between the icebreaker *CCGS Amundsen* and three science vessels of the French Fleet: the *Pourquoi Pas?*, the *Thalassa* and the *Atalante*. This sharing of research platforms will coordinate research efforts to study high latitude marine environments and their response to ongoing climate change in line with GEOTRACES research objectives.

Our new, GEOTRACES relevant scientific results, publications and presentations are summarized below.

GEOTRACES or GEOTRACES relevant cruises

- Jean-Eric Tremblay (ULaval) and Jay Cullen (UVic) conducted trace element and isotope sampling in the Canadian Arctic as part of the ArcticNet supported NTRAIN program (<u>https://arcticnet.ulaval.ca/project/nutrient-fluxes-and-living-marine-resources-in-the-inuit-nunangat/</u>) in the eastern, central and western Arctic Ocean.
- Jay Cullen (UVic), Maite Maldonado (UBC), Andrew Ross (DFO) Samples for trace elements and copper ligand measurement were collected using GEOTRACES protocols during Line P cruises in 2021 and 2022 as part of the Line P Iron Program, a GEOTRACES Process Study (GPpr07). Samples for Fukushima derived radionuclides were collected in collaboration with John N. Smith (DFO).

New projects and/or funding relevant to GEOTRACES

- A new project that overlaps with Line P (stations P16, P20 and P26) and expands monitoring of copper ligands in the subarctic NE Pacific to a zone encompassing 38 stations has been approved for funding by the North Pacific Anadromous Fish Commission (NPAFC) and BC Salmon Restoration Initiative Fund (BC SRIF):
- Cullen, J.T., Peña, A., Ross, A.R.S. 2021-2023. Linking salmon survival to climate change through its impact on primary production via nutrient and metal ligand distributions in the North Pacific. International Year of the Salmon (IYS) 2022 Pan-Pacific Winter High Seas Expedition. NPAFC/BC SRIF (\$69 K/yr).
- Funding from the new Fisheries and Oceans Canada (DFO) Competitive Science Research Fund (CSRF) to support sampling and analysis of trace metals and ligands along Line P (GEOTRACES Process Study GPpr07) has also been approved for the next 3 years:

- Ross, A.R.S., Peña, A., Christian, J. 2021-2024. Predicting marine productivity in a changing climate linking phytoplankton biomass and ecology to ocean conditions and related changes in the availability of essential trace metals. DFO/CSRF (\$43 K/yr).
- Myers, P. (U. Alberta) and 7 others 2022-23 Ecosystems and Ocean Science Contribution Framework Open Call for Proposals. Understanding the bio-physical processes impacting the evolution of Tallurutiup Imanga and Pikialasorsuaq in a warming climate DFO \$717,063
- Else, B. (U. Calgary) and others 2022. FoxSIPP: The Foxe Basin Sea Ice Pump Project. NSERC Ship Time \$210,000
- Bhatia, M. (U. Alberta) and others 2022. The changing coastal environment in the Canadian High Arctic: Past, present, and future. NSERC Ship Time \$118,000

GEOTRACES relevant workshops and meetings organized

- Waterman, S. (UBC) 55th Canadian Meteorological and Oceanographic Society (CMOS) Congress, virtual, May 202. Primary Session Chair: "The Changing Arctic Ocean"
- Waterman, S. (UBC) ArcticNet Annual Scientific Meeting, virtual, Dec 2021. Primary Session Chair: "Ocean dynamics in the Arctic: from coast to open ocean"
- Maldonado, M. (UBC). BioGeoSCAPES Ocean metabolism and nutrient cycles on a changing planet. CSIR National Institute of Oceanography, Goa, India. July 15, 2021
- Maldonado, M. BioGeoSCAPES community building in other countries. A US National Biogeoscapes Workshop supported by OCB November 10-12, 2021 (https://www.usocb.org/ocb-scoping-workshop-laying-the-foundation-for-a-potential-future-biogeoscapesprogram/)

Outreach activities conducted

• <u>Podcast (Maldonado); September 21, 2021</u>. Episode 10: Unraveling the mysteries of the Indian Ocean by Nature India (https://www.nature.com/articles/d44151-021-00050-w)

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Colombo, M., J. Li, B. Rogalla, S.E. Allen, M.T. Maldonado. 2022. Particulate trace element distributions along the Canadian Arctic GEOTRACES section: shelf-water interactions, advective transport and contrasting biological production. Geochimica et Cosmochimica Acta, 323: 183-201. doi.org/10.1016/j.gca.2022.02.013
- Colombo, M., B. Rogalla, J. Li, S.E. Allen, K.J. Orians, M.T. Maldonado. 2021. Canadian Arctic Archipelago shelf-ocean interactions: a major iron source to Pacific-derived waters transiting to the Atlantic. Global Biogeochemical Cycles 35 (10) id. e07058. https://doi.org/10.1029/2021GB007058
- Cooke M., M. Trudel, J.P. Kellogg, J.T. Cullen, J.F. Mercier and J. Chen. (2022). Radioactivity concentration measurements in fish samples collected (2011-2019) from the west coast of Canada after the Fukushima accident. Journal of Environmental Radioactivity.
- De Vera J., P. Chandan, P. Pinedo-González, S.G. John, S.L. Jackson, J.T. Cullen, M. Colombo, K.J. Orians, B.A. Bergquist. (2021) Anthropogenic lead pervasive in Canadian

Arctic seawater. Proceedings of the National Academy of Sciences. 118(24) https://doi.org/10.1073/pnas.2100023118

- Jensen, J., J.T. Cullen, S.L. Jackson, L. Gerringa, D. Bauch, R. Middag, R.M. Sherrell, J. Fitzsimmons. (2022). A novel relationship between dissolved copper and nickel in the Arctic Ocean. Journal of Geophysical Research Oceans.
- Krisch, S., M.J. Hopwood, S. Roig, L.J.A. Gerringa, R. Middag, M.M. Rutgers van der Loeff, M.V. Petrova, P. Lodeiro, M. Colombo, J.T. Cullen, S.L. Jackson, L. Heimbürger-Boavida, E.P. Achterberg. (2022). Arctic-Atlantic exchange of iron, manganese, cobalt, nickel, copper and zinc with a focus on Fram Strait. Global Biogeochemical Cycles.
- Kuang, C, M. Maldonado, J.T. Cullen, R. Francois. (2022). Factors controlling the temporal variability and spatial distribution of dissolved cadmium in the coastal Salish Sea. Continental Shelf Research.
- Meyer, A.C.S., J.T. Cullen, D. Grundle. (in revision). Nitrous oxide distributions in the oxygenated water column of the Sargasso Sea. Atmosphere-Ocean.
- Meyer, A.C.S., D. Grundle, J.T. Cullen. (2021). Selective uptake of rare earth elements in marine systems as an indicator of and control on aerobic bacterial methanotrophy. Earth and Planetary Science Letters. 558, https://doi.org/10.1016/j.epsl.2021.116756
- Nixon, R.L., M.A. Peña, R. Taves, *D.J. Janssen, J.T. Cullen, A.R.S. Ross (2021). Evidence for the production of copper-complexing ligands by marine phytoplankton in the subarctic northeast Pacific. Marine Chemistry 237 https://doi.org/10.1016/j.marchem.2021.104034
- Shaked, Y., B.S. Twining, A. Tagliabue and M.T. Maldonado. 2021. Probing the bioavailability of dissolved iron to marine eukaryotic phytoplankton using in situ single cell iron quotas. Global Biogeochemical Cycles. 35, e2021GB006979. https://doi.org/10.1029/2021GB006979
- Taves, R., D.J. Janssen, M.A. Peña, A.R.S. Ross, K.G. Simpson, W.R. Crawford, J.T. Cullen. (2022). Relationship between surface dissolved iron inventories and net community production during a marine heatwave in the subarctic northeast Pacific. Environmental Science: Processes and Impacts.
- Whitmore, L.M., A.M. Shiller, T. Horner, Y. Xiang, D. Bauch, F. Dehairs, P. Lam, J. Li, M.T. Maldonado, C. Mears, R. Newton, A. Pasqualini, H. Planquette, R. Rember, and H. Thomas. 2022. Strong Margin Influence on the Arctic Ocean Barium Cycle Revealed by Pan-Arctic Synthesis Journal of Geophysical Research: Oceans, 127, e2021JC017417. https://doi.org/10.1029/2021JC017417

GEOTRACES presentations in international conferences

- Rogalla, B., Colombo, M., Li, J., Allen, S., Orians K., Maldonado M.T. Shelf-ocean interactions in the Canadian Arctic Archipelago as a major source of iron to the pacific derived waters transiting to the North Atlantic. Ocean Sciences Meeting 2022. Honolulu, HI, USA. February 27-March 4, 2022.
- Colombo, M., Li, J., Rogalla, B., Desai, D., LaRoche, J. Allen, S. Maldonado M.T. Particulate trace element dynamics in the Canadian Arctic Ocean. Ocean Sciences Meeting 2022. Honolulu, HI, USA. February 27-March 4, 2022.

Submitted by Dr. Jay T. Cullen (jcullen@uvic.ca).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CHILE

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

• The concentration of dissolved metals (<0.45um) in surface estuarine waters of Chilean Patagonia archipielago has been recently analysed (2021). During austral spring, across a salinity front located at 50°S, the dFe concentrations can reach concentrations as low as 5nM despite the proximity of continental iron sources (e.g. Glacier discharges). Measurements of the concentration of metals in waters filtered by 0.02um suggest that most of the dFe is in the form of colloids (Fig.1).

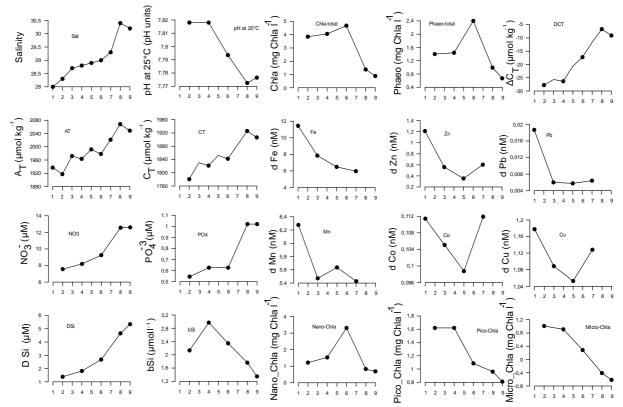


Figure 1. Concentration of dissolved metals (<0.45um), macronutrients, chlorophyll a, and carbonic acid system parameters across a salinity gradient in fiord waters of Patagonia Archipelago (50°S).

• Iron addition experiments to estuarine waters suggest that the rate of macronutrient uptake in surface waters can be increased by enrichment in 5nM of unchelated iron (Fig.2).

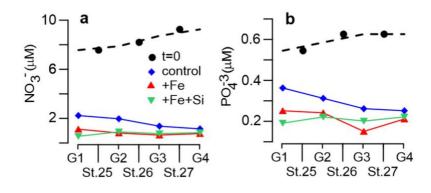


Figure 2. Surface water nitrate and phosphate at the start (t = 0) and after three days of "on-deck" incubation (t = 3). Dots depict the surface water concentration of macronutrients within a salinity gradient (shown in Fig.1) where experimental carboys (G1-G4) were filled. Coloured symbols depict the concentration of macronutrients (in controls and in + 5nM Fe and +5nM Fe+Si treatments) after 3 days of "on-deck" incubation.

GEOTRACES or GEOTRACES relevant cruises

In January-February 2022, the Fjorflux project (a cooperation project between Germany, Chile and Argentina) carried out on *R/V Meteor* (M179) explored inland waters of South Patagonia and the Drake Passage. In this campaign, phytoplankton composition, carbonate system parameters, methane, phytoplankton size structure, phytoplankton toxine content was studied, along with sampling of surface waters for metals analysis (using a towed fish) and on-deck bottles experiments. Preliminary results suggest that, in this period of the year (austral summerlate austral summer), dFe did not play a role modulating phytoplankton dynamic. However silicic acid seems modulated new productivity and pCO2 in surface waters.

Submitted by Rodrigo Torres (<u>rtorresaavedra@gmail.com</u>).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CHINA-BEIJING

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

- Surface and profile samples were collected from the western NPSG during the GP09 spring cruise and GPpr15 summer and winter cruises with an underway fish-towing system and a GEOTRACES standard rosette sampling system. N₂ fixation rates and diazotroph abundances were measured by ¹⁵N₂ gas dissolution method and *nifH* gene qPCR, respectively.
- Distribution of N₂ fixation rates in the western North Pacific is shown in Figure 1. Surface and depth-integrated rates ranged from below detection limit to 15.83 nmol N L⁻¹ d⁻¹ and below detection limit to 764.3 µmol N m⁻² d⁻¹, respectively. High rates were mostly found in between 15°N and 20°N regions in the North Pacific Subtropical Gyre (NPSG), whereas rates were around the detection limits in the areas south of 15°N. Vertically, high rates were generally found in the upper 50 m water column and decreased dramatically at deeper depths. Among seasons, N₂ fixation rates were significantly higher during the warm seasons (spring and summer) than during winter.

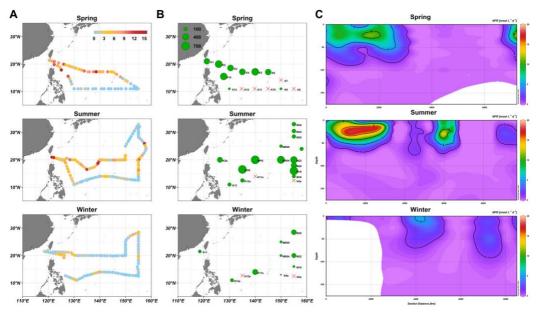


Figure 1. N_2 fixation rate in the western North Pacific during GP09 and GPpr15 summer and winter cruises. A. Surface N_2 fixation rate (nmol N L⁻¹ d⁻¹). B. Depth-integrated N_2 fixation rate (µmol N m⁻² d⁻¹). C. Vertical distribution of N_2 fixation rate (nmol N L⁻¹ d⁻¹).

• We found that iron:nitrogen (Fe:N) supply ratios are the most important factor in regulating the distribution of N₂ fixation across the tropical ocean (Figure 3). Fe:N supply ratio shows a clear spatial coherence with both depth-integrated N₂ fixation rates and *nifH* gene abundances, with elevated values for NPSG stations and low values around the NEC where Ekman divergence shoals the nitracline upward to the euphotic depth, enhancing turbulent nitrate supply from below, and aerosol Fe supply from above is reduced.

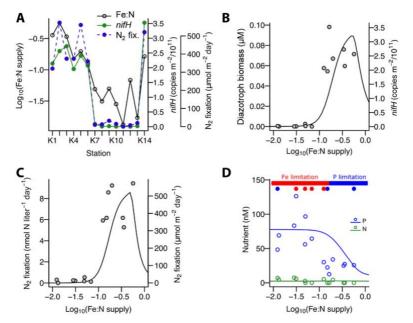


Figure 2. Regulation Fe:N supply ratios on N_2 fixation across the tropical western North Pacific.

• By conducting nutrient (iron and phosphate, Fe and P) amendment experiments across the western North Pacific, we found that switches of diazotroph nutrient limitation from the marginal north South China Sea (NSCS) to the NPSG. N₂ fixation rates were co-limited both Fe and P in the NSCS, nutrient-replete in Kuroshio, P-limited in the western Philippine Sea, and changed to Fe-limitation in the further Gyre region and the North Equatorial Current.

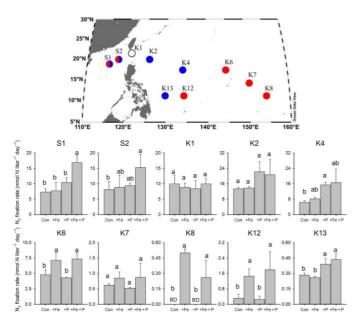


Figure 3. Response of N_2 fixation to nutrient addition. Symbols summarize the nutrient limitation of N_2 fixation found at each site: red, Fe limitation; blue, P limitation; split red/blue, Fe-P colimitation; white, Fe and P replete.

• Distribution of ²²⁶Ra in the surface and bottom layers of the world ocean is shown in Figure 4. We synthesize historical dissolved ²²⁶Ra data from multiple international research programs including GEOSECS, TTO, and GEOTRACES to build a global picture of ²²⁶Ra distribution throughout the global ocean. The activities of ²²⁶Ra in the world's ocean increase along the thermohaline circulation pathways. Deep and bottom water masses are

found with characteristic $^{226}\mathrm{Ra}$ properties confirming that $^{226}\mathrm{Ra}$ is a good thermohaline tracer.

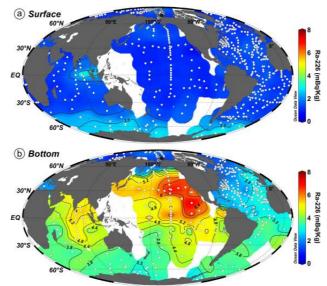


Figure 4. The white dots represent sampling stations extracted mainly from databases from multiple sources that are described with details in the Data Sources section. The original data and figure-gridding algorithms are presented in the Supplementary Information section.

- By investigating the distribution of Ra and Rn isotopes in coastal waters, submarine groundwater discharge nutrients into coastal waters were estimated. The results showed that submarine groundwater discharge plays a significant role in the nutrients cycle in coastal waters.
- We studied the reduction of Hg²⁺ mediated by microalgae and aerobic bacteria in surface marine water and microalgae cultures under dark and sunlight conditions. The comparable reduction rates of Hg²⁺ with and without light suggest that dark reduction by biological processes is as important as photochemical reduction in the tested surface marine water and microalgae cultures. The contributions of microalgae, associated free-living aerobic bacteria, and extracellular substances to dark reduction were distinguished and quantified in 7 model microalgae cultures. The results suggest it is the aerobic bacteria associated with microalgae that are directly involved in dark Hg²⁺ reduction. The aerobic bacteria in the microalgae cultures were isolated and a rapid dark reduction of Hg²⁺ followed by a decrease of Hg⁰ was observed by aerobic bacteria *Alteromonas* spp., *Algoriphagus* spp., and uncultured bacterium clone Tir12-16S. The reduction of Hg²⁺ and re-oxidation of Hg⁰ were demonstrated in aerobic bacteria *Alteromonas* spp. by using double isotope tracing (¹⁹⁹Hg²⁺ and ²⁰¹Hg⁰). These findings highlight the importance of algae-associated aerobic bacteria in Hg transformation in oxic marine water.
- Mercury isotope dilution and isotope addition techniques were utilized to determine the methylation and demethylation potential of Hg at concentrations comparable to that in natural environments by 15 common marine microalgae (8 species of Diatoms, 4 species of Dinoflagellates, 2 species of Chlorophyta and 1 species of Chrysophyte). Methylation of inorganic Hg was found to be negligible in the culture of all tested marine microalgae, while 6 species could significantly induce the demethylation of methylmercury (MeHg). The rates of microalgae-mediated MeHg demethylation were at the same order of magnitude as that of photodemethylation, indicating that marine microalgae may play an important role in the degradation of MeHg in marine environments. Further studies suggest that the demethylation

of MeHg by the microalgae may be mainly caused by their extracellular secretions (via photo-induced demethylation) and associated bacteria, rather than the direct demethylation of MeHg by microalgae cells. In addition, it was found that thiol groups may be the major component in microalgal extracellular secretions that lead to the photo-demethylation of MeHg.

GEOTRACES or GEOTRACES relevant cruises

- 2021 Northwest Pacific Ocean Multidisciplinary Cruise (May 8 to Jun 18, 2021).
- Surficial and core samples were collected to analyze Hg species and isotopes during this cruise.

New projects and/or funding

- NSFC- General Fund: Cross-shelf transport of sedimentary iron in the South China Sea, #42176037, ¥590K, 2022-2025, PI: Yihua Cai
- NSFC-Youth Fund: The source, fractionation, and flux of particulate iron, zinc, cadmium in the northwestern Pacific Ocean, #42006045, ¥240K, 2021-2023, PI: Kan Zhang
- NSFC-Youth Fund: Effect of light intensity on the release and transfer of *Trichodesmium* derived nitrogen, #42106041, ¥300K, 2022-2024, PI: Zuozhu Wen

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Wen, Z., Browning, T. J., Cai, Y., Dai, R., Zhang, R., Du, C., Jiang, R., Lin, W., Liu, X, Cao, Z., Hong, H., Dai, M., Shi, D. (2022). Nutrient regulation of biological nitrogen fixation across the tropical western North Pacific. Science Advances, 8, eab17564.
- Xu B, Li S., Burnett W C., Zhao S., Santos I R., Lian E., Chen X., Yu Z. (2022). Radium-226 in the global ocean as a tracer of thermohaline circulation: Synthesizing half a century of observations. Earth-Science Reviews, 226, 103956.
- Cao, Z., Rao, X., Yu, Y, Siebert, C, Hathorne, Ed C., Liu, B, Wang, G., Lian, E., Wang, Z., Zhang, R., Gao, L, Wei, G., Yang, S., Dai, M., Frank, M (2021). Stable barium isotope dynamics during estuarine mixing. Geophysical Research Letters, 48, e2021GL095680.
- Chen, X., Du, J., Yu, X., Wang, X. (2021). Porewater-derived dissolved inorganic carbon and nutrient fluxes in a saltmarsh of the Changjiang River Estuary. Acta Oceanologica Sinica, 40, 32-43.
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- Peng, T., Zhu, Z., Du, J., Liu, J. (2021). Effects of nutrient-rich submarine groundwater discharge on marine aquaculture: A case in Lianjiang, East China Sea. Science of the Total Environment, 786, 147388.

- Liu, J., Du, J., Yu, X. (2021). Submarine groundwater discharge enhances primary productivity in the Yellow Sea, China: Insight from the separation of fresh and recirculated components. Geoscience Frontiers, 12, 101204.
- Peng, T., Liu, J., Yu, X., Zhang, F., Du, J. (2022). Assessment of submarine groundwater discharge (SGD) and associated nutrient subsidies to Xiangshan Bay (China), an aquaculture area. Journal of Hydrology, 610, 127795.
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- Che, H., Zhang, J., Liu, Q. He, H. Zhao, Z. (2022). Refining the contribution of riverine particulate release to the global marine Nd budget. Progress in Earth and Planetary Science, 9, 22.
- Liu Q, Zhang J, He H, Ma L, Li H., Zhu, S. Matsuno T. (2022). Significance of nutrients in oxygen-depleted bottom waters via various origins on the mid-outer shelf of the East China Sea during summer. Science of the Total Environment, 826, 154083.
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- Zhang, X., Guo, Y., Liu, G., Liu, Y., Song, M., Shi, J., Hu, L., Li, Y., Yin, Y., Cai, Y, Jiang, G. (2021). Dark Reduction of Mercury by Microalgae-Associated Aerobic Bacteria in Marine Environments. Environmental Science & Technology, 55, 14258-14268.
- Li, Y, Li, D, Song, B., Li, Y. (2022). The potential of mercury methylation and demethylation by 15 species of marine microalgae. Water Research, 215, 118266.

Completed GEOTRACES Ph.D. or Master theses

• Wei Lin. Biogeochemistry of barium in the western North Pacific and its application of tracing organic carbon remineralization in the twilight zone. Master thesis, 2021.

GEOTRACES presentations in international conferences

- Zhimian Cao, Wei Lin, Yating Li, Xinting Rao.Barium concentrations and isotopes along the GEOTRACES-GP09 transect in the western North Pacific. AGU Fall Meeting, 2021, New Orleans, LA, USA (Poster).
- Jinlong Wang, Quantification of oceanic input contribution to radionuclides and trace metals in marginal seas. Ocean Science Meeting, 2022, Online (Oral Session).

Submitted by Dalin Shi (<u>dshi@xmu.edu.cn</u>).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CHINA-TAIPEI

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

- Nitrogenase is vulnerable to O2 and oxidative stress generated in photosynthesis. However, Trichodesmium carries out nitrogen fixation and photosynthesis simultaneously and possesses the capability to bloom in the surface water. Chen et al. (2022) demonstrates that nickel superoxide dismutase reduces oxidative stress generated during photosynthesis in Trichodesmium, and thus protects its nitrogen fixation process under high light conditions.
- Although aerosol sizes are highly associated with the solubilities and the deposition fluxes of aerosol Fe in the surface ocean, systematic studies for the association of the solubilities and fluxes have been limited. Using five size-fractions of dry aerosols collected at two islets in the East China Sea, Hsieh et al. (2022) found that either single or two averaged deposition velocities (fine/coarse) used in most of previous studies significantly overestimate dissolvable Fe fluxes. Aerosol sizes are essential parameters to accurately estimate the solubility and the fluxes of aerosol dissolvable Fe to the ocean.
- Bluefin tuna (BFT) is an apex predatory, long-lived, migratory pelagic fish that is widely distributed throughout the world's oceans. These fish have very high concentrations of neurotoxic methylmercury (MeHg) in their tissues, which increase with age. Tseng et al. (2021) shows that Hg accumulation rates (MARs) in BFT as a global pollution index can reveal global patterns of Hg pollution and bioavailability in the oceans and further reflect both natural and anthropogenic emissions and regional environmental features. Overall, MARs provide a means to compare Hg bioavailability among geographically distinct populations of upper trophic level marine fish across ocean subbasins, to investigate trophic dynamics of Hg in marine food webs, and furthermore, to improve public health risk assessments of Hg exposure from seafood.

GEOTRACES or GEOTRACES relevant cruises

- Scheduled Legend cruise to the Western Philippian Sea, August 2022 (9 days)
- Scheduled NORI cruise to the Western Subtropical North Pacific, August 2023 (18 days)

New projects and/or funding

- Grant Title: Anthropogenic aerosol trace metal marine biogeochemistry, funded by Academia Sinica (2021/01-2025/12, 5M NTD per year)
- Grant Title: Aerosol Fe biogeochemical cycling in the Northwestern Pacific Ocean (II): phase transformation and field validation, funding source: MOST (2022/08-2025/07, pending)
- Grant Title: The role of Ni on photosynthesis and nitrogen fixation in Trichodesmium, funding source: MOST (2022/08-2025/07, pending)
- Grant Title: The Depositional Fluxes and Impacts of Natural & Anthropogenic Aerosols in the Northwestern Pacific Ocean: Academia Sinica Thematic Research Program Proposal (2023/01-2025/12, pending).

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Chen, C.-C., I. B. Rodriguez, Y.-L. L. Chen, J. P. Zehr, Y.-R. Chen, S.-T. D. Hsu, S.-C. Yang, and T.-Y. Ho*(2022) Nickel superoxide dismutase protects nitrogen fixation in Trichodesmium. Limnology and Oceanography:Letters doi: 10.1002/lol2.10263
- Li, H.-T., S. Tuo, M.-C. Lu, and T.-Y. Ho* (2022) The effects of Ni availability on H2 production and N2fixation in a model unicellular diazotroph: the expression of hydrogenase and nitrogenase. Limnology and Oceanography doi: 10.1002/lno.12151
- Hsieh, C.-C., H.-Y. Chen, and T.-Y. Ho* (2022) The effect of aerosol size on Fe solubility and deposition flux: A case study in the East China Sea. Marine Chemistry doi: 10.1016/j.marchem.2022.104106
- Liao, W.-H., S. Takano, H.-A. Tian, H.-Y. Chen, Y. Sohrin, and T.-Y. Ho* (2021) Zn elemental and isotopic features in the sinking particles of the South China Sea: the implications to its sources and sinks. Geochimica et Cosmochimica Acta doi: 10.1016/j.gca.2021.09.013.
- Hsieh, Y.-T., Geibert, W., Woodward, E.M.S., Wyatt, N.J., Lohan, M.C., Acterberg, E.P., and Henderson, G.M. (2021) Radium-228-derived ocean mixing and trace element inputs in the South Atlantic. Biogeosciences, 18, 1645-1671.
- Hsieh, Y.-T., Bridgestock, L., Scheuermann, P.P., Seyfried, Jr., W.E., Henderson, G.M. (2021) Barium isotopes in mid-ocean ridge hydrothermal vent fluids: a source of isotopically heavy Ba to the ocean. Geochimica et Cosmochimica Acta, 292, 348-363.
- Ruo-Mei Wang, Chen-Feng You, Chuan-Hsiung Chung, Kuo-Fang Huang, Ya-Ju Hsu, (2022) Uranium isotopes in a subtropical mountainous river of Taiwan: Insight into physical and chemical weathering processes, Journal of Hydrology, 607, , 127481, ISSN 0022-1694, https://doi.org/10.1016/j.jhydrol.2022.127481.
- Huei-Ting Lin, Hong-Wei Chiang, Tsai-Luen Yu, Marcus Christl, Juan Liu, Kristine DeLong, and Chuan-Chou Shen, (2021) 236U/238U Analysis of Femtograms of 236U by MC-ICPMS, Analytical Chemistry, 93 (24), 8442-8449, DOI: 10.1021/acs.analchem.1c00409
- Su-Cheng Pai, Yu-Ting Su, Mei-Chen Lu, Yalan Chou, and Tung-Yuan Ho, Determination of Nitrate in Natural Waters by Vanadium Reduction and the Griess Assay: Reassessment and Optimization, ACS ES&T Water 2021 1 (6), 1524-1532, DOI: 10.1021/acsestwater.1c00065
- Tseng, C.-M.*, S.-J. Ang, Y.-S. Chen, J.-C. Shiao, C. H. Lamborg, X. S. He, and R. Reinfelder (2021) Bluefin tuna reveal global patterns of mercury pollution and bioavailability in the world's oceans. PNAS, 118 (38) e2111205118.
- Ho, P.-C., Okuda, N., Yeh, C.-F., Wang, P.-L., Gong, G.-C. and Hsieh, C.-h. (2021) Carbon and nitrogen isoscape of particulate organic matter in the East China Sea. Progress in Oceanography, 197, 102667 (https://doi.org/10.1016/j.pocean.2021.102667).

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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN COLOMBIA

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

- Technical report to environmental authorities about:
 - C3 Parameters as total cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, vanadium, zinc and mercury, to support a technical concept of the possible effects that the "Restoration Project of the degraded ecosystems of the dike channel" would produce on the ecosystems of mangroves, seagrasses and coral reefs in the coastal marine area between Boca Cerrada and the mouth of Caño Correa.
 - C3 Parameters as total mercury, lead, cadmium, chromium, copper, zinc, iron, manganese, gamma-emitting radioactive isotopes of the ²³⁸U chain, topics of interest to support the sustainable development of the offshore hydrocarbon sector.
 - C3 Parameters as lead, cadmium, chromium, copper, nickel, zinc in suspended particulate material, sediments and organisms, in "Monitoring of environmental conditions and structural and functional changes in plant communities and fisheries resources during the rehabilitation of Ciénaga Grande de Santa Marta, an important coastal lake in the Colombian Caribbean".

GEOTRACES or GEOTRACES relevant cruises

- Cruise in an off-shore exploration block in the Colombian Caribbean where water and sediment samples were taken to measure key parameters such as micronutrients essential to life in the ocean and other related with anthropogenic pollution.
- Environmental assessment of the underwater hills and lomas of the north Pacific basin.
- Declaration of the Marine Protected Area cordillera Submarina Beata as a landscape restoration strategy in the Colombian Caribbean 2022.

New projects and/or funding

- Regional Cooperation Project with International Atomic Energy Agency "Strengthening regional capabilities of Latin America and the Caribbean in the use and application of nuclear and isotopic techniques to increase knowledge about stressors that affect coastal zones and to contribute to the sustainable management of marine resources".
- Regional Cooperation Project with International Atomic Energy Agency "Evaluating the Impact of Heavy Metals and Other Pollutants on Soils Contaminated by Anthropogenic Activities and Natural Origin".

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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CROATIA

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

The Croatian GEOTRACES activities were related to:

• application of improved electrochemical methods (in combination with ICPMS) for determination of number of trace metals, their speciation, fractionation and interaction with organic matter and sulphur species in natural waters, including monitoring of the coastal and open waters of the Adriatic Sea;

mercury speciation and determination by CV-AAS in natural waters, including monitoring of the coastal and open waters of the Adriatic Sea;

- study of geochemistry of redox proxies and redox transformations in seawater under a range of critical environmental conditions (Cu, V, Re, Mo and U);
- study of geochemistry of technology critical elements (Li, Nb, Sc, Ga, Y, La, Sb, Ge, Te and W) in marine sediments;
- geochemical research and biological response in different environmental systems (coastal and open sea, marine lakes, anchialine caves, submarine groundwater discharge);
- development of new methods for ex- and in-situ determination of natural and anthropogenic radionuclides (focus is on 86/87Sr, 89,90Sr and 210Pb);
- development of electroanalytical method for determination and characterization of polysulfides in anoxic seawater conditions;
- study of interactions between surface water chemistry, phytoplankton, atmospheric chemistry, and climate;
- characterization of atmospheric precipitation (rain, aerosols PM2.5) regarding presence of major cations and anions, organic matter, sulphur species and trace metals;
- measurements of activity concentration of 7Be and 210Pb in atmospheric precipitation (rain, aerosols PM2.5) in order to monitor dynamics of particle transport, metrological information, origin of air mass transfer and seasonal variation of aerosol deposition;
- work on advanced technologies for water quality control/monitoring and prediction purposes.

New projects and/or funding

Current projects supported by the Croatian Ministry of Science, Education and Sport and Croatian Science Foundation (CSF):

- 2018-2022, CSF project: Biochemical REsponses of oligotrophic Adriatic surface ecosystems to atmospheric Deposition Inputs (BiREADI) (PI. Sanja Frka)
- 2018-2022, CSF project: MARine lake (Rogoznica) as a model for EcoSystem functioning in a changing environment (PI. I. Ciglenečki-Jušić)
- 2018-2022, CSF project: Geochemistry and Records of Redox Indicators in Different Environmental Conditions: Towards a better understanding of redox conditions in the past (PI: E. Bura-Nakić)

- 2020-2024, CSF project: Marine (micro)plastic litter and pollutant metals interaction: a possible pathway from marine environment to human (METALPATH) (PI Vlado Cuculić)
- 2020-2024: SNSF/CSF: Understanding copper speciation and redox transformations in seawater (PI: E. Bura-Nakić)

Other projects:

2020-2023: HAMAG-BICRO: "Application of artificial intelligence in advanced predictive technologies for online water quality control". (PI. D. Omanović)

2020-2023: INTERREG CRO-ITA: InnovaMare - "Model of innovation ecosystem in the field of underwater robotics and sensors for control and monitoring purposes with a mission focused on the sustainability of the Adriatic Sea". (PI. M. Mlakar)

2021-2022: Providing a service of systematic testing of the state of transitional and coastal waters in the Adriatic Sea (Croatia) (PI. I. Ciglenečki-Jušić)

2020-2022: INTERREG ADRION: "SEAVIEWS - Sector Adaptive Virtual Early Warning System for marine pollution". (AP. D. Omanović)

2020-2022: SKLEC China Open Research Fund: "Eco-environmental impacts of submarine groundwater discharge-derived nutrients, carbon and metal in oligotrophic karstic estuary of the Krka River (Adriatic Sea, Croatia)". (PI. N. Cukrov)

2020-2021: Partnerships between scientists and fishermen (1. cooperation in Ploče: PI. V. Filipović Marijić; 2. cooperation in Gradac: PI. D. Kapetanović).

Other GEOTRACES activities

- D. Omanović is a member of the new GESAMP working group 45 Climate Change and Greenhouse Gas Related Impacts on Contaminants in the Ocean.
- I.Ciglenečki-Jušić is appointed Croatian representative in the Oceans Knowledge Hub within the JPI Oceans initiative Ocean Carbon Capacities
- I. Ciglenečki-Jušić is a member of the new European Marine Board Working Group on Ocean Oxygen

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Elvira Bura-Nakić, Lucija Knežević, Jelena Mandić, Chromatographic and spectrophometric studies of vanadate (+V) reduction by 3-mercaptopropionic acid, *Journal of Inorganic Biochemistry*, 230 (2022) 111747.
- Saša Marcinek, Ana Marija Cindrić, Jasmin Pađan and Dario Omanović, Trace Metal Partitioning in the Salinity Gradient of the Highly Stratified Estuary: A Case Study in the Krka River Estuary (Croatia), *Applied Sciences*, 12 (2022) 5816.
- Duc Huy Dang, Dario Omanović, Alfonso Mucci, Wei Wang, Allison Sikma, Anique Chatzis, The winter estuarine geochemistry of platinum in the Estuary and Gulf of St. Lawrence, *Marine Chemistry*, 242 (2022) 104123.
- Abra Penezić, Blaženka Gašparović, Vlado Cuculić, Slađana Strmečki, Tamara Djakovac and Marina Mlakar, Dissolved trace metals and organic matter distribution in the Northern Adriatic, an increasingly oligotrophic shallow sea, *Water*, 14 (2022) 349.

- Nevenka Mikac, Ivan Sondi, Neda Vdović, Kristina Pikelj, Maja Ivanić, Mavro Lučić, Niko Bačić, Martina Turk Furdek, D. Srečo Škapin, Slađana Krivokapić, Origin and history of trace elements accumulation in recent Mediterranean sediments under heavy human impact. A case study of the Boka Kotorska Bay (Southeast Adriatic Sea), *Marine pollution bulletin*, 179 (2022), 113702.
- Anđela Bačinić, Sanja Frka and Marina Mlakar, A study of cobalt (II) complexes involved in marine biogeochemical processes: Co(II)-1,10-Phenanthroline and Co(II)-1,10-Phenanthroline-L-α-Phosphatidylcholine, *Bioelectrochemistry*, 144 (2022) 108009.
- Boris Mifka, Maja Telišman Prtenjak, Josipa Kuzmić, Milan Čanković, Sarah Mateša and Irena Ciglenečki, Climatology of dust deposition in the Adriatic Sea; a possible impact on marine production, *Journal of Geophysical Research: Atmospheres*, 127 (2022) e2021JD035783.
- Katarina Kajan, Neven Cukrov, Nuša Cukrov, Renée Bishop-Pierce and Sandi Orlić, Microeukaryotic and prokaryotic diversity of anchialine caves from eastern Adriatic Sea Islands, *Microbial Ecology*, 83 (2021) 257-270.
- Robert Casotto, Ana Cvitešić Kušan, Deepika Bhattu, Tianqu Cui, Manousos-Ioannis Manousakas, Sanja Frka, Ana Kroflič, Irena Grgić, Irena Ciglenečki, Urs Baltenspergera, Jay G. Slowik, Kaspar R. Daellenbacha and Andre S. H. Prévôta, Chemical composition and sources of organic aerosol on the Adriatic coast in Croatia, *Atmospheric Environment: X*, 13 (2022) 100159.
- Palma Orlović-Leko, Niki Simonović, Ivan Šimunić, and Irena Ciglenečki, Fast methodology (warning tools) for tracking changes of the aquatic organic material, *Reliability: Theory & Applications*, 17 (2022) 168-171.
- Slađana Strmečki, Lora Pereža, Electrochemistry of chitosan amino-glycan and BSA protein mixture under seawater conditions, *Journal of Electroanalytical Chemistry*, 898 (2021) 115630.
- Andrea Milinković, Asta Gregorič, Vedrana Grgičin, Sonja Vidič, Abra Penezić, Ana Cvitešić Kušan, Saranda Alempijević, Anne Kasper-Giebl, Sanja Frka, Variability of black carbon aerosol concentrations and sources at a Mediterranean coastal region, *Atmospheric Pollution Research*, 12 (2021) 101221.
- Hrvoje Carić, Neven Cukrov, Dario Omanović, Nautical tourism in marine protected areas (MPAs): evaluating an impact of copper emission from antifouling coating, *Sustainability*, 13 (2021) 11897.
- Niko Bačić, Nevenka Mikac, Mavro Lučić and Ivan Sondi, Occurrence and distribution of technology-critical elements in recent freshwater and marine pristine lake sediments in Croatia: A case study, *Archives of environmental contamination and toxicology*, 81 (2021) 574-588.
- Irena Ciglenečki, Paolo Paliaga, Andrea Budiša, Milan Čanković, Jelena Dautović, Tamara Djakovac, Mathieu Dutour-Sikirić, Romina Kraus, Nataša Kužat, Davor Lučić, Daniela Marić Pfannkuchen and Jakica Njire, Dissolved organic carbon accumulation during a bloom of invasive gelatinous zooplankton *Mnemiopsis leidyi* in the northern Adriatic Sea; case of the anomalous summer in 2017, *Journal of Marine Systems*, 222 (2021) 103599.
- Paolo Paliaga, Andrea Budiša, Jelena Dautović, Tamara Djakovac, Mathieu Andre Dutour-Sikirić, Hrvoje Mihanović, Nastjenjka Supić, Igor Celić, Neven Iveša, Moira Buršić, Ivan Balković and Lara Jurković, Microbial response to the presence of invasive ctenophore

Mnemiopsis leidyi in the coastal waters of the Northeastern Adriatic." *Estuarine, Coastal and Shelf Science* 259 (2021): 107459.

- Ivana Jakovljević, Iva Šimić, Gordana Mendaš, Zdravka Sever Štrukil, Silva Žužul, Valentina Gluščić, Ranka Godec Gordana Pehnec, Ivan Bešlić, Andrea Milinković, Saranda Alempijević and Martin Šala, Pollution levels and deposition processes of airborne organic pollutants over the central Adriatic area: Temporal variabilities and source identification, *Marine Pollution Bulletin*, 172 (2021) 112873.
- Elvira Bura-Nakić, Lucija Knežević, Jelena Mandić, Ana-Marija Cindrić and Dario Omanović, Rhenium distribution and behavior in the salinity gradient of a highly stratified estuary and pristine riverine waters (the Krka River, Croatia), *Archives of Environmental Contamination and Toxicology*, 81 (2021) 564-573.
- Leja Rovan, Tea Zuliani, Barbara Horvat, Tjaša Kanduč, Polona Vreča, Qasim Jamil, Branko Čermelj, Elvira Bura-Nakić, Neven Cukrov, Marko Štrok and Sonja Lojen, Uranium isotopes as a possible tracer of terrestrial authigenic carbonate, *Science of the Total Environment*, 797 (2021) 149103.
- Željka Fiket, Martina Furdek Turk, Maja Ivanić and Goran Kniewald, Non-traditional stable isotope signatures in geological matrices as a tool for interpreting environmental changes–a review, *Geologia Croatica* 74 (2021) 177-187.
- Milan Čanković, Mathieu Dutour-Sikirić, Iris Dupčić Radić, and Irena Ciglenečki, Bacterioneuston and bacterioplankton structure and abundance in two trophically distinct marine environments - a marine lake and the adjacent coastal site on the Adriatic Sea, *Microbial ecology*, (2021) 1-15.
- Abra Penezić, Adrea Milinković, Saranda Alempijević, Silva Žužul and Sanja Frka, Atmospheric deposition of biologically relevant trace metals in the eastern Adriatic coastal area, *Chemosphere*, 283 (2021) 131178.

Completed GEOTRACES PhD or Master theses

- Doctoral Thesis: Saša Marcinek, Multimethodological study of trace metal speciation and organic matter in estuarine waters, University of Zagreb, December 2021. (URL: https://www.bib.irb.hr/1199097/download/1199097.Marcinek-PhD_Thesis.pdf)
- Master Thesis: Iva Dešpoja, Electrochemical determination of cooper complexing capacity in the surface layer of the coastal middle Adriatic ea, University of Split, April 2021.

GEOTRACES presentations in international conferences

- *The Iron at the Air-Sea Interface Workshop*, Asheville, USA, July 2021; Diel variability of iron in the estuarine surface microlayer a preliminary study. Marcinek, S., Cindrić, A. M., Pađan, J. and Omanović, D.
- ASLO 2021 Aquatic Sciences Meeting; Virtual Meeting, June 2021; Atmospheric deposition impacts on the sea surface microlayer in the coastal environment. Penezić A., Milinković A., Alempijević S., Žužul S. and Frka S.
- International scientific conference 'Marine Ecosystems: Research and Innovations', Odessa, Ukraine, October 2021; Differences in metal accumulation and condition of marine fish species potentially impacted by the port of Ploče in the eastern Adriatic Sea. Mijošek

T. Filipović Marijić V., Redžović Z., Erk M., Ivanković D., Lučev A.J., Brkić A., Kapetanović D., Gavrilović A., Radočaj T., Omanović, D., Cindrić, A.-M. and Dragun Z.

- Copper speciation by anodic stripping voltammetry in the surface layers of the oligotrophic sea influenced by atmospheric deposition. Strmečki, S.; Dešpoja, I.; Alempijević, S and Frka S.; 72nd Annual Meeting of the International Society of Electrochemistry, Jeju Island, Korea, September 2021
- *EGU General Assembly 2021*, Virtual Meeting, April 2021; Impact of specific atmospheric depositions on Cu-organic matter interaction in the sea-surface microlayer of the Middle Adriatic. Strmečki, S.; Dešpoja, I. and Alempijević, S.
- *Goldschmidt*, Lion France, July 2021; Polysulfide dynamics in a marine euxinic environment (Rogoznica Lake, Croatia); importance of anoxygenic photosynthesis. Mateša S., Šegota S., Čanković M. and Ciglenečki I.
- *Goldschmidt*, Lion France, July 2021; Geochemical evidence for water column sulfidic holomixia in the sediment of a marine lake. Ciglenečki I., Čanković M., Marguš M., Mateša S., Simonović N., Dutour Sikirić M. and Mikac N.
- Complexation of V(IV) and V(V) with succinic and oxalic acids in aqueous acid solution using affinity capillary electrophoresis. Bura-Nakić E., Knežević L., Nowak A., Medina M., Tulashi N. and Vorlicek P. T.; *NECTARs Spring Web meeting*, March 2021
- Complexation of V(IV) and V(V) with succinic and oxalic acids in aqueous acid solution using affinity capillary electrophoresis. Knežević L., Zanda E, Bura-Nakić E. and Sladkov V.; *NECTARs Spring Web meeting*, March 2021
- 28th AMOS Annual Conference: 'Science for Impact'; Virtual Meeting, February 2021; Atmospheric deposition of biologically relevant trace metals in an oligotrophic Adriatic Sea area. Penezić A., Milinković A., Alempijević S., Žužul S. and Frka S.
- 27th Croatian Meeting of Chemists and Chemical Engineers, with international participation, Veli Lošinj, Croatia, October 2021; Application of the electrochemical method for monitoring polysulfides (S_x²⁻) in marine euxinic environment (Rogoznica Lake, Croatia). Mateša S. and Ciglenečki I.
- 27th Croatian Meeting of Chemists and Chemical Engineers, with international participation, Veli Lošinj, Croatia, October 2021; Dynamics of organic matter in Rogoznica lake as an indication of global change. Simonović N., MargušM., Dutour-Sikirić M. and Ciglenečki I.
- 27th Croatian Meeting of Chemists and Chemical Engineers, with international participation, Veli Lošinj, Croatia, October 2021; Long-term (30 years) study of dissolved organic matter in te Northern Adriatic Sea; an indication of global changes and the BiOS variations. Ciglenečki I., Vilibić I., Dautović J., Simonović N., Vojvodić V., Ćosović B., Zemunik P., Dunić N. and Mihanović H.

Submitted by Saša Marcinek (<u>smarcin@irb.hr</u>).

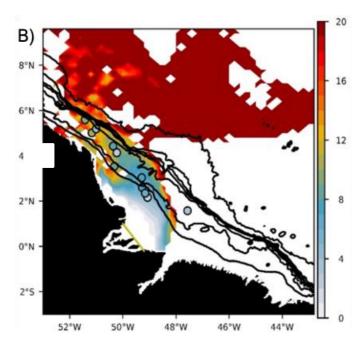
ANNUAL REPORT ON GEOTRACES ACTIVITIES IN FRANCE

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

• The residence time of Amazon waters on the Brazilian continental shelf based on radium

Radium isotopes are used as a tracer of the Amazon plume that enters into the Atlantic Ocean. We combined data collected in the framework of three large projects: i) AmasSeds (1991), ii) AMANDES/ GEOTRACES process study GApr01 (2007–2008) and iii) M147 (2018). The result revels that it takes between 9 and 14 days for the waters of the Amazon to reach the northwestern limit of the Brazilian continental shelf (off French Guiana) and between 12 and 21 days to reach the northwestern limit, east of the Brazilian continental. The average transport



velocity towards the northwest along the Brazilian coast is thus estimated at 30 cm/s. Residence times obtained from radium isotopes agree with those estimated from high-resolution numerical simulations based on the NEMO model (Léon et al., 2022).

Figure 1. Age (in days) of the Amazon plume determined using NEMO model for AMANDES 4 (July 2008). The water parcels are released in the model along the green line. The colored circles show the radium apparent ages (in days). From Léon et al. (2022).

• Early winter barium excess in the Southern Indian Ocean as an annual remineralisation proxy (GEOTRACES GIPr07 cruise)

The Southern Ocean (SO) is of global importance to the carbon cycle, and processes such as mesopelagic remineralisation that impact the efficiency of the biological carbon pump in this region need to be better constrained. During the study by van Horsten et al (2022), early austral winter barium excess (Baxs) concentrations were measured for the first time, along 30°E in the Southern Indian Ocean. Winter Baxs concentrations of 59 to 684 pmol L⁻¹ were comparable to those observed throughout other seasons. The expected decline of the mesopelagic Baxs signal to background values during winter was not observed, supporting the hypothesis that this remineralisation proxy likely has a longer timescale than previously reported. A compilation of available SO mesopelagic Baxs data, including data from this study, shows an accumulation rate of ~ 0.9 µmol m⁻² d⁻¹ from September to July that correlates with temporally integrated remotely sensed primary productivity (PP), throughout the SO from data spanning ~ 20 years, advocating for a possible annual timescale of this proxy. The percentage of mesopelagic POC remineralisation as calculated from estimated POC remineralisation fluxes over integrated remotely sensed PP was approximately 2-fold higher south of the polar front (19±15 %, n=39) than north of the polar front (10±10 %, n=29), revealing the higher surface carbon export

efficiency further south. By linking integrated remotely sensed PP to mesopelagic Baxs stock we could obtain better estimates of carbon export and remineralisation signals within the SO on annual and basin scales.

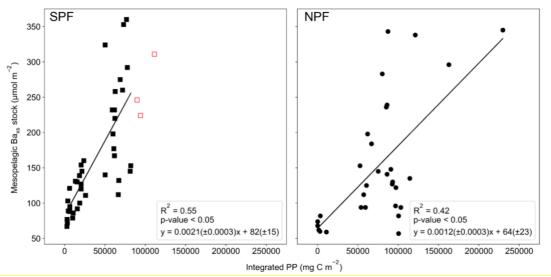


Figure 2. Integrated mesopelagic Baxs stock plotted against integrated remotely sensed PP from the preceding September up to one month prior to sampling, all available literature data and winter data from this study, (a) South of the PF (SPF, black squares) and (b) North of the PF (NPF, black circles). Red open squares are data points from our winter dataset where there was not sufficient remote sensing PP data to integrate up to 1 month prior to sampling and available data up to 3 months prior to sampling was plotted but not included in the statistical analysis (van Horsten et al., 2022).

• Influence of metamorphic rocks and ice cover in the rivers' watersheds on river-borne neodymium isotope signatures and REE concentrations: in the case of the Canadian Arctic Archipelago (GN02 cruise)

Dissolved REEs and Nd isotopes were measured in thirteen rivers draining in the Canadian Arctic Archipelago (CAA) (GN02 cruise, August 2015). Results show that dissolved REE concentrations increase with increasing fractions of metamorphic rocks and ice cover in the rivers' watersheds, while ε_{Nd} and PAAS-normalized REE patterns are inherited from the watershed's bedrock lithology (Fig. 3). The CAA river Nd flow is equivalent to the Nd marine input from the Canada Basin. Depending on the percentage of Nd removal during mixing with seawater, the impact of river water on the ε_{Nd} of seawater exiting the CAA could potentially impart a climate-sensitive ε_{Nd} signature to the seawater reaching Baffin Bay, with possible implications for the use of ε_{Nd} in paleoceanographic reconstructions of water mass distribution.

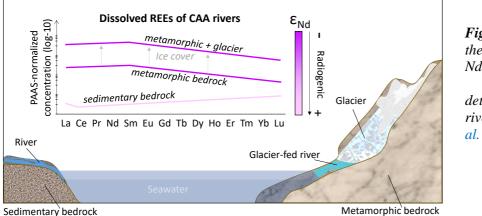


Figure 3. Schematics of the dissolved REE and Nd isotope characteristics determined in the CAA rivers. From Grenier et al. (2022).

• <u>Analytical development. Interferences and matrix effects on iron isotopic composition</u> measurements by MC-ICPMS: influence of Calcium and Aluminium Interferences

This work presents for the first time a study of the impact of Cr, Ni, Ca, Si, and Al interferences and Na, Mg, Ca, K, and Mo matrix effects on Fe isotope measurements using Neptune and Neptune Plus MC-ICPMS with desolvation and a ⁵⁷Fe-⁵⁸Fe double-spike. These results document thresholds below which reliable measurements could be obtained, and point toward elements, which require particular attention. They should provide a useful framework for future Fe isotope analyses. The figure illustrates the case of Ca perturbations.

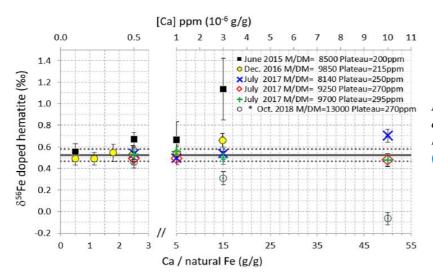


Figure 4. The influence of Ca on d54Fe measurements by MC-ICP-MS. From Lacan et al. (2021)

• <u>Phytoplanktonic response to simulated volcanic and desert dust deposition events in the South</u> <u>Indian and Southern Oceans</u>

Contrasting concentrations of macronutrients and micronutrients induce different nutrient limitations of the oceanic productivity and shape the composition of the phytoplankton communities of the South Indian Ocean and Indian sector of the Southern Ocean. To assess the phytoplankton response to nutrient release by desert dust and volcanic ash aerosols in these distinct biogeochemical regions, we conducted a process study with microcosm incubation experiments. A dry or wet deposition of either dust from Patagonia or ash from the Icelandic volcano Eyjafjallajökull or dissolved nutrients (Si, Fe, N and/or P) were added to trace metal clean incubations of surface seawater collected from five stations. These deposition experiments enabled the measurement of the biological response along with solubility calculations of nutrients. Both types of aerosols alleviated the iron deficiency occurring in the

Southern Ocean during austral summer and resulted in a 24–110% enhancement of the primary production, depending on the station. The release of dissolved silicon may also have contributed to this response, although to a lesser extent, whereas neither the dust nor the ash relieved the nitrogen limitation in the low-nutrient and low-chlorophyll area. Diatom growth was responsible for 40% to 100% of the algal biomass increase within the responding stations, depending on the region and aerosol type. The high particle concentrations that are characteristic of ash deposition following volcanic eruptions may be of equal or higher importance to phytoplankton compared to desert dust, despite ashes' lower nutrient solubility to the ocean (Geisen et al. 2022).

• A silicon isotopic perspective on the contribution of diagenesis to the sedimentary silicon budget in the Southern Ocean

Diatoms are known to fractionate silicon isotopes during the formation of their frustules causing the silicon isotopic composition of biogenic silica to track the degree of silicic acid consumption in surface waters. Despite a growing body of work that uses this proxy to reconstruct past changes in silicic acid utilization, the understanding of the benthic silicon cycle, particularly the identification and quantification of the processes that potentially alter the silicon isotopic composition of biogenic silica during early diagenesis is still lacking. We investigated these processes by comparing the silicon isotopic composition of pore water silicic acid, biogenic silica and, for the first time, lithogenic silica from five sediment cores collected in the deep basin of the Southern Ocean representing a diversity of sedimentation regimes. Silicic acid concentrations and the isotopic composition of Southern Ocean pore waters were the result of a dynamic balance between the dissolution of biogenic silica, reactive lithogenic silica phases and Si re-precipitation with the relative importance of each processes differing significantly between regions. The results are consistent with the formation of authigenic alumino-silicates derived from dissolved biogenic silica in the Sub-Antarctic Zone and in the Antarctic Zone (on average $12 \pm 5\%$ and $17 \pm 13\%$, respectively). Since this latter process can fractionate silicon isotopes, this implies that, even if the silicon isotopic composition of diatoms preserved in the sediments is a reliable proxy for silicic acid utilization in the past ocean, care must be taken to extract a clean biogenic silica phase free of authigenic clays and lithogenic phases from sediments to eliminate this potential bias when interpreting isotopic records (Closset et al. 2022).

Special issue in the framework of PEACETIME

In the frame of the PEACETIME project, a special issue BIOGEOSCIENCES and ATMOSPHERIC CHEMISTRY and PHYSICS was completed in 2022 (see here: https://bg.copernicus.org/articles/special_issue1040.html). 21 papers were published following the PEACETIME cruise, a process-study endorsed by GEOTRACES (GApr09 PROCESS STUDY – CRUISE PEACETIME; MEDITERRANEAN SEA. The most relevant new papers to GEOTRACES are marked with # in the publication list.

GEOTRACES or GEOTRACES relevant cruises

• Resilience cruise (*Marion Dufresne*), 19/04/2022- 23/05/2022: surface samples collected with the towed fish for dissolved, soluble and particulate trace metals and iron isotopes in the Mozambique Channel. This cruise might seek for GEOTRACES compliant data endorsement.

GEOTRACES workshops and meetings organized

• SWINGS post-cruise meeting (May 9-12, 2022, 36 attendees) was organized by C. Jeandel and H. Planquette in Auxerre (France)

Outreach activities conducted

- Many post cruise interviews and conferences about SWINGS. A list of SWINGS outreach activities is available here: <u>https://www.geotraces.org/geotraces-french-swings-gs02-cruise-press-review/</u>
- As GEOTRACES IPO, C. Jeandel realized with Elena Masferrer and Adrian Artis of 3 videos describing: 1) The GEOTRACES Programme (<u>https://youtu.be/IGUt4OZL2Z8</u>); 2) The Pb scientific challenges and results; (3) The Isotopes.
- Rencontre EchoScientifique: Le Réveilleur & Cécile Guieu and Sophie Bonnet: <u>https://www.youtube.com/watch?v=9HGYQQAWuXY</u> (interview in French about the TONGA project)
- Le Réveilleur: Why does life struggle in the ocean? Scientific reflections on what limits life in the ocean, particularly in the region covered by the TONGA project and campaign. https://www.youtube.com/watch?v=3105ScO53fo (in French)

Other GEOTRACES activities

- As IPO senior scientist, C. Jeandel is preparing all the highlights posted on the GEOTRACES website: <u>https://www.geotraces.org/category/science/newsflash/</u> and also assist Elena Masferrer to miscellaneous tasks, on request.
- Co-organization of a session in AGU 2021 fall meeting. PP024. Refinement of paleo-proxies in the GEOTRACES era (Co-conveners: Christopher Hayes, Kazuyo Tachikawa, Kassandra Costa and Jesse R Farmer)

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Artigue L., Wyatt N.J., Lacan F., Mahaffey C., Lohan M.C. 2021. The importance of water mass transport and dissolved-particle interactions on the dissolved aluminum cycle in the subtropical North Atlantic. Global Biogeochemical Cycles. doi.org/10.1029/2020GB006569
- #Bressac, M., Wagener, T., Leblond, N., Tovar-Sánchez, A., Ridame, C., Taillandier, V., Albani, S., Guasco, S., Dufour, A., Jacquet, S. H. M., Dulac, F., Desboeufs, K., and Guieu, C., 2021. Subsurface iron accumulation and rapid aluminum removal in the Mediterranean following African dust deposition, Biogeosciences, 18, 6435-6453, https://doi.org/10.5194/bg-18-6435-2021.
- Cloete, R., Loock, J.C., van Horsten, N.R., Menzel Barraqueta J.-L., Fietz, S., Mtshali, T.N., Planquette, H., García-Ibáñez, M.I., Roychoudhury, A.N., 2021. Winter dissolved and particulate zinc in the Indian Sector of the Southern Ocean: Distribution and relation to major nutrients (GEOTRACES GIpr07 transect). Marine Chemistry, 236, 104031. https://doi.org/10.1016/j.marchem.2021.104031.

- Cloete, R., Loock, J. C., van Horsten, N. R., Fietz, S., Mtshali, T. N., Planquette, H., and Roychoudhury, A. N., 2021. Winter Biogeochemical Cycling of Dissolved and Particulate Cadmium in the Indian Sector of the Southern Ocean (GEOTRACES GIpr07 Transect). Frontiers in Marine Science 8, https://www.frontiersin.org/article/10.3389/fmars.2021.656321.
- Closset**, I., Brzezinski, M. A., Cardinal, D., Dapoigny, A., Jones, J. L., & Robinson, R. S., 2022. A silicon isotopic perspective on the contribution of diagenesis to the sedimentary silicon budget in the Southern Ocean. Geochimica et Cosmochimica Acta, 327, 298–313. https://doi.org/10.1016/J.GCA.2022.04.010 (1 post-doc **)
- #Desboeufs, K., Fu, F., Bressac, M., Tovar-Sánchez, A., Triquet, S., Doussin, J.-F., Giorio, C., Chazette, P., Disnaquet, J., Feron, A., Formenti, P., Maisonneuve, F., Rodríguez-Romero, A., Zapf, P., Dulac, F., and Guieu, C., 2022: Wet deposition in the remote western and central Mediterranean as a source of trace metals to surface seawater, Atmos. Chem. Phys., 22, 2309-2332, https://doi.org/10.5194/acp-22-2309-2022.
- Fourrier*, P., G. Dulaquais, C. Guigue, P. Giamarchi, G. Sarthou, H. Whitby & R. Riso, 2022. Characterization of the vertical size distribution, composition and chemical properties of dissolved organic matter in the (ultra)oligotrophic Pacific Ocean through a multi-detection approach, Mar. Chem, https://doiorg.inee.bib.cnrs.fr/10.1016/j.marchem.2021.104068. (1 Ph. D. student *)
- Garcia-Orellana J., Rodellas V., Tamborski J., Diego-Feliu M., van Beek P., Weinstein Y., Charette M., Alorda-Kleinglass A., Michael H.A., Stieglitz T., Scholten J., 2021. Radium isotopes as submarine 1 groundwater discharge (SGD) tracers: review and recommendations. Earth Science Reviews, https://doi.org/10.1016/j.earscirev.2021.103681
- Geisen*, C., Ridame, C., Journet, E., Delmelle, P., Marie, D., Lo Monaco, C., ... Cardinal, D., 2022. Phytoplanktonic response to simulated volcanic and desert dust deposition events in the South Indian and Southern Oceans. Limnology and Oceanography, 9999, 1–17. https://doi.org/10.1002/LNO.12100 (1 Ph. D. student *)
- González**, A.G., Bianco A., Boutorh J., Cheize M., Mailhot G., Delort A.-M., Planquette H., Chaumerliac, N., Deguillaume L., Sarthou G, 2022. Influence of strong iron-binding ligands on cloud water oxidant capacity, STOTEN, https://doi.org/10.1016/j.scitotenv.2022.154642. (1 post-doc **)
- Grenier**, M., Brown, K. A., Colombo, M., Belhadj, M., Baconnais, I., Pham, V., Soon, M., Myers, P. G., Jeandel, C., and François, R., 2022. Controlling factors and impacts of riverborne neodymium isotope signatures and rare earth element concentrations supplied to the Canadian Arctic Archipelago. Earth and Planetary Science Letters 578, 117341, https://doi.org/10.1016/j.epsl.2021.117341. (1 post-doc **)
- Hamilton, D. S., Perron, M. M., Bond, T. C., Bowie, A. R., Buchholz, R. R., Guieu, C., ... & Mahowald, N. M., 2022. Earth, wind, fire, and pollution: aerosol nutrient sources and impacts on ocean biogeochemistry. Annual review of marine science, 14, 303-330.
- Hodel F., R. Grespan, M. De Rafélis, G. Dera, C. Lézin, E. Nardin, D. Rouby, M. Aretz, M. Steinnman, M. Buatier, F. Lacan, C. Jeandel et V. Chavagnac., 2021. Drake Passage Gateway opening and Antarctic Circumpolar Current onset 31 Ma ago: the message of foraminifera and reconsideration of the Neodymium isotope record Chemical Geology, Volume 570. https://doi.org/10.1016/j.chemgeo.2021.120171 (hal-03358760)

- Horner T., S. Little, T. Conway, J. Farmer, J. Hertzberg, et al., 2021. Bioactive trace metals and their isotopes as paleoproductivity proxies: An assessment using GEOTRACES-era data. Global Biogeochemical Cycles, 35, e2020GB006814. (10.1029/2020GB006814).
- Lacan F., Artigue L., Klar J.K., Pradoux C., Chmeleff J., Freydier R. 2021. Interferences and matrix effects on iron isotopic composition measurements by 57Fe-58Fe double-spike multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS); the importance of calcium and aluminium interferences. Frontiers in Environmental Chemistry. doi:10.3389/fenvc.2021.692025
- Léon M., van Beek P., Scholten J., Moore W., Souhaut M., DeOliveira J., Jeandel C., Seyler P., Jouanno J., 2022. Use of 223Ra and 224Ra as chronometers to estimate the residence time of Amazon waters on the Brazilian continental shelf, Limnology & Oceanography 00, 1-15, doi: 10.1002/lno.12010
- Levier*, M., Roy-Barman, M., Colin, C., and Dapoigny, A., 2021. Determination of low level of actinium 227 in seawater and freshwater by isotope dilution and mass spectrometry. Marine Chemistry, 233, 103986. (1 Ph. D. student *)
- Lory, C., Van Wambeke, F., Fourquez, M., Barani, A., Guieu, C., Tilliette, C., ... & Bonnet, S., 2022. Assessing the contribution of diazotrophs to microbial Fe uptake using a group specific approach in the Western Tropical South Pacific Ocean. ISME Communications, 2(1), 1-11.
- Michael S., Resing J., Lacan F., Buck N., Pradoux C., Jeandel C. 2021. Constraining the Solomon Sea as a source of Al and Mn to the Equatorial Undercurrent. Deep Sea Research Part I: Oceanographic Research Papers, Elsevier, 174, pp.103559. (10.1016/j.dsr.2021.103559). (hal-03358780)
- #Pulido-Villena, E., Desboeufs, K., Djaoudi, K., Van Wambeke, F., Barrillon, S., Doglioli, A., Petrenko, A., Taillandier, V., Fu, F., Gaillard, T., Guasco, S., Nunige, S., Triquet, S., and Guieu, C., 2021. Phosphorus cycling in the upper waters of the Mediterranean Sea (PEACETIME cruise): relative contribution of external and internal sources, Biogeosciences, 18, 5871-5889, https://doi.org/10.5194/bg-18-5871-2021.
- Rodellas V., Stieglitz T., Tamborski J., van Beek P., Andrisoa A., Cook P., 2021. Conceptual uncertainties in groundwater and porewater fluxes estimated by radon and radium mass balances, Limnology & Oceanography 9999, 1–19, doi: 10.1002/lno.11678
- Silori*, S., Sharma*, D., Chowdhury, M., Biswas, H., Cardinal, D., & Mandeng-Yogo, M., 2021. Particulate organic matter dynamics and its isotopic signatures (δ13CPOC and δ15NPN) in relation to physical forcing in the central Arabian Sea during SW monsoon (2017–2018). Science of The Total Environment, 785, 147326. https://doi.org/10.1016/j.scitotenv.2021.147326 (2 Ph. D Students *)
- Silori*, S., Sharma*, D., Chowdhury, M., Biswas, H., Bandyopadhyay, D., Shaik, A. U. R., Cardinal, D., Mandeng-Yogo, M., & Narvekar, J., 2021. Contrasting phytoplankton and biogeochemical functioning in the eastern Arabian Sea shelf waters recorded by carbon isotopes. Marine Chemistry, 232, 103962. https://doi.org/10.1016/j.marchem.2021.103962 (2 Ph. D. students*)
- Thibon F., Weppe L., Montanes M., Telouk P., Vigier N., 2021. Lithium isotopic composition of the organic-rich reference materials TORT-2, DORM-2, TORT-3, DORM-4, SRM-1400 and ERM-CE278k, J. Anal. At. Spectrom. 36, 1381-1388 doi: 10.1039/D1JA00045D.

- Thibon F., Metian M., Oberhaensli F., Montanes M., Vasileva E., Orani A-M, Telouk P., Swarzenski P. and Vigier N., 2021. Bioaccumulation of lithium isotopes in mussels and implications for coastal environments, ACS Earth and Space Chemistry, doi: 10.1021/acsearthspacechem.1c00045
- Van Horsten*, N, Planquette, H., Sarthou, G., Mtshali, T. N, Roychoudhury, A., Bucciarelli. E., 2022. Early winter barium excess in the Southern Indian Ocean as an annual remineralisation proxy (GEOTRACES GIPr07 cruise). Biogeosciences, https://doi.org/10.5194/bg-2021-42. (1 Ph. D. student *)
- #Van Wambeke, F., Taillandier, V., Desboeufs, K., Pulido-Villena, E., Dinasquet, J., Engel, A., Marañón, E., Ridame, C., and Guieu, C., 2021. Influence of atmospheric deposition on biogeochemical cycles in an oligotrophic ocean system, Biogeosciences, 18, 5699-5717, https://doi.org/10.5194/bg-18-5699-2021.
- Yeghicheyan, D., Grinberg, P., Alleman, L., Belhadj, M., Causse, L., Chmeleff, J., Cordier, L., Djouraev, I., Dumoulin, D., Dumont, J., Freydier, R., Mariot, H., Cloquet, C., Kumkrong, P., Malet, B., Jeandel, C., Marquet, A., Riotte, J., Tharaud, M., and Mester, Z., 2021. Collaborative determination of trace element mass fractions and isotope ratios in AQUA-1 drinking water certified reference material. Anal. Bioanal. Chem. 413 10.1007/s00216-021-03456-8.

Completed GEOTRACES PhD or Master theses

- Carla Geisen (PhD): Macro- and micronutrient dissolution from desert and volcanic aerosols in rain and seawater: impact on phytoplankton in the Southern Indian Ocean, Sorbonne Université, defended on 27 September 2021. Available from 27 September 2022 on www.theses.fr
- Natasha van Horsten (PhD): Insights into early winter Southern Indian Ocean dissolved iron distributions and remineralization using excess barium (GEOTRACES GIPr07 cruise), in Brest in cotutelle with Stellenbosch University (South Africa), defended on 16 November 2021.
- Martin Levier (PhD): Development and use of Actinium 227 as a tracer of deep ocean mixing, Université Paris-Saclay, defended on 21 March 2022.

GEOTRACES presentations in international conferences

Goldschmidt 2021, 4-9 July 2021, virtual

- Iron (II) oxidation kinetics variability in the Atlantic Ocean and development of an improved theoretical equation. *Submitted by D. Gonzalez-Santana, <u>david.gonzalez@fpct.ulpgc.es</u> at the time Postdoc at LEMAR*
- Particulate Trace Metals from Shallow Hydrothermal Vents. Submitted by M.-E. Vorrath, <u>maria-elena.vorrath@awi.de</u> at the time Postdoc at LEMAR
- 227 Ac and 231 Pa in the southeast sector of Southern Ocean (Bonus GoodHope–GEOTRACES cruise. Levier, M., Roy-Barman, M., & Dapoigny, A. M. Levier was a PhD student at LSCE at the time

European Aerosol Conference, 30 August – 3 September, 2021:

• Influence of Fe-binding ligands on cloud water oxidant capacity: a study on samples collected at puy de Dôme (France). Bianco, Angelica, Aridane G. González, Julia Boutorh, Marie Cheize, Anne-Marie Delort, Gilles Mailhot, Hélène Planquette, Laurent Deguillaume, Géraldine Sarthou. *Submitted by A. Bianco, <u>A.Bianco@opgc.fr</u>*

AGU 2021, 13-17 December 2021, New Orleans and online everywhere

• Neodymium isotope budget in the Mediterranean Sea inferred from core-top sediments, seawater data synthesis and box model calculation. Submitted by K. Tachikawa, kazuyo@cerege.fr

Ocean Sciences 2022, 24 February- 4 March 2022, Hawaii and online everywhere

- The distribution of size-fractionated particulate cadmium in the North Atlantic Ocean along the GEOVIDE section (GEOTRACES GA01): linking Cd and phytoplankton community structure. *Submitted by H. Planquette*, <u>helene.planquette@univ-brest.fr</u>
- Lost mercury: High mercury release and rapid scavenging from deep hydrothermal vent sites at the Mid-Atlantic Ridge. N. Torres Rodriguez. Submitted by N Torres Rodriguez, natalia.torres-rodriguez@mio.osupytheas.fr
- 3D study of the TAG hydrothermal plume: interaction between hydrodynamics and geochemistry. *Submitted by C. Cathalot*, <u>*Cecile.Cathalot@ifremer.fr*</u>
- dFe pattern impacted by shallow hydrothermal sources along a transect through the Tonga-Kermadec arc, Ocean Science Meeting, Hawaï, 2022. Submitted by C. Tilliette, <u>chloe.tilliette@imev-mer.fr</u>
- An oasis in the desert: shallow hydrothermal iron triggers massive diazotroph blooms in the subtropical Pacific Ocean. Bonnet S., Guieu C. and the TONGA team, [sophie.bonnet@mio.osupytheas.fr; cecile.guieu@imev-mer.fr]
- dFe pattern impacted by shallow hydrothermal sources along a transect through the Tonga-Kermadec arc. Tilliette C. et al., [chloe.tilliette@imev-mer.fr]
- Distribution of thiol and humic substances during the 2019 Tonga cruise. Portlock G. et al., [g.portlock@liverpool.ac.uk]
- Lithium concentration and Li isotope composition of plankton from the Tonga volcanic arc: influence of shallow hydrothermal fluids. Vigier N. et al. Submitted by nathalie.vigier@imev-mer.fr

Submitted by Kazuyo Tachikawa (kazuyo@cerege.fr).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN GERMANY

May 1st, 2021 to April 30th, 2022

GEOTRACES or GEOTRACES relevant cruises

- Research cruise RainbowPlume ('Rainbow non-boyant hydrothermal plume GEOTRACES study') as part of German Corona Cruise Proposal Round. Cruise M176/2 (Emden_Germany Emden_Germany) was sailed in period September 1 to October 5, 2021 (*RV Meteor*) and investigated plume geochemistry at Rainbow vent field (mid Atlantic Ridge). PIs Achterberg, Koschinsky, Browning, Frank, and important involvement by Jan Scholten and Walter Geibert. We will apply for GEOTRACES Compliant status.
- GP21 section cruise on FS Sonne (SO289, 'Biogeochemistry of trace metals and their isotopes in the South Pacific Ocean. Ocean Region: South Pacific between Chile and New Zealand') has been sailed in the period February 18-April 8 2022 PIs Achterberg, Frank, Koschinsky, and important involvement by Jan Scholten, Walter Geibert, S Galer, W Abouchami. Valparaiso_Chile – Nouméa_New Caledonia
- SO290 Nouméa-Nouméa, southeastern Tasman Sea (PI: K.Pahnke). Water column sampling for Nd and Si isotopes and REE (plus hydrography and nutrients) at 20 stations.
- GP11 section cruise on *FS Sonne* (SO298), in the Equatorial Pacific Ocean is scheduled for the period April 11- May 30 2023 PIs Achterberg, Frank, Koschinsky, and important involvement by Walter Geibert, S Galer, W Abouchami.
- Polarstern cruises PS133/1 and PS133/2 South Georgia and the adjoining Antarctic Circumpolar Current ('IslandImpact') are scheduled for late 2022. Process study application is under consideration.
- Heincke training cruise HE603 is scheduled for 12 July-15 July 2022 (GEOTRACES Summer School).

New projects and/or funding

- DFG Funding for Jan Scholten (Kiel Uni), Eric Achterberg & Aaron Beck (GEOMAR) and Walter Geibert (AWI) for two postdocs to conduct Ra, Th and He isotope work on GEOTRACES cruises. Postdocs (Dr L Vieira and Dr. X. Chen) started in September 2021 and February 2022, respectively.
- Funding of one Postdoc for 18 months with project 'Rainbow non-boyant hydrothermal plume GEOTRACES study', related to research cruise M176/2
- Funding of one Postdoc for 26 months within project 'Biogeochemistry of trace metals and their isotopes in the South Pacific Ocean. Ocean Region: South Pacific between Chile and New Zealand', related to research cruise SO289
- Funding for GEOTRACES Summer School 2022 (92k€) was received from Volkswagen Stiftung. Additional support by US GEOTRACES and SCOR for travel bursaries.

GEOTRACES workshops and meetings organised

The GEOTRACES Summer School 2022 was largely organized in the reporting period but will only take place in July 2022.

Outreach activities conducted

• Press release for South Pacific GEOTRACES cruise GP21. https://www.geomar.de/en/news/article/tracing-trace-elements

Other GEOTRACES activities

- Leading role in creation of the IDP2021 (R.Schlitzer)
- Leading role in committee work (E. Achterberg: SSC. W. Geibert: co-chair S&I committee, now SSC

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Ardiningsih, Indah, Zhu, Kechen, Lodeiro, Pablo, Gledhill, Martha, Reichart, Gert-Jan, Achterberg, Eric P., Middag, Rob and Gerringa, Loes J. A. (2021) Iron Speciation in Fram Strait and Over the Northeast Greenland Shelf: An Inter-Comparison Study of Voltammetric Methods Frontiers in Marine Science, 7. Art.Nr. 609379. DOI 10.3389/fmars.2020.609379.
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Completed GEOTRACES PhD or Master theses

- Kechen Zhu (2021). Impact of pH, temperature and dissolved organic matter on iron speciation and dissolved iron inventories in seawater. University of Kiel/GEOMAR
- Wanxuan Yao (2021) Implications of iron model complexity for the projection of global biogeochemical cycles. University of Kiel/GEOMAR
- Stephan Krisch (2021) Iron Biogeochemistry in Fram Strait and on the Northeast Greenland Shelf. University of Kiel/GEOMAR

GEOTRACES presentations in international conferences

- Hollister, A.P., Gledhill, M., Koschinsky-Fritsche, A. Distribution and Flux of Trace Metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in the Amazon and Pará River Estuary and Mixing Plume (cruise M147). Online poster presentation. Statuskonferenz Forschungsschiffe, February 2022, Oldenburg, Germany. (online meeting due to COVID-19)
- Hollister, A. P., Gledhill, M., Koschinsky-Fritsche, A. Distribution and Flux of Trace Metals in the Amazon Estuary and Plume. Online oral presentation. Virtual Ocean Sciences Meeting, February 2022, Hawaii, USA. (online meeting due to COVID-19)
- Mara Sutorius, The coupling of REE and organic matter cycling during a phytoplankton spring bloom. ASLO Aquatic Sciences Meeting, online, 2021.
- Schlitzer, Reiner, GEOTRACES IDP2021. What does it include and how can it be accessed, IDP2021 online Release Event, Nov 2021.
- Schlitzer, Reiner, Accessing and utilizing the GEOTRACES 2021 Intermediate Data Product, Ocean Sciences Meeting Town Hall TH33, Feb 2022.

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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN INDIA

May 1st, 2021 to April 30th, 2022

Various research activities under the Indian GEOTRACES program are being pursued vigorously in India. Last year no new sampling was done. However, the samples collected in previous oceanographic research cruises in the Indian Ocean are being analyzed for trace elements and isotopes. Major stress is being given to understanding the sources of key trace elements in the Indian Ocean to assess their role in various processes operating in the region.

New results:

Dissolved Mn in the Indian Ocean

Biogeochemical cycling of dissolved Mn has been studied in the Indian Ocean, the Arabian Sea and the Bay of Bengal, the Andaman Sea and the southern Indian Ocean. Atmospheric dust deposition, riverine discharge, shelf sediments and hydrothermal sources seem to contribute significantly to the Mn budget of the Indian Ocean whereas Mn-oxy hydroxides, particle scavenging and biological uptake through biology and their export are important sinks of dissolved Mn.

Benthic Fluxes of Trace elements in the Indian Ocean

The importance of benthic fluxes to dissolved trace element budgets in the Indian Ocean has been evaluated by studying their distribution in the bottom and pore waters. Abundances of some of the trace elements are significantly elevated and controlled by redox conditions. The benthic fluxes of some of them are significantly higher in the central Indian Ocean.

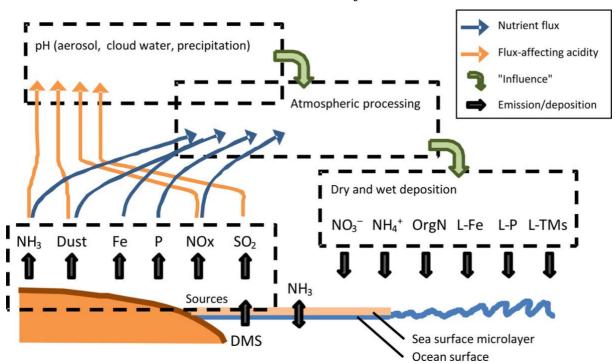
New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- ND Singh, SK Singh, Distribution and cycling of dissolved aluminium in the Arabian Sea and the Western Equatorial Indian Ocean. Marine Chemistry 243, 104122, 2022
- V Chinni, SK Singh, Dissolved iron cycling in the Arabian Sea and sub-tropical gyre region of the Indian Ocean. Geochimica et Cosmochimica Acta 317, 325–348, 2022
- V Goswami, SK Singh, R Bhushan, VK Rai, Spatial distribution of Mo and δ98Mo in waters of the northern Indian Ocean: Role of suboxia and particle-water interactions on lighter Mo in the Bay of Bengal. Geochimica et Cosmochimica Acta 324, 174-193, 2022.
- Damodararao K., Singh S.K., Substantial Submarine Groundwater Discharge in the Estuaries of the East Coast of India and Its Impact on Marine Strontium Budget, Geochim. Cosmochim. Acta, 324, 66-85, 2022.

Submitted by Vineet Goswami (vineetg@prl.res.in) and Sunil Kumar Singh (sunil@nio.org).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN IRELAND

May 1st, 2021 to April 30th, 2022



New GEOTRACES or GEOTRACES relevant scientific results

Baker et al. *Changing atmospheric acidity as a modulator of nutrient deposition and ocean biogeochemistry* Science Advances (2021).

Anthropogenic emissions to the atmosphere have increased the flux of nutrients, especially nitrogen, to the ocean, but they have also altered the acidity of aerosol, cloud water, and precipitation over much of the marine atmosphere. For nitrogen, acidity-driven changes in chemical speciation result in altered partitioning between the gas and particulate phases that subsequently affect long-range transport. Other important nutrients, notably iron and phosphorus, are affected, because their soluble fractions increase upon exposure to acidic environments during atmospheric transport. These changes affect the magnitude, distribution, and deposition mode of individual nutrients supplied to the ocean, the extent to which nutrient deposition interacts with the sea surface microlayer during its passage into bulk seawater, and the relative abundances of soluble nutrients in atmospheric deposition. Atmospheric acidity change therefore affects ecosystem composition, in addition to overall marine productivity, and these effects will continue to evolve with changing anthropogenic emissions in the future.

GEOTRACES or GEOTRACES relevant cruises

• There were no GEOTRACES or GEOTRACES relevant cruises during the reporting period. This was in part due to the ongoing covid situation limiting shipboard personnel and activities.

New projects and/or funding

• A new SEAL AA500 nutrient analyzer was funded in the 2nd phase of the Irish Centre for research in Applied Geoscience (iCRAG2). This is scheduled to be installed at the National University of Ireland Galway in Sept 2022 and will be available to Irish researchers on a cost share basis.

GEOTRACES workshops and meetings organized

• There were no GEOTRACES specific workshops run in Ireland during the reporting period. A joint SCOR Ireland workshop is planned for late 2022 or early 2023.

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Baker, A.R., Kanakidou, M., Nenes, A., Myriokefalitakis, S., Croot, P.L., Duce, R.A., Gao, Y., Guieu, C., Ito, A., Jickells, T.D., Mahowald, N.M., Middag, R., Perron, M.M.G., Sarin, M.M., Shelley, R., Turner, D.R., 2021. Changing atmospheric acidity as a modulator of nutrient deposition and ocean biogeochemistry. Science Advances 7, eabd8800.
- Duerschlag, J., Mohr, W., Ferdelman, T.G., LaRoche, J., Desai, D., Croot, P.L., Voß, D., Zielinski, O., Lavik, G., Littmann, S., Martínez-Pérez, C., Tschitschko, B., Bartlau, N., Osterholz, H., Dittmar, T., Kuypers, M.M.M., 2021. Niche partitioning by photosynthetic plankton as a driver of CO2-fixation across the oligotrophic South Pacific Subtropical Ocean. The ISME Journal.
- Hanna, G.S., Choo, Y.-M., Harbit, R., Paeth, H., Wilde, S., Mackle, J., Verga, J.-U., Wolf, B.J., Thomas, O.P., Croot, P., Cray, J., Thomas, C., Li, L.-Z., Hardiman, G., Hu, J.-F., Wang, X., Patel, D., Schinazi, R.F., O'Keefe, B.R., Hamann, M.T., 2021. Contemporary Approaches to the Discovery and Development of Broad-Spectrum Natural Product Prototypes for the Control of Coronaviruses. Journal of Natural Products.
- Jordan, C., Cusack, C., Tomlinson, M.C., Meredith, A., McGeady, R., Salas, R., Gregory, C., Croot, P.L., 2021. Using the Red Band Difference Algorithm to Detect and Monitor a Karenia spp. Bloom Off the South Coast of Ireland, June 2019. Frontiers in Marine Science 8.
- Lyons, W.B., Carey, A.E., Gardner, C.B., Welch, S.A., Smith, D.F., Szynkiewicz, A., Diaz, M.A., Croot, P., Henry, T., Flynn, R., 2021. The geochemistry of Irish rivers. Journal of Hydrology: Regional Studies 37, 100881.
- Rocha, C., Robinson, C.E., Santos, I.R., Waska, H., Michael, H.A., Bokuniewicz, H.J., 2021. A place for subterranean estuaries in the coastal zone. Estuarine, Coastal and Shelf Science 250, 107167.
- Savatier, M., Guerra, M.T., Murphy, J.E., Rocha, C., 2021. Radium isotope ratios as a tool to characterise nutrient dynamics in a variably stratified temperate fjord. Marine Chemistry 231, 103934.
- Savatier, M., Rocha, C., 2021. Rethinking tracer-based (Ra, Rn, salinity) approaches to estimate point-source submarine groundwater discharge (SGD) into coastal systems. Journal of Hydrology 598, 126247.
- Xu, H., Croot, P., Zhang, C., 2021. Discovering hidden spatial patterns and their associations with controlling factors for potentially toxic elements in topsoil using hot spot analysis and K-means clustering analysis. Environment International 151, 106456.

Completed GEOTRACES PhD or Master theses

• Maxime Savatier, Trinity College Dublin (PhD). *Effect of groundwater-surface interactions on coastal areas hosting aquaculture activities.*

GEOTRACES presentations in international conferences

• **Croot, P.**, Nicholas, S., Heller, M. "Dissolved titanium as a tracer for dust input in the Southern Hemisphere", Proceedings of the Blowing South: Southern Hemisphere Dust Symposium, Argentina, 8-10 Nov, 2021.

Submitted by Prof. Peter Croot (peter.croot@nuigalway.ie).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN ISRAEL

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

• <u>Eastern Mediterranean transects</u>: Inputs from continental margins and anthropogenic activities exert strong controls over trace metal biogeochemical cycles with oceanic Pb being a primary tracer of anthropogenic inputs to the marine environment, and its isotopic composition widely used to distinguish and quantify its different sources. Although the Mediterranean Sea was extensively sampled for trace metals, observations regarding its eastern margins remain scarce. During June 2021, we performed a transect between Haifa and the central Levant Basin (120 km offshore) on board the *R.V. Bat Galim*. Sampling included surface water (short lived U-nuclides) and vertical profiles (dissolved trace element concentrations, Pb isotopes (^{208,207,206,204}Pb), ²³⁰Th and ²³²Th). These data are coupled with a similar transect performed during 2018, to constrain shelf to depth fluxes of particulates, nutrients and trace elements (PIs: Weinstein and Torfstein).

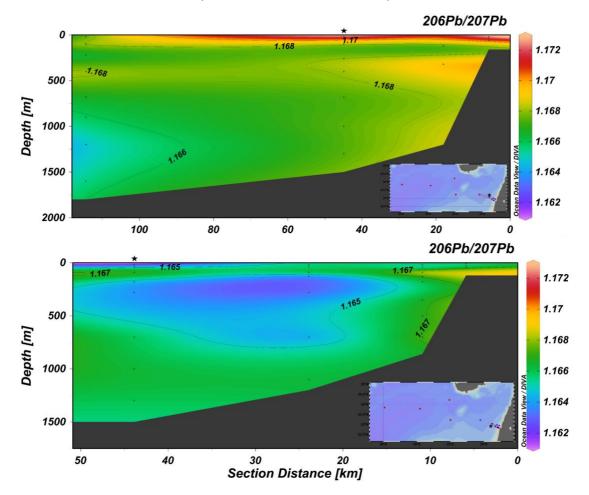


Figure 1. Pb isotopic composition of seawater across two transects in the eastern Mediterranean

Monitoring of marine heavy metals 1: One of the challenges in monitoring the marine coastal environments is quantifying the magnitude and duration of pollution events. Hoober et al. (2022) introduce a new concept of defining heavy metal (HM) baseline assessment levels (BALs) in coastal environments using foraminiferal shells. We demonstrated the potential of this approach by examining a nature reserve along the Mediterranean coast of Israel. Our previous investigation of this site in 2013-2014 using foraminiferal single-chamber LA-ICPMS created a large dataset consisting of HM measurements of two species, Lachlanella and Pararotalia calcariformata. This database was used to establish the BAL of Zn, Cu and Pb, associated with anthropogenic sources. In February 2021, a significant tar pollution event affected the entire Mediterranean coast of Israel, derived from an offshore oil spill. This event provided a unique opportunity to test the applicability of the foraminiferal BAL by comparing it to whole-shell ICPMS measurements of the two species collected in winter and summer 2021. Results reveal a significant increase (2–34 -fold) in the three HMs between 2013–2014 and 2021, with Pb/Ca displaying the most prominent increase in both species. This suggests a possible linkage between the oil spill event and the significantly elevated metal/Ca ratios in 2021.

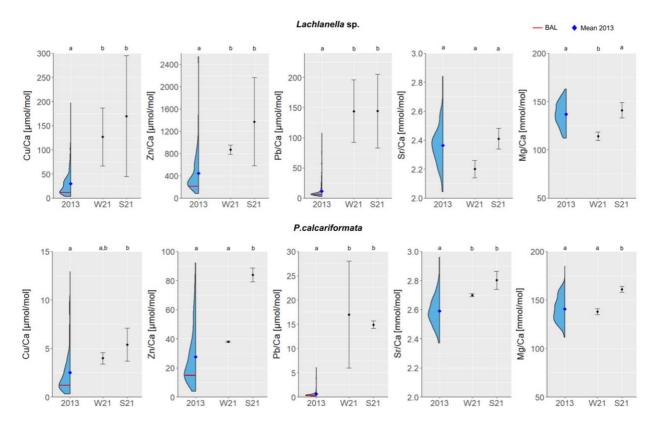


Figure 2. Violin plots of metal/Ca ratios in benthic foraminifera (from: Hoober et al., 2022). Singlechamber 2013–2014 LA-ICPMS records are compared with mean whole-shell winter (W21) and summer (S21) 2021 ICPMS ratios. Red horizontal lines mark the BAL ratio for each anthropogenic metal, Cu, Zn and Pb. The blue diamond indicates the average metal/Ca of all single-chamber 2013– 2014 LA-ICPMS analyses. Error bars represent 1 SD. Letters represent the results of the groups' comparison test. Note the different concentration scales (y axes) of the HMs between the two species.

Monitoring of marine heavy metals 2: Mussels are considered highly efficient marine biomonitors, tracing anthropogenic and natural variations in heavy metals and various organic compounds. While heavy metals depuration processes in biomonitors are of growing interest, less knowledge is available regarding their Pb isotopes and rare earth elements (REEs) accumulation- release dynamics, and their response to short-term anthropogenic and terrigenous perturbations. Benaltabet et al. (2021) report the results of a relocation experiment where a group of mussels (Brachidontes pharaonis) were extracted from a contaminated lagoon in the Gulf of Aqaba, northern Red Sea, and placed in water tanks that were flushed continuously with fresh, uncontaminated seawater. Specimens were removed periodically from the water table over a period of 13 weeks and trace and REEs and Pb isotopic compositions were determined separately for mussel's shells and soft tissues. The results display a clear decrease over time in the concentrations of various heavy metals and REEs in the soft tissue, in concert with a similar shift in the Pb isotopic compositions toward seawater values. By contrast, the elemental and Pb isotopic composition of the shell presents little change over time. Coupling between the Pb isotopic composition of corresponding soft tissue and shell samples allows back-calculation of the timing and magnitude of abrupt pollution events and presents a novel approach for monitoring short-term pollution events. Given the coastal setting of the studied samples, it is important to consider the effects of terrigenous material on the results. Accordingly, Al-normalized element concentrations, Pb isotopes and calculated Ce anomalies, are used to identify two distinct terrigenous end members controlling the contaminated lagoon and the pristine site. The study demonstrates the potential of using mussels as robust biomonitors of natural and anthropogenic environmental perturbations through the combination between elemental concentrations and the isotopic composition of Pb.

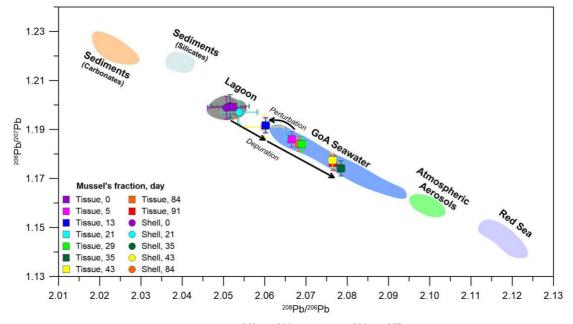


Figure 3. The isotopic composition of ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁶Pb/²⁰⁷Pb in soft tissue (squares) and shells (circles) (from Benaltabet et al., 2021). Colored markers represent the different samples through the length of the experiment. Shaded areas represent the regional end members: GoA seawater (blue field; Benaltabet et al., 2020, Mar. Chem.), atmospheric aerosols (Chien et al., 2019, Env.Sci. Tech.), GoA leached and residual sediment fractions (Benaltabet et al., 2020, Mar. Chem.), which represent the carbonate (orange field) and silicate (light blue field) fractions of bottom sediments, respectively. Red Sea seawater compositions (purple field) are assumed to correspond with Arabian Sea compositions (after Lee et al., 2015, GCA). For more information regarding the suggested end members the reader is referred to Chien et al. (2019, Env.Sci. Tech.) and Benaltabet et al. (2020, Mar. Chem.). The day 0 shell and soft tissue composition represents the lagoon end member (gray field).

GEOTRACES or GEOTRACES relevant cruises

- The National Monitoring Program (NMP) for the Gulf of Eilat/Aqaba operates out of the IUI (http://www.iui-eilat.ac.il/Research/NMPAbout.aspx). Activities include monthly cruises across the north Gulf of Eilat/Aqaba, during which physical, chemical and biological measurements are performed in depth profiles (at a water depth of 700 meters) together with spatial-surface coverage. The main-relevant parameters monitored are: Temperature, salinity, dissolved oxygen, pH, alkalinity, POC, NO₂, NO₃, Si(OH)₄, PO₄, Chl-a. The samples are collected with the IUI Research Vessel, which has a powder coated aluminium Rosette (SeaBird) with 12 niskin bottles (12 liters each), and a CTD (SeaBird electronics). These measurements have been performed continuously since the year 2000.
- The National Monitoring Program of Israel's Mediterranean waters –Hydrographic and sedimentological cruises on board R.V. Bat Galim along E-W transects across the Israeli Mediterranean EEZ (Water bi-annual (nutrients, alkalinity, pH, DO, Chl-a, pico-phytoplancton, PP, BP); Sediments annual).
- Marine particulate fluxes are studied in the oligotrophic Gulf of Aqaba (GOA), northern Red Sea as part of the *Red Sea Dust, Marine Particulates and Seawater Time Series* (*REDMAST*, *GIpr09*). This includes a monthly–rotated bottom tethered mooring mounted with 5 sediment trap stations (KC Denmark Inc.) at approximately equal depth intervals between 120 and 570 m (water depth of ~610 m).

New projects and/or funding

- Yeala Shaked: Israel Science Foundation (ISF) research grant. Dust as a source of Phosphorus to Trichodesmium a globally important marine N2-fixer.
- Yeala Shaked: United States Israel Binational Science Foundation (BSF) research grant (with Rene Boiteau). Ocean Fertilization by Dust Studying how marine microorganisms 'mine' nutrients from dust.

Outreach activities conducted (please list any outreach/educational material available that could be shared through the GEOTRACES web site)

• Public talk (Adi Torfstein): "Climate change and global warming: where we came from and where we are heading", Yeruham, 2021

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Banc-Prandi G., Baharier N., Benaltabet T., Torfstein A., Antler G. and Fine M. (2022) Elevated temperatures reduce the resilience of the Red Sea branching coral styllophora pistillata to copper pollution. Aquatic Toxicology 244, 106096.
- Benaltabet T., Gunter-Hoch E. and Torfstein A. (2021) Heavy metal, rare earth element and Pb isotope dynamics in mussels during a depuration experiment in the Gulf of Aqaba, northern Red Sea. Frontiers in Marine Science 8, 669329
- Hoober L., Titelboim D., Abramovich S., Herut B., Teutsch N., Benaltabet T. and Torfstein A. (2022) Establishing baseline assessment levels for monitoring coastal heavy metals using foraminiferal shells: A case study from the Southeastern Mediterranean. Water 14, 1352

- Kolker, D., Bookman, R., Herut, B., David, N., Silverman, J. (2021). An Initial Assessment of the Contribution of Fresh Submarine Ground Water Discharge to the Alkalinity Budget of the Mediterranean Sea. Journal of Geophysical Research: Oceans, 126(8):p.e2020JC017085. https://doi.org/10.1029/2020JC017085
- Ozer, T., Gertman, I., Gildor, H., Herut, B. (2022). Thermohaline temporal variability of the SE Mediterranean coastal waters (Israel) -long-term trends, seasonality, and connectivity. Frontiers in Marine Sciences, 8:799457.
- Shaked Y, Twining B, Tagliabue A, and Maldonado MT. 2021. Probing the bioavailability of dissolved iron to ocean phytoplankton using in situ single cell iron quotas. Global Biogeochemical Cycles. e2021GB006979. https://doi.org/10.1029/2021GB006979
- Guy Sisma-Ventura, Or M. Bialik, Yizhaq Makovsky, Eyal Rahav, Tal Ozer, Mor Kanari, Sophi Marmen, Natalia Blekin, Tamar Guy-Haim, Gilad Antler, Barak Herut, Maxim Rubin-Blum (2022). Cold seeps alter the near-bottom biogeochemistry in the ultraoligotrophic Southeastern Mediterranean Sea. Deep–Sea Research I 183: 103744. ttps://doi.org/10.1016/j.dsr.2022.103744
- Sisma-Ventura G, Kress N, Silverman J, Gertner Y, Ozer T, Biton E, Lazar A, Gertman I, Rahav E and Herut B. (2021). Post-eastern Mediterranean Transient Oxygen Decline in the Deep Waters of the Southeast Mediterranean Sea Supports Weakening of Ventilation Rates. Front. Mar. Sci. 7:598686. https://doi.org/10.3389/fmars.2020.598686

GEOTRACES presentations in international conferences

- Yeala Shaked: Invited and funded speaker at SOLAS/SCOR Workshop: "Iron at the Air-Sea Interface". Ashville, US. (July, Remote).
- Yeala Shaked: Invited keynote speaker at: American Society for Limnology and Oceanography, Palma de Mallorca, Spain. Session chair (June, virtual meeting).
- Adi Torfstein: Co-convener of session in the Goldschmidt Meeting, Lyon, 2021: "Marine biogeochemistry: Particle fluxes and dissolved trace element cycling from source to sink"

Presentations:

- Lapid G., Torfstein A., Teutsch N. and Erel Y. (2021) Constraints on the provenance and weathering rates of atmospheric dust from the U and Nd isotopic compositions of carbonate and silicate phases. Goldschmidt meeting.
- Benaltabet T., Lapid G. and Torfstein A. (2021) Seawater aluminium seasonal dynamics and response to short-term perturbations in the Gulf of Aqaba, northern Red Sea. Goldschmidt meeting.
- Levy N., Torfstein A., Schiebel R., Chernihovsky N., Jochum K.P., Weis U., Stoll B., and Haug G.H. (2021) Time series of trace element distributions in planktonic foraminifer shells from the oligotrophic Gulf of Aqaba, northern Red Sea. Goldschmidt meeting.
- Kienast S.S. and Torfstein A. (2022) First estimate of biological carbon pump efficiency in the subtropical Gulf of Aqaba. Ocean Sciences meeting

Submitted by Adi Torfstein (adi.torf@mail.huji.ac.il).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN JAPAN

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

• Zheng et al. (2021) reported on basin-scale full-depth sectional distributions of total dissolvable, dissolved, and labile particulate Cd, Ni, Zn, and Cu along three transects including the GEOTRACES GP18 and GP02. In the North Pacific Ocean, it was indicated that there were strong differences in the relationships between dissolved trace metals and nutrients from those reported in other oceans. Dissolved Cd is influenced by biological processes and water circulation. Although this was also the case for dissolved Ni, Zn, and Cu, these metals were affected by scavenging. The effects of scavenging of the four metals were detected due to the internal formation of the Pacific Deep Water in the North Pacific Ocean and its long residence time. Judging from the stoichiometry among trace metals and major nutrients, scavenging was the important factor that significantly affects the distributions of dissolved Zn, Ni, and Cu, of which the magnitude of influence increases in the order of Cd < Ni, Zn < Cu.

Citation: Zheng, L., T. Minami, S. Takano, T-. Y. Ho, Y. Sohrin (2021), Sectional distribution patterns of Cd, Ni, Zn, and Cu in the North Pacific Ocean: relationships to nutrients and importance of scavenging, Global Biogeochemical Cycles, 35, doi: 10.1029/2020GB006558.

GEOTRACES workshops and meetings organized

- Domestic GEOTRACES session was held during the fall meeting of The Oceanographic Society of Japan 2021 (September 13 17, 2021) online for pursuing scientific discussion on recent Japanese GEOTRACES studies. We had 10 presentations including those given by 4 students.
- Domestic session entitled "Marine Geochemistry" related to GEOTRACES studies was held during the annual meeting of Geochemical Society of Japan 2021 (September 12 26, online and partially in person at Hirosaki University). We had 9 presentations including those by 4 students.

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

During the past year, Japan GEOTRACES investigators published 25 peer-reviewed journal articles and one article. The underlined first author is the ECR.

Peer-reviewed journal articles

- Alam, M., M. Tripti, G. P. Gurumurthy, Y. Sohrin, M. Tsujisaka, A. D. Singh, S. Takano, K. Verma (2022), Palaeoredox reconstruction in the eastern Arabian Sea since the late Miocene: Insights from trace elements and stable isotopes of molybdenum (δ^{98/95}Mo) and tungsten (δ^{186/184}W) at IODP Site U1457 of Laxmi Basin. Paleogeography, Palaeoclimatology, Paleoecology, 587, 110790. DOI: 10.1016/j.palaeo.2021.110790.
- <u>Ikhsani, I.</u> Y., R. Muhammad, J. Xu, K. H. Wong, S. Takeda, H. Obata (2021), Sources and transport of dissolved Mn, Fe, Cu, and Co in a semi-enclosed bay (Ariake Sea) in Japan. Estuarine, Coastal and Shelf Science, 259, 107475: doi.org/10.1016/j.ecss.2021.107475.

- Inoue, M., S. Hanaki, H. Kameyama, Y. Kumamoto, S. Nagao (2022), Unique current connecting Southern and Indian Oceans identified from radium distributions, Scientific Reports, 12, 1781.
- Kamidaira, Y., Y. Uchiyama, H. Kawamura, T. Kobayashi, S. Otosaka (2021), A modeling study on the oceanic dispersion and sedimentation of radionuclides off the coast of Fukushima. Journal of Environmental Radioactivity, 238–239, 106724. doi: 10.1016/j.jenvrad.2021.106724.
- Kumamoto, Y., M. Aoyama, Y. Hamajima, H. Nagai, T. Yamagata, A. Murata (2022), Zonal and vertical transports of Fukushima-derived radiocesium in the subarctic gyre of the North Pacific until 2014. Journal of Environmental Radioactivity, 247, 106864.
- Kurisu, M., K. Sakata, M. Uematsu, A. Ito, Y. Takahashi (2021), Contribution of combustion Fe in marine aerosols over the northwestern Pacific estimated by Fe stable isotope ratios. Atmospheric Chemistry and Physics. 21, 16027–16050. <u>https://doi.org/10.5194/acp-2021-460</u>
- Mashio, A. S., T. Tanimura, H. Hasegawa, S. Takeda, H. Obata (2021), Budgets and sources of dissolved platinum in the inland seas of Japan. Estuarine, Coastal and Shelf Science, 253, 107293.
- Misumi, K., J. Nishioka, H. Obata, D. Tsumune, T. Tsubono, M. C. Long, K. Lindsay, J. K. Moore (2021), Slowly Sinking Particles Underlie Dissolved iron transport across the Pacific Ocean, Global Biogeochemical Cycles, doi:10.1029/2020GB006823.
- Nakaguchi, Y., A. Sakamoto, T. Asatani, T. Minami, K. Shitashima, L. Zheng, Y. Sohrin (2022), Distribution and stoichiometry of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the Seas of Japan and Okhotsk. Marine Chemistry, 241, 104108. DOI: <u>https://doi.org/10.1016/j.marchem.2022.104108</u>.
- Nakajima, M. T. E., N. Takahata, K. Shirai, T. Kagoshima, K. Tanaka, H. Obata, Y. Sano (2022), Monitoring the magmatic activity and volatile fluxes of an actively degassing submarine caldera in southern Japan. Geochimica et Cosmochimica Acta, 317, 106-117.
- Nishioka, J., T. Hirawake, D. Nomura, Y. Yamashita, K. Ono, A. Murayama, A. Shcherbinin, Y. N. Volkov, H. Mitsudera, N. Ebuch, M. Wakatsuchi, I. Yasuda (2021), Iron and nutrient dynamics along the East Kamchatka current, western Bering sea basin and Gulf of Anadyr, Progress in Oceanography, doi:10.1016/j.pocean.2021.102662.
- Nomura, D., H. Ikawa, Y. Kawaguchi, N. Kanna, T. Kawakami, Y. Nosaka, S. Umezawa, M. Tozawa, T. Horikawa, R. Sahashi, T. Noshiro, I. Kaba, M. Ozaki, F. Kondo, K. Ono, I. S. Yabe, E. Y. Son, T. Toyoda, S. Kameyama, C. Wang, H. Obata, A. Ooki, H. Ueno, A. Kasai (2022), Atmosphere–sea ice–ocean interaction study in Saroma-ko Lagoon, Hokkaido, Japan 2021. Bulletin of Glaciological Research, 40, 1–17, doi: 10.5331/bgr.21R02.
- Oka, A., H. Tazoe, H. Obata (2021), Global distribution of rare earth elements in the ocean simulated by an ocean general circulation model. Journal of Oceanography, 77, 413–430.
- Otosaka, S., Y. Kamidaira, T. Ikenoue, H. Kawamura (2021), Distribution, dynamics, and fate of radiocesium derived from FDNPP accident in the ocean. Journal of Nuclear Science and Technology, 59, 409-423, doi: 10.1080/00223131.2021.1994480.
- Sasaki, Y., H. Kobayashi, A. Oka (2022), Global simulation of dissolved ²³¹Pa and ²³⁰Th in the ocean and the sedimentary ²³¹Pa/²³⁰Th ratios with the ocean general circulation model COCO ver4.0. Geoscientific Model Development, 15(5), 2013-2033.

- Sato, M., J. Nishioka, K. Maki, S. Takeda (2021), Chemical speciation of iron in the euphotic zone along the Kuroshio Current. Marine Chemistry, 233, doi:10.1016/j.marchem.2021.103966.
- Takano, S., M. Tsuchiya, S. Imai, Y. Yamamoto, F. Yusuke, K. Suzuki, Y. Sohrin (2021), Isotopic analysis of nickel, copper, and zinc in various freshwater samples for source identification. Geochemical Journal, 55 (3), 171-183. DOI: 10.2343/geochemj.2.0627.
- Tazoe, H., H. Amakawa, K. Suzuki, J. Nishioka, T. Hara, H. Obata (2021), Analysis of Nd isotopic composition in seawater using newly developed solid phase extraction and MC-ICP-MS. Talanta, 232, 122435: doi.org/10.1016/j.talanta.2021.122435.
- Tazoe, H., H. Obata, T. Hara, M. Inoue, T. Tanaka, J. Nishioka (2022), Vertical profiles of ²²⁶Ra and ²²⁸Ra concentrations in the western Subarctic Gyre of the Pacific Ocean, Frontiers in Marine Science, in press.
- Wong, K. H., H. Obata, I. Y. Ikhsani, R. Muhammad (2021), Controls on the distributions of dissolved Cd, Cu, Zn, and Cu-binding organic ligands in the East China Sea. Journal of Geophysical Research-Oceans, 126, e2020JC016997: doi.org/10.1029/2020JC016997.
- Wong, K. H., J. Nishioka, T. Kim, H. Obata (2022), Long-range lateral transport of dissolved manganese and iron in the subarctic Pacific. Journal of Geophysical Research-Oceans, 127, e2021JC017652: doi.org/10.1029/2021JC017652.
- Yamada, M., J. Zheng (2021), Temporal trend of ²⁴⁰Pu/²³⁹Pu atom ratios in water columns in the western North Pacific Ocean and its marginal seas. Journal of Environmental Radioactivity, 240, 106737. <u>https://doi.org/10.1016/j.jenrad.2021.106737</u>
- Yamada, M., J. Zheng (2021), Distributions of ²³⁹Pu and ²⁴⁰Pu concentrations and ²⁴⁰Pu/²³⁹Pu atom ratios and ²³⁹⁺²⁴⁰Pu inventories in a water column in the eastern Indian Ocean: Transport of Pacific Proving Grounds-derived Pu via the Indonesian Throughflow. Environmental Science and Technology, 55(20), 13849-13859. https://doi.org/10.1021/acs.est.1c03575
- Yamada, M., S. Oikawa (2022), Biomonitoring of Pu isotopes in liver of North Pacific giant octopus (*Enteroctopus dofleini*) collected off the Rokkasho Nuclear Fuel Reprocessing Plant, western North Pacific margin. Journal of Sea Research, 183, 102201. https://doi.org/10.1016/j.seares.2022.102201
- Zheng, L., T. Minami, S. Takano, T.-Y. Ho, Y. Sohrin (2021), Sectional distribution patterns of Cd, Ni, Zn, and Cu in the North Pacific Ocean: Relationships to nutrients and importance of scavenging. Global Biogeochemical Cycles, 35 (7), e2020GB006558, https://doi.org/10.1029/2020GB006558.

Non-peer-reviewed article

• Wong, K. H., H. Obata, J. Nishioka, Y. Yamashita, Y. Kondo, T. Kim, A. Mashio, H. Hasegawa (2022), Subarctic Pacific Intermediate Water: An Oceanic Highway for the Transport of Trace Metals in the North Pacific, Limnology and Oceanography Bulletin, https://doi.org/10.1002/lob.10490

Completed GEOTRACES PhD or Master theses

- Idha Yulia Ikhsani (2022), "Dynamics of trace metal biogeochemistry in the estuary and open ocean: Studies from Ariake Sea, Bay of Bengal and Eastern Indian Ocean", Ph.D. Agriculture. Thesis, The University of Tokyo.
- Wiwit (2021), "Copper-binding organic ligands and their relationship with phytoplankton growth in Japanese coastal waters", Ph.D. Agriculture. Thesis, The University of Tokyo.
- Koki Yamanaka (2022), "Redox status of Fe in the North Pacific Ocean and its adjacent seas", M. F. Sc. Thesis, Nagasaki University.
- Ryota Hirabayashi (2022), "Mass cycle mechanisms in the Eastern Indian Ocean", Master's thesis, Graduate School of Agriculture, Meiji University.

GEOTRACES presentations in international conferences

- Chan, C-. Y., L. Zheng, Y. Sohrin (2021), North-south (145°W) and east-west (47°N) sectional distributions of dissolved trace metals during GEOTRACES Japan KH-17-3 cruise in the Pacific Ocean, Goldschmidt2021 Virtual Conference, July 2021.
- Kurisu, M., K. Sakata, M. Uematsu, A. Ito, Y. Takahashi (2021), Estimation of the contribution of combustion Fe in marine aerosols over the North Pacific using Fe stable isotope ratios, PICES-2021 Annual Meeting, October 2021.
- Kumamoto, Y., A. Michio, Y. Hamajima, M. Inoue, S. Nishino, T. Kikuchi, K. Sato (2022), Radiocesium in the western subarctic area of the North Pacific Ocean, Bering Sea, and Arctic Ocean in 2019 and 2020, the 6th International Conference on Environmental Radioactivity (ENVIRA 2021), online, December 2021.
- Tang, C., S. Aoki, Y. Maruo, F. Kondo, S. Komiya, K. Noborio (2021), Methane exchange in the sea–air interface of Indian Ocean, AGU Fall Meeting 2021, 884317, New Orleans & online, December 2021.

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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN MEXICO

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

The results presented are from an impacted area of the Gulf of Mexico and a protected area on the Pacific mexican region in front of Baja California peninsula.

• **Gulf of Mexico**. Surface water samples from the Yucatan shelf presented Cd concentrations similar to those reported internationally for non-polluted coastal and marine waters. V concentrations, on the other hand, fall within the range of anthropogenically polluted waters (25% of the sampling sites). In the study area, the probable sources of V could be: (1) carbonate sediments leaching V into the water column and co-transported with fine sediments resuspending as a result of the complex hydrodynamics in the area or, (2) accidental spills from cargo ships transporting oil between the Atlantic and the Gulf of Mexico. Significant spatial and temporal differences were found for both metals; therefore, a regional interval concentration is suggested for V from 1.28 to 1.84 μ g L⁻¹and Cd from 0.003 to 0.09 μ g L⁻¹. These differences could primarily be the result of the observed hydrology and hydrodynamics created by the Yucatan current, submarine groundwater discharges and upwelling.

From: Arcega-Cabrera et al. (2021).

Pacific (protected area). Surficial sediment quality in the Ojo de Liebre Lagoon (OLL), Mexico, was evaluated via five geochemical indices. Results indicate that concentrations of the elements Ag, As, Cu, Fe, Mn, Mo, Ni, Sb, U, V and Zn do not exert adverse biological effects in this ecosystem. However, minor enrichment was observed for Ba (mean ± SD: 1.09 ± 0.17) and Co (1.57 ± 0.22) and was moderately severe for Cd (9.3 ± 2.0), possibly due to natural processes. The adverse effect index was >1 only for Hg, suggesting that concentrations of this element are sufficiently high (0.40 to 1.13 nmol g⁻¹) to potentially elicit adverse effects on local organisms in contact with sediments. This result is particularly important for grey whales (*Eschrichtius robustus*), given that they ingest large quantities of benthic organisms during their seasonal stay in the OLL. From: Valdivieso-Ojeda et al. (2021).

New projects and/or funding

• Biological response of phytoplankton community to iron and vitamin B12 and their implication to the formation and presistence of Harmful Algal Blooms in Mexican coastal waters. Multidisciplinary project financed by CONACyT. PI: Dr. Mary Carmen Ruiz de la Torre (2017 - 2022).

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

• Arcega-Cabrera, F., Gold-Bouchot, G., Lamas-Cosío, E. et al. 2021. Spatial and Temporal Variations of Vanadium and Cadmium in Surface Water from the Yucatan Shelf. Bulletin of Environmental Contamination and Toxicology 108, 43–48. https://doi.org/10.1007/s00128-021-03234-3

- Cervantes-Díaz, G.Y., Hernández-Ayón, J.M., Zirino, A., Herzka, S.Z., Camacho-Ibar, V., Norzagaray, O., Barbero, L., Montes, I., Sudre, J., Delgado, J.A. 2022. Understanding upper water mass dynamics in the Gulf of Mexico by linking physical and biogeochemical features. Journal of Marine Systems, 225, 103647. https://doi.org/10.1016/j.jmarsys.2021.103647.
- Dótor-Almazán A., Gold-Bouchot G., Lamas-Cosío E., Huerta-Diaz M.A., Ceja-Moreno V., Oceguera-Vargas I., Zapata-Pérez O., Arcega-Cabrera F. 2022. Spatial and temporal distribution of trace metals in shallow marine sediments of the Yucatan Shelf, Gulf of Mexico. Bulletin of Environmental Contamination and Toxicology 108, 3-8. doi: 10.1007/s00128-021-03170-2.
- Dótor-Almazán A., Gold-Bouchot G., Lamas-Cosío E., Huerta-Diaz M.A., Ceja-Moreno V., Oceguera-Vargas I., Zapata-Pérez O., Arcega-Cabrera F. 2022. Vanadium and cadmium in shallow marine sediments: Spatial and temporal behavior in the Tamaulipas Continental Platform, Gulf of Mexico, Mexico. Bulletin of Environmental Contamination and Toxicology 108, 30-36. doi: 10.1007/s00128-021-03213-8.
- Hernández-Sánchez, O.G., Camacho-Ibar, V.F., Fernández-Álamo, M.A., Herzka, S.Z. 2022. Nitrogen sources (NO3– vs N2 fixation) inferred from bulk δ15N values of zooplankton from the deep water region of the Gulf of Mexico. Journal of Plankton Research, 44, 48-87. https://doi.org/10.1093/plankt/fbab089
- Lee-Sánchez, E., Camacho-Ibar, V.F., Velásquez-Aristizábal, J.A., Valencia-Gasti, J.A., Samperio-Ramos, G. 2022. Impacts of mesoscale eddies on the nitrate distribution in the deep-water region of the Gulf of Mexico. Journal of Marine Systems, 229, 103721. https://doi.org/10.1016/j.jmarsys.2022.103721.
- Olimón-Andalón V, Valdés-Flores J, Ley-Quiñonez CP, Zavala-Norzagaray AA, Aguirre AA, León-Sicairos N, Velázquez-Román J, Flores-Villaseñor H, Acosta-Smith E, Sosa-Cornejo I, Valdez-Flores M, Hart CE, Canizalez-Román A. 2021. Essential and trace metals in a post-nesting olive ridley turtles (Lepidochelys olivacea) in Ceuta beach, Sinaloa, Mexico. Environmental Science and Pollution Research International, 28(23):29998-30006. doi: 10.1007/s11356-021-12819-8.
- Valdivieso-Ojeda J.A., Huerta-Diaz M.A., Delgadillo-Hinojosa F., Otero X.L., Arenas-Islas D. and García-Orozco J. (2021) Sediment trace metal levels in the Ojo de Liebre Lagoonal Complex (Baja California, Mexico), a marine wildlife protected area. Mar. Pollut. Bull. 165, 112097. DOI: 10.1016/j.marpolbul.2021.112097. ISSN Impreso: 0025326X, ISSN Electrónico: 0025326X.
- Velásquez-Aristizábal, J.A. Camacho-Ibar, V.F., Durazo, R., Valencia-Gasti, J.A., Lee-Sánchez, E., Trasviña-Castro, A. 2022. Nitracentric/Hydrographic classification and prediction of nitrate profiles for oceanographic stations under the influence of mesoscale eddies in the Gulf of Mexico. Frontiers in Marine Science, 9, 827574 doi: 10.3389/fmars.2022.827574

Completed GEOTRACES PhD or Master

• Gutiérrez, R.A. 2022. Spatial and temporal variability of dissolved manganese in Todos Santos Bay (summer 2008 - spring 2009). MSc thesis Oceanografía Costera - Universidad Autónoma de Baja California. 94 pp • Naranjo-Ortiz, D.A. 2022. Spatial and temporal distribution of nickel and cadmium in relation to the abundance of Synechococcus spp. and Prochlorococcus spp. in the Mexican region of the Gulf of Mexico. MSc thesis, CICESE. 177 pp

Submitted by Maria Lucila Lares (<u>llares@cicese.mx</u>).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN THE NETHERLANDS

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

- Progress is being made with the interpretation and publication of results from cruises ANA08B and PS117
- Sample analysis of the Metalgate cruise samples is ongoing

GEOTRACES or GEOTRACES relevant cruises

• Metalgate cruise 64PE474 Reykjavik (Iceland) 17-07-2021 to Reykjavik (Iceland) 16-08-2021. GEOTRACES process study GApr16

Outreach activities conducted (please list any outreach/educational material available that could be shared through the GEOTRACES web site)

• Session in the Bètapartnersconferentie for high school teachers 'Chemie en Natuurkunde in de Oceaan; De basis van het leven. (in Dutch; 17/03/2021)

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Joy-Warren, H.L., Alderkamp, A.-C., van Dijken, G.L., J. Jabre, L., Bertrand, E.M., Baldonado, E.N., Glickman, M.W., Lewis, K.M., Middag, R., Seyitmuhammedov, K., Lowry, K.E., van de Poll, W. and Arrigo, K.R., 2022. Springtime phytoplankton responses to light and iron availability along the western Antarctic Peninsula. Limnology and Oceanography, 67(4): 800-815.
- Krisch, S., Hopwood, M.J., Roig, S., Gerringa, L.J.A., Middag, R., Rutgers van der Loeff, M.M., Petrova, M.V., Lodeiro, P., Colombo, M., Cullen, J.T., Jackson, S.L., Heimbürger-Boavida, L.-E. and Achterberg, E.P., 2022. Arctic – Atlantic Exchange of the Dissolved Micronutrients Iron, Manganese, Cobalt, Nickel, Copper and Zinc with a Focus on Fram Strait. Global Biogeochemical Cycles, 36(5): e2021GB007191Kleint, C., Zitoun, R., Neuholz, R., Walter, M., Schnetger, B., Klose, L., Chiswell, S.M., Middag, R., Laan, P., Sander, S., and Koschinsky, A., in press. Trace metal dynamics in shallow hydrothermal plumes at the Kermadec arc. accepted in Frontiers in Marine Science.
- Middag, R., Rolison, J.M., George, E., Gerringa, L.J.A., Rijkenberg, M.J.A. and Stirling, C.H., 2022. Basin scale distributions of dissolved manganese, nickel, zinc and cadmium in the Mediterranean Sea. Marine Chemistry, 238: 104063.
- Seyitmuhammedov, K., Stirling, C.H., Reid, M.R., van Hale, R., Laan, P., Arrigo, K.R., van Dijken, G., Alderkamp, A.-C., and Middag, R., 2022. The distribution of Fe across the shelf of the Western Antarctic Peninsula at the start of the phytoplankton growing season. Marine Chemistry: 104066.
- Gerringa, L.J.A., Rijkenberg, M.J.A., Slagter, H.A., Laan, P., Paffrath, R., Bauch, D., Rutgers van der Loeff, M. and Middag, R., 2021. Dissolved Cd, Co, Cu, Fe, Mn, Ni, and Zn in the Arctic Ocean. Journal of Geophysical Research: Oceans, 126(9): e2021JC017323.

- Baker, A.R., Kanakidou, M., Nenes, A., Myriokefalitakis, S., Croot, P.L., Duce, R.A., Gao, Y., Guieu, C., Ito, A., Jickells, T.D., Mahowald, N.M., Middag, R., Perron, M.M.G., Sarin, M.M., Shelley, R. and Turner, D.R., 2021. Changing atmospheric acidity as a modulator of nutrient deposition and ocean biogeochemistry. Science Advances, 7(28): eabd8800
- Zitoun, R., Achterberg, E.P, Browning, T.J., Hoffmann, L.J., Kirsch, S., Sander, S. G., and Koschinsky, A. (2021). The complex provenance of Cu-binding ligands in the South-East Atlantic. Marine Chemistry, 237, 104047
- Lenstra, W.K., N.A.G.M van Helmond, O.M. Żygadłowska, R. Van Zummeren, R. Witbaard, C.P. Slomp. 2022. Sediments as a source of iron, manganese, cobalt and nickel to continental shelf waters (Louisiana, Gulf of Mexico). Frontiers in Marine Science. Front. Mar. Sci. 9:811953. doi: 10.3389/fmars.2022.811953

GEOTRACES presentations in international conferences

- Dale, D., Macrander, A., Ólafsdóttir, S., Middag, R., Casacuberta Arola, N.. Using anthropogenic radionuclides to trace ocean circulation around Iceland. Poster presentation at the 2022 Arctic-Subarctic Ocean Fluxes meeting, 9-11 May, Hafnarfjörður (Iceland).
- Jones, R.L., Annett, A., Jariel, C., Lohan, M., Middag, R.. Investigating the behaviour of iron during sediment resuspension along the Denmark Strait and the Greenland Shelf. Goldschmidt 2022.
- Eich, C., Middag, R., and Brussaard, C.P.D. Ecological importance of viral lysis as a loss factor for phytoplankton in the Amundsen Sea. Poster presentation at the 2022 Marine Microbes GRC, 29-05-2022, Switzerland.
- Middag, R., Ardiningsih, I., Bertrand, E.M., Brussaard, C.P.D., Eich, C.U.M, Jung, J., Kim, T., Lee, S., Lee, Y., van Manen, M.H., McCain, J.S.P., Tian, H.A. Effects of Iron and Temperature on Antarctic Phytoplankton. Oral Presentation at the 2022 Ocean Science Meeting, 28-02-2020, online, USA.

Submitted by Rob Middag (<u>rob.middag@nioz.nl</u>) on behalf of all Dutch GEOTRACES participants

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN NORWAY

May 1st, 2021 to April 30th, 2022

GEOTRACES or GEOTRACES relevant cruises

- NTNU Nansen Legacy Project spring cruise in the Northern Barents Sea (bio-essential and toxic element and DOC characterization) in the water column and sediments. April -May 2021.
- NTNU Nansen Legacy Project late summer cruise from Northern Barents Sea the Nansen Basin (bio-essential, toxic and rate earth elements) in the water column and sediments. August September 2021.
- NTNU Best- Siberian project participation in a Russian Arctic cruise on board the RV "Akademik Mstislav Keldysh" (bio-essential and toxic elements) in the water column and sediments. October-November 2021.

New Funded projects

• NTNU participation in the NEXUS-MONARC project: Capacity Building Nexus for Monitoring Water Quality in Multi-Stressor Areas: Pilot Study at the Hellenic Volcanic Arc. HORIZON-WIDERA-2021-ACCESS-03 (EU funded).

Other GEOTRACES activities

• The Biogeochemistry group at NTNU led by Dr. Ardelan have strengthened their trace element lab by adding a new DMA-80 and a Brooks Rand total Hg and MeHg determination instruments.

GEOTRACES presentations in international conferences

• Seasonal scavenging of inorganic mercury during transition to Arctic polar night. Stephen G. Kohler, Lars-Eric Heimburger-Boavida, Mariia V. Petrova, Murat V. Ardelan. Arctic Frontiers 2021 conference presentation.

Submitted by Nicolas Sanchez (<u>nicolas.sanchez@ntnu.no</u>).

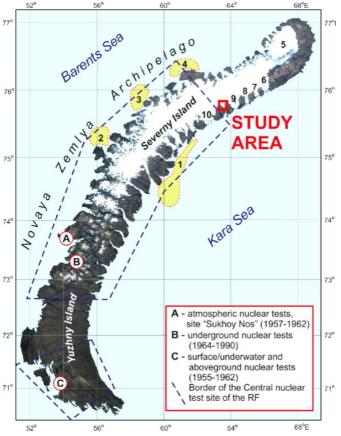
ANNUAL REPORT ON GEOTRACES ACTIVITIES IN RUSSIA

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

Arctic Ocean

In recent years, cryoconite has received growing attention from a radioecological point of view, since several studies have shown that this material is extremely efficient in accumulating natural and anthropogenic radionuclides. The Novaya Zemlya Archipelago (Russian Arctic) hosts the second largest glacial system in the Arctic. From 1957 to 1962, numerous atmospheric nuclear explosions were conducted at Novaya Zemlya, but to date, very little is known about the radioecology of its ice cap. Analysis of radionuclides and other chemical elements in cryoconite holes on Nalli Glacier reveals the presence of two main zones at different altitudes that present different radiological features. The first zone is 130-210 m above sea level (a.s.l.), has low radioactivity, high concentrations of lithophile elements and a chalcophile content close to that of upper continental crust clarkes. The second zone (220–370 m a.s.l.) is characterized by high activity levels of radionuclides and "inversion" of geochemical behavior with lower concentrations of lithophiles and higher chalcophiles. In the upper part of this zone (350–370 m a.s.l.), ¹³⁷Cs activity reaches the record levels for Arctic cryoconite (5700–8100 Bq/kg). High levels of Sn, Sb, Bi and Ag, significantly exceeding those of upper continental crust clarkes, also appear here. We suggest that a buried layer of contaminated ice that formed during atmospheric nuclear tests serves as a local secondary source of radionuclide contamination. Its melting is responsible for the formation of this zone (Miroshnikov et al., 2022).



- *Figure 1.* Location of the sampling site on Nalli Glacier (red box). Zones of high ¹³⁷Cs activity in bottom sediments: 1–4 (*Miroshnikov et al.*, 2022).
- Glaciers: 5 northern icecap; 6 Roze, 7 – Sredny, 8 – Rozhdestvensky, 9 – Vershinsky, and 10 – Moshchny.

In high latitude regions, thawing of snow provides a sizable contribution of dissolved • trace metals to the hydrological network. Towards a better understanding of natural and anthropogenic control on heavy metals and metalloid input from the atmosphere to the inland waters of Siberian Arctic and subarctic regions, the chemical composition of dissolved (<0.22 µm) fractions of snow across a 2800 km south–north gradient in Western Siberia was measured (Figure 2) (Krickov et al., 2022). Fe, Mn, Co, Ni, and Cd demonstrated sizable (by a factor of 4-7) decrease in concentration northward, which can be explained by a decrease in overall population density and the influence of dry aerosol deposition. Many elements (Mn, Ni, Cu, Cd, Pb, As, and Sb) exhibited a prominent local maximum (a factor of 2-3) in the zone of intensive oil and gas extraction (61–62° N latitudinal belt), which can be linked to gas flaring and fly ash deposition. Overall, the snow water chemical composition reflected both local and global (long-range) atmospheric transfer processes. Based on mass balance calculation, we demonstrate that the winter time atmospheric input represents sizable contribution to the riverine export fluxes of dissolved (<0.45 µm) Mn, Co, Zn, Cd, Pb, and Sb during springtime and can appreciably shape the hydrochemical composition of the Ob River main stem and tributaries.

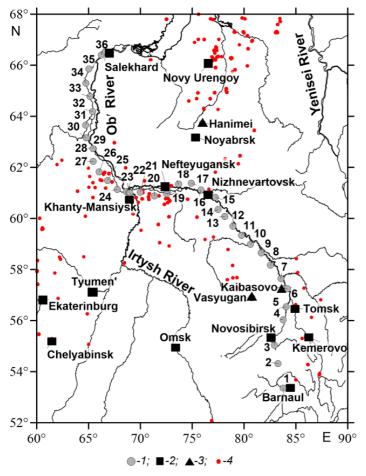


Figure 2. Studied area of the Western Siberian Lowland (Krickov et al., 2022): 1 –sampling sites; 2 – large cities; 3 – scientific stations of Tomsk State University; 4 – the position of gas flaring on 25 July 2020 taken from: https://firms.modaps.eosdis.nasa.g ov/download/accessed

• The first-order principles of seep carbonate formation are currently quite well constrained, little is known regarding the duration or mode of carbonate formation in the Siberian Arctic shelf. Currently available data on carbonate formation in the Siberian Arctic seas have reported that the methane-derived carbonates (MDACs) can form in recent subsurface sediments but cannot form pavements or large carbonate slabs at the sediment/water interface. Newly discovered crusts of methane-derived authigenic carbonate deposits were observed on the seafloor and sampled at the cold seep field with an area of approximately 13 km² on the outer shelf of the Laptev Sea (Kravchishina et al., 2021). Seafloor observations

indicated evidence of gas flares, and microbial colonies were recorded in the southern area, suggesting that the seep field is currently active. The retrieved carbonates are the result of paleomethane seepage. The crusts containing fingerprints of gas mixtures could be the result of the physical mixing of different methane pools in response to the vertical and lateral diffusion of gas. This mixing involves admixtures of thermogenic and microbial gases as well as an admixture of bicarbonate from seawater. Therefore, both thermogenic methane and microbial methane participated in the carbonate precipitation. Methane cold seepage is related to deep-seated faults belonging to the Laptev Sea Rift System and the Khatanga-Lomonosov Fracture Zone. A similar origin of methane seepage has been reported in sediment deposits within Arctic seas at $72^{\circ}-79^{\circ}$ N. The methane seepage could have been controlled by the last deglaciation that triggered changes in the fault system and favored gas migration from offshore hydrocarbon reservoir.

The ecosystems of the Arctic Ocean and their expected changes in a context of Global climate processes are crucially dependent on the freshwater input. The freshwater signal is assumed to be the main structuring factor for the marine fauna on the shallow shelf of the Siberian Arctic seas. The Laptev Sea is a key area for understanding the land-ocean interaction in high latitude regions. The largest freshwater input is provided by the deltaic Lena River followed by the estuarine Khatanga River. The plumes of these rivers differ considerably in their hydrophysical characteristics, suggesting differential impacts on ecosystems of the adjacent shelf. The key component of pelagic ecosystems is zooplankton, which transfers energy from primary producers to higher trophic levels and modifies sedimentations processes. This study is focused on the influence of river discharge on zooplankton in the Laptev Sea at the end of productive season in August–September 2017. Despite large spatial extension of the Khatanga plume, the impact of river discharge on zooplankton species composition was restricted mainly to the inner Gulf where the brackish species shaped the community. Contrary to the Khatanga input, the Lena freshwater inflow was highly variable and under certain conditions (discharge rate, wind forcing) governed the structure of zooplankton community over a vast shelf area. Analysis of demographic structure of Calanus glacialis suggests that seasonal development of the population was largely controlled by the time of ice retreat. Observed climatic changes in the Arctic were not reflected in the total zooplankton biomass and composition of the dominant species (Pasternak et al., 2022).

The important information on the impact of a riverine discharge and time of ice retreat on the magnitude and biogeochemical composition of the vertical particle fluxes on the Laptev Sea shelf was provided in the paper by Drits et al. (2021). The effect of the river discharge was manifested by the increase of the total particle flux dominated by the lithogenic component and a higher share of lithogenic organic carbon in the total particulate organic carbon flux than outside the river plume (Figure 3). A high share of freshwater phytoplankton species in the trapped material indicated that phytoplankton was transported onto the shelf by the river plume and subsequently exported to the underlying water column. The most pronounced influence of the freshwater discharge was observed close to the river mouth and the plume signature decreased progressively towards its periphery. The large contribution of the lithogenic matter to the vertical particle flux on the Laptev Sea shelf is suggested to result not only from the riverine discharge but also from sediment resuspension, lateral offshore transport of sediment just above the seabed, and coastal abrasion. The timing of ice cover retreat appears crucial in determining the patterns of vertical particle export, with the higher fluxes observed soon after the sea ice break up. The ice-released matter and phytoplankton bloom in the marginal ice zone are expected to contribute to the increase of the particle flux. The timing of ice retreat determined also the biogenic carbon composition. The observed changes in the vertical flux magnitude and composition which result from different time of ice retreat are similar to seasonal succession in the pelagic communities.

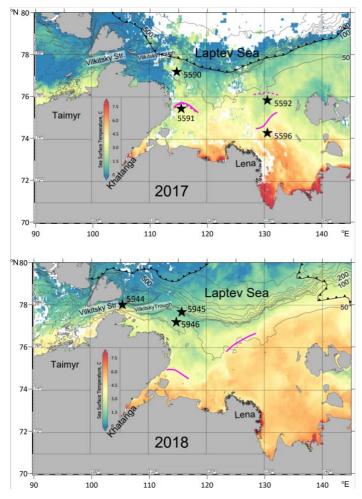


Figure 3. Map of the study area with location of the stations (Drits et al., 2021). Sea surface temperature (°C) distribution: average for 29 August -62017 September (MODIS-Aqua_L3_SST_8d_4km vR2019.0) (Berrick et al., 2009). Bold lines show the position of the ice edge (http://www.aari.ru). Magenta lines indicate river plume extension (isohaline of 25): solid line – at the time of first sampling (31.08-3.09. 2017), dashed line - at the time of the repeated sampling (14.09- 20.09.2017). Contour depths in meters. When sampling was repeated, the Lena plume considerably extended to the north, while Khatanga plume remained at the same position.

Spring processes in phytoplankton communities in the Arctic shelf seas, when the primary production is increased up to 50% of the annual bulk value, are extremely poorly studied. The hotspots of huge primary production in the northern Eurasian seas are correlated with regional climatic changes, a significant reduction of sea ice cover, a decrease in ice thickness, and a prolonged period of open water (Sergeeva et al., in prep.). Early spring communities are formed by a few species of diatoms. These species massively form resting spores which settle down to the upper sediment layer under the biogenic depletion and lack of light. The species composition and abundance of diatoms resting spores in the sediment surface layer can correlate with the intensity and composition of spring blooms. The aim was to study the composition and intensity of the early spring sea ice-associated phytoplankton bloom in the Kara Sea areas affected and not affected by Atlantic waters. The planktonic diatoms viable spores from the upper sediment layer were studied in 2020 and 2021. The results of two-year variability in the number and composition of viable spores demonstrate the relationship with sea ice conditions. On the continental slope (ice melting in May) with pronounced influence of warm waters of Atlantic origin the diatom taxa is more diverse, and prevail species: Thalassiosira constricta, Thalassiosira oceanica, and Detonula confervacea. On the shelf (ice melting in mid-June) the species of Navicula pelagica and Thalassiosira constricta are predominate. The dense sea ice on the shelf during a winter leads to Chaetoceros socialis predominate, what can form massive blooms associated with spring melting of sea ice.

The relationship between the composition of the microbial community and the processes • of methane and sulfur cycling was established in the northern Barents Sea (Begmatov et al., 2021). The data revealed differences between microbial communities and processes in the upper and deep layers of sediments, probably reflecting oxic versus anoxic conditions (Figure 4). The upper layer was dominated by autotrophic ammonium-oxidizing Crenarchaeota and various groups of typical aquatic aerobic heterotrophic bacteria of the phyla Actinobacteria, Proteobacteria, Verrucomicrobia, and Bacteroidetes fed by falling organics. In the deep sediments, the sulfur and nitrogen cycles seemed to be linked. Nitrate formed as a result of ammonia oxidation is utilized by Campilobacterota, which oxidize sulfide formed by sulfate reducers back to sulfate. Nitrate, in turn, is reduced to gaseous nitrogen, and possibly to ammonia. Methane arriving from sediment layers located below the sulfate-rich zone is oxidized by ANME archaea in the anoxic zone in a process coupled to sulfate reduction and denitrification, or by aerobic methanotropic bacteria in the upper oxygenated layer. Methane concentrations and rates of microbial biogeochemical processes in sediments in the northern Barents Sea are noticeably higher than in oligotrophic areas of the Arctic Ocean, indicating that an increase in methane concentration significantly activates microbial processes in sediments.

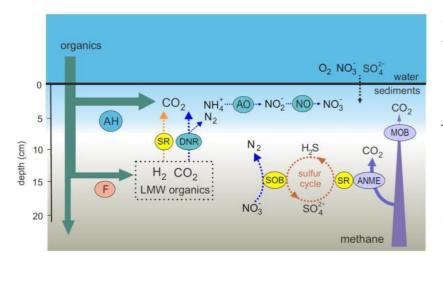


Figure 4. Microbial related processes to sulfur methane, and cycling in nitrogen the Barents Sea sediments. AH, aerobic heterotrophs; F, fermentative microorganisms; SOB. sulfur-oxidizing bacteria; SR. sulfate-reducing bacteria; ANME, anaerobic methane oxidizing archaea; MOB, aerobic methaneoxidizing bacteria; AO, ammonia oxidizing microorganisms; NO. nitrite-oxidizing microorganisms; DNR, dissimilatory nitrate reducers: LMW. low molecular weight (*Begmatov et al.*, 2021).

The Yamal tundra lakes (Yamal Peninsula, Kara Sea, Arctic) were found to exhibit high phytoplankton production (340–1200 mg Cm⁻² d⁻¹) during the short summer season (Savvichev et al., 2021). The research was carried out in four lakes in August 2019. Organic matter was deposited onto the bottom sediments, where methane (33–990 µmol CH₄ dm⁻³) was the main product of anaerobic degradation. The rates of hydrogenotrophic methanogenesis appeared to be higher in the sediments of the deep lakes than in those of the shallow ones. In the sediments, Methanoregula and Methanosaeta were predominant in the archaeal methanogenic community. Methane oxidation $(1.4-9.9 \ \mu mol \ dm^{-3} \ d^{-1})$ occurred in the upper sediment layers simultaneously with methanogenesis. *Methylobacter* tundripaludum (family *Methylococcaceae*) predominated in the methanotrophic community of sediments and water column. The activity of methanotrophic bacteria in deep mature lakes resulted in a decrease in the dissolved methane concentration in lake water from 0.8-4.1 to 0.4μ mol CH₄ L⁻¹ d⁻¹, while in shallow thermokarst lakes the geochemical effect of methanotrophs was much less

pronounced (Figure 5). Thus, only small, shallow Yamal lakes may contribute significantly to the overall diffusive methane emissions from the water surface during the summer season. The water column of large, deep lakes on Yamal acts, however, as a microbial filter preventing methane emission. Climate warming will lead to an increase in the total area of thermokarst lakes, which will enhance the effect of methane release into the atmosphere.

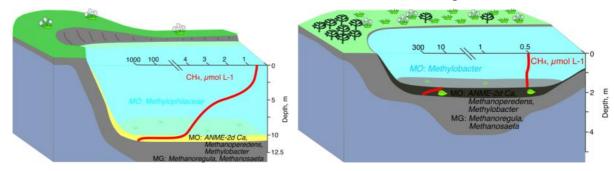


Figure 5. Microbial processes and microbial communities of the methane cycle in the water columns and bottom sediments of deep (a) and shallow tundra lakes (b) of the Yamal Peninsula (Savvichev et al., 2021).

• Relationship between long-term variability of sea ice cover in the Barents Sea with changes in current velocity and surface temperature in the North Atlantic was revealed (Krasheninnikova et al., 2022).

• The study of aliphatic (AHCs) and polycyclic aromatic hydrocarbons (PAHs) of bottom sediments was carried out in the Norwegian and Barents seas. The anthropogenic input of HCs into bottom sediments leads to an increase in their content in the composition of C_{org}. The fluids influence on the Svalbard shelf and in the Medvezhinsky Trench determines the specificity of local anomalies in the content and composition of HCs. This is reflected in the absence of a correlation between HCs and the grain size composition of sediments and C_{org} content as well as a change in hydrocarbon molecular markers. The bottom sediments are enriched in light alkanes and naphthalenes due to discharge of gas fluids (Nemirovskaya, Khramtsova, 2021).

Atlantic Ocean

To clarify one more mechanism of the Fe, Mn, Cu, Zn, and Pb accumulation in the biogenic foraminiferal-coccolite sediments, the metalliferous sediment core 184k was taken at the hydrothermal vent cluster Pobeda (17° N, Mid-Atlantic Ridge), and the background core 215k of carbonate sediments from the Central Atlantic were examined (Demina et al., 2022). In metalliferous sediment core the main Fe mineral phase was goethite FeOOH (37-44% on a carbonate-free basis, cfb). Rather small quantities ($\leq 10-12\%$) of talc, serpentine, quartz whose total amounts increased down the core reaching up to 50% (cfb). Down the 184k core, the calcite CaCO₃ content decreases sharply from 77% to 20% which was obviously due to its substitution with authigenic goethite, on the one side, and an increase in the number of modified ultrabasite fragments, on the other side. The metal enrichment factor (EF) in 184k core relative to background values reached up to 125 for Cu, while for Mn, no increased EF was recorded. The Fe total content (cfb) increased down the 184k core and reached maximum 41% (on a carbonate-free basis, cfb) in the deep layers, wherein the elevated concentrations of the rest metals were recorded, an observation that might be attributed to influence of hydrothermal diffused fluids. Essential mass of Fe (up to 70% of total content) was found in the residual fraction composed of crystallized goethite, aluminosilicates. Among geochemically mobile fractions, 90–97% of total Fe was determined in the form of authigenic oxyhydroxides. The same fraction was the predominant host for Mn in both metalliferous and background sediments (55–85%). In sum, 40–96 % of Cd, Cu, Zn, and Pb were associated with the Fe-Mn oxyhydroxides. A substitution of Ca in foraminiferal tests with the Fe oxy-hydroxides, might serve one of the mechanisms of the ore metals, primarily Fe, accumulation in the biogenic carbonate sediments at the hydrothermal vent field.

• Vertical particle fluxes at hydrothermal vent fields of the southernmost Mohns Ridge (Arctic Mid-Ocean Ridge) are discussed in Klyuvitkin et al. (2021). Sediment traps were deployed at the Trollveggen and Soria Moria hydrothermal vent fields in June 2019. The particles were deposited in the near bottom layer under a dominant northeastern water flow. Numerous short-period positive temperature anomalies up to 0.86 °C were registered in the study area. The values of particle fluxes in the near bottom layer are much lower than at the hydrothermal vent fields of the Mid-Atlantic Ridge. A significant amount of hydrothermal minerals (barite, sulfides, etc.) were detected in trapped material of the near bottom layer.

GEOTRACES or GEOTRACES relevant cruises

• The 84th cruise of the RV *Akademik Mstislav Keldysh* was carried out in the western Eurasian Arctic from July 24 to August 26, 2021 (Figure 6). Dr. Marina Kravchishina and Dr. Alexey Klyuvitkin are the cruise leaders, Shirshov Institute of Oceanology, Russian Academy of Sciences. The research of processes of paleo and modern sedimentation and reconstructions of past *climate* conditions were carried out in the regions where cold Polar and warm Atlantic water masses are contacted, and in the areas under the influence of cold (seep) and hot (hydrothermal) fluids in the western Eurasian Arctic. The consequences of atlantification are 'recorded' in all components of the ecosystems of the studied area, as well as the reverse effect of the Arctic amplification on the ecosystems of the Northern North Atlantic, occurring both at the present days and in the Pleistocene–Holocene (Kravchishina et al., 2022).

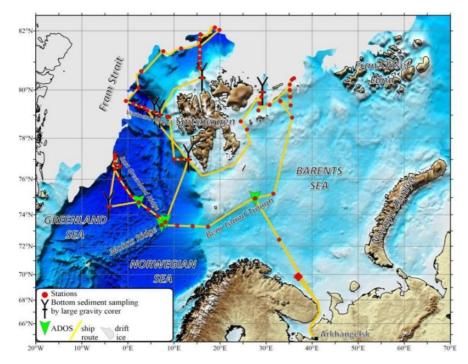


Figure 6. The map of the route and sampling stations carried out in the cruise in July–August 2021. An analysis of the Arctic sea ice for the sampling area was carried out according to https://cryo.met.no/

New projects and/or funding

• The grant of the *Ministry* of *Science* and Higher *Education* of the Russian Federation (grant no. 075-15-2021-934) "Study of anthropogenic and natural factors of changes in the composition of air and environmental objects in Siberia and the Russian sector of the Arctic in conditions of rapid climate change using unique scientific facility "Airplane Lab *Tu-134 Optic*", 2021–2023. Dr. Boris Belan is a project leader, V.E. Zuev Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Science, Tomsk.

• The project of the Russian Science Foundation (no. 21-77-10064) "Variability of the composition of dissolved organic matter in the Arctic shelf seas of Russia according to long-term observations of the optical properties of sea water", 2021–2023. Dr. Anastasia Drozdova is a project leader, early career researcher, Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow.

• The project of the Russian Science Foundation (no. 21-17-00235) "Natural Events of the Late Holocene (neoglaciation) in the subpolar North Atlantic and seas of northern Eurasian as reflection on global climate variability", 2021–2023. Dr. Alexander Matul is a project leader, Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow.

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

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1 PhD student involved.

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1 PhD student involved.

- Klyuvitkin, A. A., Kravchishina, M. D., & Boev, A. G. (2021). Particle Fluxes in Hydrothermal Vent Fields of the Southern Part of the Mohns Ridge. *Doklady Earth Sciences*, 497(1), 200–205. <u>https://doi.org/10.1134/S1028334X21030053</u>
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2 PhD students involved.

• Sakerin, S.M., Kabanov, D.M., Kopeikin, V.M., Kruglinsky, I.A., Novigatsky, A.N., Pol'kin, V.V., Shevchenko, V.P., and Turchinovich, Y.S. (2021). Spatial distribution of black carbon concentrations in the atmosphere of the North Atlantic and the European sector of the Arctic ocean. *Atmosphere*, *12*(8). <u>https://doi.org/10.3390/atmos12080949</u>

1 PhD student involved.

 Savvichev A., Rusanov I., Dvornikov Y., Kadnikov V., Kallistova A., Veslopolova E., Chetverova A., Leibman M., Sigalevich P., Pimenov N., Ravin N., Khomutov A. (2021). The water column of the Yamal tundra lakes as a microbial filter preventing methane emission. *Biogeosciences*, 18(9), 2791–2807. <u>https://doi.org/10.5194/bg-18-2791-2021</u>

Completed GEOTRACES PhD or Master theses

• Svetlana Krasheninnikova completed PhD thesis at A.O. Kovalevsky Institute of Biology of the Southern Seas of Russian Academy of Sciences. Krasheninnikova S. revealed correlation between temperature and velosity of surface currents in the North Atlantic and reduction of sea ice cover in European Arctic, using the oceanic reanalysis ORA-S4 and data from 1958 to 2014 (Krasheninnikova et al., 2022). The correlation coefficient between mean annual temperature of water in the Barents Sea with the temperature and velocity of the Gulf Stream current is 0.9 and 0.8, respectively. The correlation between water temperature of the Barents Sea and the velocity of the current northwest of Spitsbergen is –0.7. Current velocity in the area of northern border of the Gulf Stream and the South Equatorial Current, temperature in the Gulf Stream

and the Barents Sea have positive trends in interannual variability, and the velocity in the *Transpolar* Drift Stream and the sea ice extent of the Barents Sea are negative.

GEOTRACES presentations in international conferences

• 27th International Symposium on Atmospheric and Ocean Optics, Atmospheric Physics, 15 December 2021:

Turchinovich Y.S., Kopeikin V.M., Novigatsky A.N., Pol'kin V.V., Sakerin S.M., Shevchenko V.P., Shmargunov V.P. Comparison of measurements of black carbon concentrations in aerosols, using two aethalometry methods. *Proceedings of SPIE*. V. 11916. doi:10.1117/12.2600593.

Sakerin S.M., Kabanov D.M., Kopeikin V.M., Kruglinsky I.A., Novigatsky A.N., Pol'kin V.V., Shevchenko V.P., Turchinovich Y.S. Variations in black carbon concentrations in European sector of the Arctic Ocean and seas of the North Atlantic. *Proceedings of SPIE*. V. 11916. doi:10.1117/12.2601518.

Sakerin S.M., Kabanov D.M., Kruglinsky I.A., Novigatsky A.N., Pol'kin V.V., Pochufarov A.O., Shevchenko V.P., Turchinovich Y.S. Measurements of aerosol characteristics in three expeditions on board RV *Akademik Msticlav Keldysh*: from the Baltic to Barents Sea. *Proceedings of SPIE*. V. 11916. doi:10.1117/12.2601743.

Submitted by Marina Kravchishina (kravchishina@ocean.ru).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SLOVENIA

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

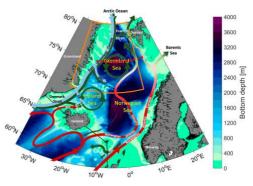
The results of two relevant topics can be considerd:

Study of the fate and processes of Hg and its speciation in marine ecosystems. The published Critical Review updates current knowledge on the sources, biogeochemical cycling, and mass balance of Hg in the Mediterranean and identifies perspectives for future research especially in the context of global change. Concentrations of Hg in the Western Mediterranean average 0.86 ± 0.27 pmol L⁻¹ in the upper water layer and 1.02 \pm 0.12 pmol L⁻¹ in intermediate and deep waters. In the Eastern Mediterranean, Hg measurements are in the same range but are too few to determine any consistent oceanographical pattern. The Mediterranean waters have a high methylation capacity, with MeHg representing up to 86% of the total Hg, and constitute a source of MeHg for the adjacent North Atlantic Ocean. The highest MeHg concentrations are associated with low oxygen water masses, suggesting a microbiological control on Hg methylation, consistent with the identification of *hgcA*-like genes in Mediterranean waters. MeHg concentrations are twice as high in the waters of the Western Basin compared to the ultra-oligotrophic Eastern Basin waters. This difference appears to be transferred through the food webs and the Hg content in predators to be ultimately controlled by MeHg concentrations of the waters of their foraging zones. Many Mediterranean toppredatory fish still exceed European Union regulatory Hg thresholds. The review also points out other insufficiencies of knowledge of Hg cycling in the Mediterranean Sea, including temporal variations in air-sea exchange, hydrothermal and cold seep inputs, point sources, submarine groundwater discharge, and exchanges between margins and the open sea. Future assessment of global change impacts under the Minamata Convention Hg policy requires long-term observations and dedicated high-resolution Earth System Models for the Mediterranean region.

The second research is subject to interconversions via (photo)chemical and (micro)biological processes that determine the extent of dissolved gaseous mercury (DGM) (re)emission and the production of monomethylmercury in seawater. We investigated Hg speciation in the South Atlantic Ocean on a GEOTRACES cruise along a 40°S section between December 2011 and January 2012. Using statistical analysis, concentrations of methylated mercury (MeHg, geometric mean 35.4 fmol L⁻¹) were related to seawater temperature, salinity and fluorescence. DGM concentrations (geometric mean 0.17 pmol L⁻¹) were related to water column depth, concentrations of macronutrients and dissolved inorganic carbon (DIC). The first-ever observed linear correlation between DGM and DIC obtained from high-resolution data indicates possible DGM production by organic matter remineralization via biological or dark abiotic reactions. DGM concentrations projected from literature DIC data using the newly discovered DGM–DIC relationship agreed with published DGM observations.

• Distribution, mobility and fate of trace elements in an estuarine and lagoonal systems. The accumulation of contaminants and their potential mobility represent two of the main environmental issues facing coastal environments. Sediments often act as "reservoirs" of contaminants, including potentially toxic trace elements, but they can also be considered a secondary source of contamination due to remobilisation processes at the sediment-water interface which may affect the quality of the coastal water and aquatic biota. Our research provide a geochemical characterisation of the estuarine system of the Timavo/Reka River, focusing on the occurrence of trace elements in different environmental matrices with the purpose of highlighting potential critical conditions in terms of environmental quality. The surface sediments were found to be enriched in several trace elements especially in the innermost sector of the area. There, sulphate-reductive conditions in the bottom saltwater testify to potential anoxia at the sediment-water interface, driving trace element accumulation in the residual fraction of the sediments. However, Fe and Mn redox behaviour appears to play a crucial role in the recycling of dissolved trace elements in the water column. With the lone exception of the saltwater in the innermost sector, trace elements were found to be mainly associated with suspended particles due to oxidation and precipitation processes, whereas a common lithogenic origin was identified for Cr, Ni, and Co, which are significantly correlated both in the surface sediments and in the suspended particles.

The cycling of metal(loid)s at the sediment–water interface (SWI) was evaluated at two selected sites (VN1 and VN3) in an active fish farm in the Grado Lagoon (Northern Adriatic, Italy). Despite sediments at two sites exhibiting high total metal(loid) concentrations and moderate effluxes at the SWI, the results suggest that they are hardly remobilized from the



sediments. Recycling of metal(loid)s from the SWI would not constitute a threat for the aquatic trophic chain in the fish farm.

GEOTRACES or GEOTRACES relevant cruises

CASSANDRA project: AdvanCing knowledge on the present Arctic Ocean by chemical-phySical, biogeochemical and biological obServAtioNs to preDict the futuRe chAnges

Period of the cruise: 29/08/2021, Longyearbyen (NO) – 14/09/2021, Bergen (NO)

The project was financially supported by the Italian Program of Research In Arctic. The measurements and results are in progress.

New projects and/or funding

- The new MSCA IT project GMOS-Train started already in 2020, but should be mentioned in this report. The GMOS-Train: Global Mercury Observation and Training network in support to the Minamata Convention started in 2020 and is coordinated by M. Horvat (JSI). With the purpose to better understand the global exchange of Hg between atmosphere, hydrosphere, lithosphere, and biosphere, the next generation of young researchers will gain expertise through a network-based, highly interdisciplinary research training programme including atmospheric chemistry and physics, aquatic chemistry, ecology, analytical chemistry, multimedia modelling, and the use of science results for policy making.
- A new national project IsoCont Innovative Isotopic Techniques for Identifying Sources and Bigeochemical Cycles of Mercury on Contaminated Areas started in October 2010.

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- COSSA, Daniel, HORVAT, Milena, et al. Mediterranean mercury assessment 2022: An Updated budget, health consequences, and research perspectives. Environmental science & technology. [Print ed.]. [in press] 2022, 23 str. ISSN 0013-936X. DOI: 10.1021/acs.est.1c03044.
- ŽIVKOVIĆ, Igor, GAČNIK, Jan, JOZIĆ, Slaven, KOTNIK, Jože, ŠOLIĆ, Mladen, HORVAT, Milena. A simplified approach to modeling the dispersion of mercury from precipitation to surface waters—The Bay of Kaštela case study. Journal of marine science and engineering. 2022, vol. 10, no. 4, str. 539-1-539-13. ISSN 2077-1312. DOI: 10.3390/jmse10040539.
- KOTNIK, Jože, ŽAGAR, Dušan, NOVAK, Gorazd, LIČER, Matjaž, HORVAT, Milena. Dissolved gaseous mercury (DGM) in the gulf of Trieste, Northern Adriatic Sea. Journal of marine science and engineering. 2022, vol. 10, no. 5, str. 587-1-587-18, ilustr. ISSN 2077-1312. DOI: 10.3390/jmse10050587.
- ŽIVKOVIĆ, Igor, KOTNIK, Jože, BEGU, Ermira, FAJON, Vesna, HORVAT, Milena, et al. Enhanced mercury reduction in the South Atlantic Ocean during carbon remineralization. Marine pollution bulletin. 2022, vol. 178, str. 1-113644-10-113664. ISSN 0025-326X. DOI: 10.1016/j.marpolbul.2022.113644.
- PETRANICH, Elisa, CROSERA, Matteo, PAVONI, Elena, FAGANELI, Jadran, COVELLI, Stefano. Behaviour of metal(loid)s at the sediment-water interface in an aquaculture lagoon environment (Grado Lagoon, Northern Adriatic Sea, Italy). Applied sciences. 2021, iss. 5, [article] 2350, str. 1-16. ISSN 2076-3417. https://www.mdpi.com/2076-3417/11/5/2350, DOI: 10.3390/app11052350.
- PAVONI, Elena, CROSERA, Matteo, PETRANICH, Elisa, FAGANELI, Jadran, KLUN, Katja, OLIVERI, Paolo, COVELLI, Stefano, ADAMI, Gianpiero. Distribution, mobility and fate of trace elements in an estuarine system under anthropogenic pressure: the case of the karstic Timavo River (Northern Adriatic Sea, Italy). Estuaries and coasts. 2021, vol. 44, str. 1831-1847. ISSN 1559-2723. https://link.springer.com/article/10.1007/s12237-021-00910-9, DOI: 10.1007/s12237-021-00910-9.
- FAGANELI, Jadran, OGRINC, Nives, TAMŠE, Samo, KRANJC, Bor, TURK, Valentina, MALEJ, Alenka, KOVAČ, Nives. "Kisanje" severnega Jadrana. Acta chimica slovenica. [Spletna izd.]. 2021, vol. 68, no. 3, str. s87-s93, ilustr. ISSN 1580-3155. DOI: 10.17344/acsi.2021.7002.

GEOTRACES presentations in international conferences

• HORVAT, Milena. Towards a better understanding of mercury dynamics within a between land, atmosphere, and ocean systems to support the effectiveness evaluation of the Minamata Convention. V: Goldschmidt Virtual Conference 2021, 4-9 July, 2021.

https://2021.goldschmidt.info/goldschmidt/2021/meetingapp.cgi.

Submitted by Nives Ogrinc (<u>nives.ogrinc@ijs.si</u>).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SOUTH AFRICA

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

• Cloete et al. 2021 https://doi.org/10.1016/j.marchem.2021.104031: First winter dissolved zinc (dZn) and particulate zinc (pZn) concentrations were measured at seven stations between 41 and 58°S in the Indian Sector of the Southern Ocean. This unique spatial and seasonal dataset provided the opportunity to investigate Zn biogeochemical cycling in a region which is extremely data scarce and during a period when conditions are unfavourable for phytoplankton growth. Surface comparisons of our winter dZn and pZn to previous measurements during spring and summer revealed that Zn seasonality is most pronounced at the higher latitudes where higher dZn (and higher ratios of dZn to phosphate; dZn:PO₄) and lower pZn in winter reflect decreased biological uptake and preferential dZn resupply (relative to PO₄) to surface waters through deep winter mixing. The composition of pZn was biogenic localised maiorly however lithogenic inputs were attributed potential hydrothermal activity and transport of continental sediment via Agulhas waters.

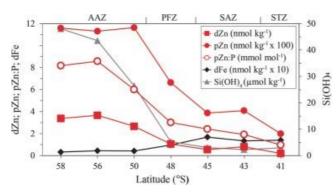
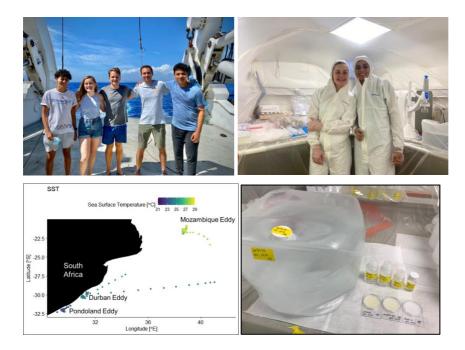


Figure 1. Surface water (~25 m) dZn, pZn, pZn:P, dFe and Si(OH)4 across the transect. Note: where necessary units were converted to plot on a single vertical axis for direct comparison. The biogeochemical zones crossed during the transect are shown on the top horizontal axis. Source: Cloete et al. 2021 https://doi.org/10.1016/j.marchem.2021.104031

GEOTRACES or GEOTRACES relevant cruises

Participation in intl. cruises

• Oceanographic campaign 'Resilience' in the Mozambique channel April - May 2022 on board RV Marion Dufresne. South African team members on board: Dr Ryan Cloete, Dr Saumik Samanta, MSc candidate Lide Jansen van Vuuren, MSc candidate Nadine Ellis (Stellenbosch University). During RESILIENCE, the TracEx team sampled roughly 100 stations from the South West Indian Ocean using a towed fish. The primary focus was high resolution (2 hrs) surface trace metal measurements (including soluble, dissolved and particulate size fractions as well as isotopic composition) across contrasting (in terms of origin and direction of rotation) mesoscale eddies in the Mozambique Channel and Agulhas Current.



• TARA Mission Microbiomes, part of the European AtlantECO project, June 2022. South African chief scientist: Prof Thulani Makhalanyane (University of Pretoria)



Ongoing/extended projects and/or funding

• Dr T. Ryan-Keogh (Early Career Researcher), National Research Foundation of South Africa (NRF; 2021-2023): "Seasonal iron speciation in the Southern Ocean, from open ocean environments to naturally fertilised sub-Antarctic Islands"

Outreach activities conducted

• Mkandla A, Fietz S, Marine and Environmental science promotion. Debating competition & Career Expo. CLS-SA, Cape Town, October 2021.

Other GEOTRACES activities

- Vichi, Marcello; Ryan-Keogh, Thomas, SCALE Cruise report 2019 (Winter and Summer Cruise); Southern Ocean Seasonal Experiment, http://hdl.handle.net/123456789/28739
- Zenodo data upload, SCALE 2019, https://zenodo.org/communities/scale_south_africa

New GEOTRACES or GEOTRACES-relevant publications

- Cloete R., J.C. Loock, N.R. van Horsten, J-L. Menzel Barraqueta, S. Fietz, T.N. Mtshali, H. Planquette, M.I. García-Ibáñez, A.N. Roychoudhury (2021). Winter dissolved and particulate zinc in the Indian Sector of the Southern Ocean: Distribution and relation to major nutrients (GEOTRACES GIpr07 transect). Marine Chemistry 236, #104031. https://doi.org/10.1016/j.marchem.2021.104031
- Cloete R, Loock JC, van Horsten N, Fietz S, Mtshali TN, Planquette H, Roychoudhury AN (2021). Winter biogeochemical cycling of dissolved and particulate cadmium in the Indian sector of the Southern Ocean (GEOTRACES GIpr07 transect). Front. Mar. Sci. 8:656321. https://doi.org/10.3389/fmars.2021.656321
- Ogundare, M.O., Fransson, A., Chierici, M., Joubert, W.R., Roychoudhury, A.N. Variability of Sea-Air Carbon Dioxide Flux in Autumn Across the Weddell Gyre and Offshore Dronning Maud Land in the Southern Ocean. Frontiers in Marine Science, 2021, 7, 614263. https://doi.org/10.3389/fmars.2020.614263
- Mdutyana, M., Sun, X., Burger, J.M., ...Ward, B.B., Fawcett, S.E. The kinetics of ammonium uptake and oxidation across the Southern Ocean. Limnology and Oceanography, 2022, 67(4), pp. 973–991. https://doi.org/10.1002/lno.12050
- Ryan-Keogh, T.J., Smith, W.O. Temporal patterns of iron limitation in the Ross Sea as determined from chlorophyll fluorescence. Journal of Marine Systems, 2021, 215, 103500. https://doi.org/10.1016/j.jmarsys.2020.103500

Completed GEOTRACES PhD or Master theses

PhD

- Asmita Singh, Stellenbosch University/CSIR: Southern Ocean phytoplankton response to iron, https://scholar.sun.ac.za/handle/10019.1/124657
- Natasha van Horsten, Stellenbosch University/CSIR: Dissolved iron and remineralisation, https://scholar.sun.ac.za/handle/10019.1/124817
- Kakauruaee Ismael Kangueehi, Stellenbosch University: Southern African dust aerosols, https://scholar.sun.ac.za/handle/10019.1/123923
- Mhlangabezi Mdutyana, University of Cape Town: Southern Ocean biogeochemistry, http://hdl.handle.net/11427/35931

MSc

- Andile Mkandla, Stellenbosch University: Molybdenum in the Southern Ocean , https://scholar.sun.ac.za/handle/10019.1/123826
- Tara de Jongh, Stellenbosch University: Dissolved aluminum in the surface Southern Ocean

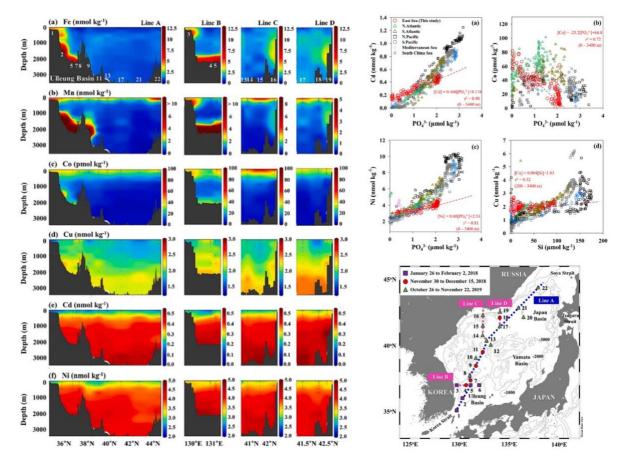


From left to right: Dr Asmita Singh, Dr Kakauruaee Ismael Kangueehi, Dr Mhlangabezi Mdutyana, Mr Andile Mkandla

Submitted by Susanne Fietz (<u>sfietz@sun.ac.za</u>).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SOUTH KOREA

May 1st, 2021 to April 30th, 2022



New GEOTRACES or GEOTRACES relevant scientific results

• Seo and his colleagues (2022, *Marine Chemistry*) reported the distributions of dissolved iron (Fe), manganese (Mn), cobalt (Co), copper (Cu), cadmium (Cd), and nickel (Ni) in the entire East Sea (Japan Sea). In this study, distinct atmospheric and shelf inputs of trace elements, except for Ni, were observed. In addition, unusually high concentrations of Fe and Mn (13 and 57 nmol kg⁻¹, respectively) are observed in the bottom layer of the Ulleung Basin (southwestern part of the East Sea), owing to large benthic inputs. These inputs might be related with the diffusion of dissolved organic matter (DOM) complexed Fe and Mn from the sediment to the overlying seawater. In contrast, the Co concentrations in the East Sea show the lowest value ever reported at similar depths in the oceans (2-8 pmol kg⁻¹), while the surface water concentrations of the same element are 2-5 fold higher than in the major oceans.

• Seo et al. (2022) examined the cycling of particulate organic carbon (POC) in continental shelf regions of the Yellow Sea (YS) and the East China Sea (ECS) was investigated by analyzing the ²³⁴Th, POC and its isotopes (δ^{13} C and Δ^{14} C), and particulate aluminum (pAl) over the period 10-20 August 2020. The continental shelf of YS and ECS is one of the largest continental shelves on the global ocean. This shelf receives and extraordinarily large volume of terrestrial material from rivers, groundwater, and the atmosphere (below figure).

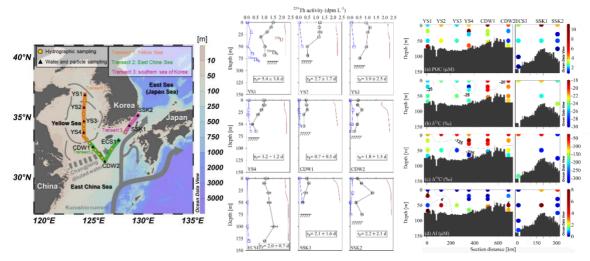


Figure. Bathymetric map showing the locations of sampling stations in the study region (left figure). Vertical distributions of 234 Th in the Yellow Sea (YS), the East China Sea (ECS), and southern Sea of Korea (SSK) (center figure). Distributions of (a) POC concentration, (b) δ^{13} C, (c) Δ^{14} C, and (d) pAl in the study region (right).

The deficit of 234 Th relative to 238 U varied from 30% to 90%, indicating short residence times in the water column (2.6 ± 2.2 d). The POC flux to the seafloor were estimated to be 47 – 125 mmol m⁻² d⁻¹. This POC settling flux was one to two orders of magnitude higher than the POC burial rates, suggesting effective oxidation (> 90%) via repeated resuspension/re-deposition cycle before burial. Based on the three-endmember mixing model for the dual carbon isotopes, the estimated contribution of resuspended sedimentary organic carbon to POC was 65% in the bottom layer (> 50 m). Overall, our study revealed the complex nature of POC cycling on this shelf, quantified the relative importance of each source of POC, and determined POC flux to the sediment.

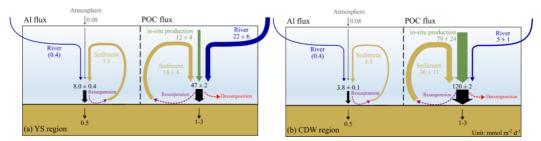


Figure. Schematics of Al and POC fluxes in (a) the Yellow Sea (YS) and (b) the Changjiang Diluted Water (CDW) regions.

• The sources and fluxes of dissolved organic carbon (DOC) were estimated by using the multiple tracers including ²²⁸Ra, fluorescent dissolved organic matter (FDOM), and dual carbon isotope (¹³C and ¹⁴C) analysis of DOC in the northwestern Pacific continental shelf. In this study, additional supplies of DOC (instead of riverine input) were found to be produced from the shelf-water based on a significant correlation between DOC and ²²⁸Ra, which suggests that DOC is mainly from the shelf sediments and enriched in the shelf-water over the water residence time. Furthermore, the potential source of additional DOC was found to be produced in the shelf-water based on the marine δ^{13} C signature together with the younger radiocarbon age of DOC than that of the Kuroshio Current water. The flux of the shelf-borne DOC was estimated to be ~1.9±0.8 Tg C yr⁻¹, which is almost comparable to that from the Changjiang discharge.

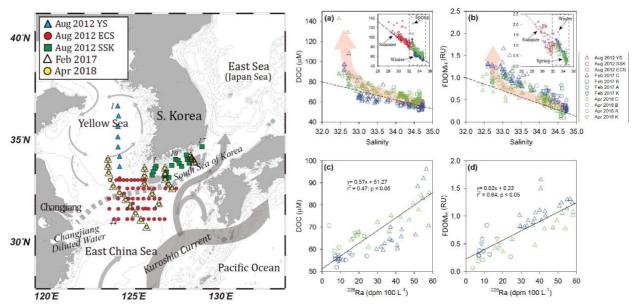


Figure 1. Map of total sampling stations in the northwestern Pacific continental shelf in the East China Sea and the Yellow Sea (left) and correlations between the concentrations of (a) DOC and (b) $FDOM_H$ against the salinity and the concentration of (c) DOC and (d) $FDOM_H$ against the activities of ²²⁸Ra in the continental shelf waters during the sampling periods. (right)

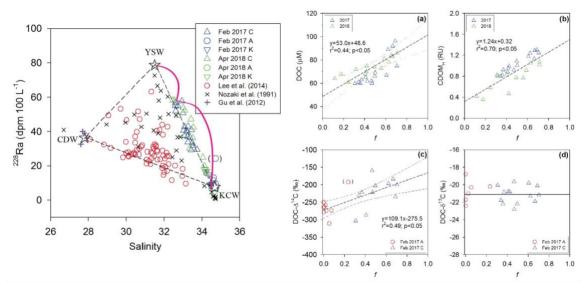
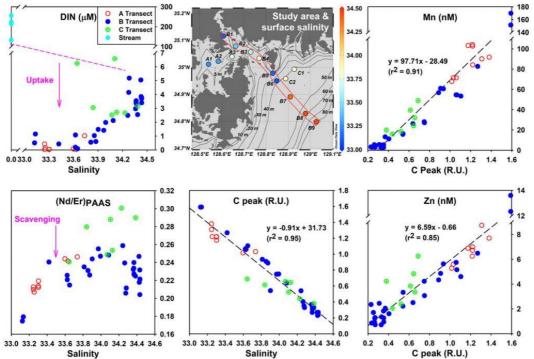


Figure 2. A mixing diagram between ²²⁸Ra and salinity. (YSW, Yellow Sea water; CDW, Changjiang diluted water; KCW, Kuroshio Current water.) (left) Correlations between the mixing fraction, f, (f=0 for KCW and f=1 for YSW) against (a) DOC, (b) FDOM_H, (c) DOC- Δ^{14} C, and (d) DOC- δ^{13} C values. Dashed lines represent the end-member mixing lines. (right)

• Chen and co-workers (2021, see reference below) analyzed an array of trace metals (manganese, iron, nickel, copper and zinc) together with Rare Earth Elements (REE) in a salinity gradient in the Jinhae Bay, the largest semi-enclosed bay in South Korea. Despite the occurrence of a significant scavenging activity revealed by the REE behaviors and intensive biological removal processes revealed by dissolved inorganic nutrients depletion, these trace elements showed higher concentrations in lower salinity waters and significant positive correlations with terrestrial humic substances. This thorough speciation study led the authors to hypothesize that when associated with terrestrial humic substances, these trace elements survive particle scavenging and biological consumption in the coastal mixing zone. This shuttling effect of terrestrial trace elements by humic substances in a coastal ocean is

challenging the current paradigm assessing that trace elements are intensively removed in such salinity gradient.

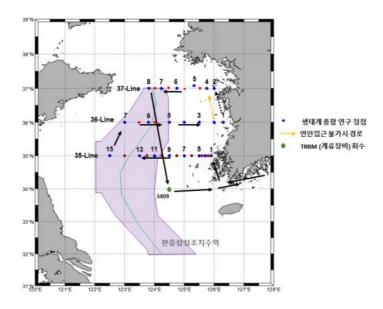


The salinity plots for REE fractionation ((Nd/Er)PAAS) values and dissolved inorganic nitrogen (DIN) concentrations revealed significant particle scavenging of REE and biological removal of DIN in the inner Jinhae bay. However, trace elements (e.g. Mn and Zn) showed a good positive correlation with terrestrial humic substances (C peak), which behaved conservatively throughout the bay.

GEOTRACES or GEOTRACES relevant cruises

• There was research cruise of *R/V Isabu* (of the Korea Institute of Ocean Science and Technology (KIOST)) in the Yellow Sea, the marginal sea in the western part of the Korean Peninsula in the Feb. – Mar. in 2022 (Chief scientist Dr. Dong-Han Choi, the biologist in the KIOST) (see the below cruise track and sampling map). The researchers of KIOST (Dr. Intae Kim and Ms. Jaeeun Lee and Ms. Huisu Lee) conducted the trace metal-clean water sampling in this cruise (>10 stations) using PRISTINE Ultra Clean CTD (UCC) equipped in R/V Isabu. The measurements of dissolved-/and particulate trace elements were now in progress. The Korea-GEOTRACES relevant members expect the first trace element report in the water column of the Yellow Sea as outcome of this project.

Sampling map in the Yellow Sea (2022. 02.~2022.03)



New GEOTRACES or GEOTRACES-relevant publications (published or in press)

Seo, H., Kim, G., Kim, T., Kim, I., Ra, K., & Jeong, H. (2022). Trace elements (Fe, Mn, Co, Cu, Cd, and Ni) in the East Sea (Japan Sea): Distributions, boundary inputs, and scavenging processes. *Marine Chemistry*, 239, 104070. doi:10.1016/j.marchem.2021.104070

The authors, Seo, H. and Jeong.H, are the Ph.D. students

• Han, H., Na, T., Cho, H.-M., Kim, G., and Hwang, J. (2022) Large fluxes of continentalshelf-borne dissolved organic carbon in the East China Sea and the Yellow Sea. Marine Chemistry, 240, 104097.

The author, Han H. is post doc at the Seoul National University

• Seo, J., Kim, G., & Hwang, J. Sources and behaviors of particulate organic carbon in the Yellow Sea and the East China Sea based on 13C, 14C, and 234Th. *Frontiers in Marine Science*, 361.

The author, Seo J. is post doc at the Seoul National University

• Chen, X., Seo, H., Han, H., Seo, J., Kim, T., & Kim, G. (2021). Conservative behavior of terrestrial trace elements associated with humic substances in the coastal ocean. *Geochimica et Cosmochimica Acta*. https://doi.org/10.1016/J.GCA.2021.05.020

The authors, Chen X and Seo, H. are Ph.D students Han, H and Seo, are the post doc at the Seoul National University

Submitted by Dr. Intae Kim, KIOST (ikim@kiost.ac.kr).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SPAIN

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

- <u>QUIMA-ULPGC Group. Trace Metals</u> (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.
- <u>Applied Physic Department (Sevilla University)</u> (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.

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€

Outreach activities conducted

- 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)

- 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

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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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SWITZERLAND

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES-relevant scientific results (highlights)

- <u>An updated view of the marine Cr cycle</u>: Observational work led by Dr. David Janssen combined incubation experiments, water-column, bottom-water, pore-water and sediment sampling with literature data to update our view of the global marine biogeochemical cycle of Cr (Janssen et al., 2021, *Earth and Planetary Science Letters*). This work was complemented by a modelling study into the first-order controls on the marine Cr cycle (Pöppelmeier et al., 2021, *Biogeosciences*).
- <u>A re-assessment of controls on the marine Cd cycle</u>: A review article led by researchers at ETH Zurich critically assessed the evidence in water-column and particulate data for the proposed loss of dissolved Cd to particle-associated sulphide formation, and found that stoichiometric variability in biological Cd uptake is in fact the major driver of trends observed in the marine Cd-PO₄ relationship (de Souza et al., 2022, *Geochimica et Cosmochimica Acta*).

GEOTRACES or GEOTRACES-relevant cruises

- Doctoral student Delphine Gilliard (University of Lausanne, supervised by Prof. S. L. Jaccard & Dr. D. J. Janssen) participated in FS Meteor cruise M176-2 to collect samples for analysis of seawater Cr isotopes (□53Cr); she will also analyse samples collected on FS Sonne cruise SR289.
- Prof. S. L. Jaccard participated in the Arctic Century Expedition to the Russian Arctic (Barents, Laptev and Kara Seas) in August/September 2021, funded by the Swiss Polar Institute and partner organisations.
- Prof. D. Vance collaborated with the Max Planck Institut für Chemie (MPIC) Mainz to collect seawater samples on S/V Eugen Seibold cruise ES22C01 (February 2022, eastern tropical Atlantic) for analysis of Ni concentration and isotopes at ETH Zurich.

New projects and/or funding

• Prof. S. L. Jaccard is involved in the project "GreenFjord – Greenlandic Fjord ecosystems in a changing climate: socio-cultural and environmental interactions" funded by the Swiss Polar Institute Flagship Initiative. CHF 1,500k.

GEOTRACES workshops and meetings organized

• Dr. D. J. Janssen co-convened a session at Ocean Sciences Meeting 2022 (Hawai'i and virtual) entitled "Sources, sinks and cycling of trace elements in coastal and near-shore systems".

Outreach activities conducted

• Prof. S. L. Jaccard participated in creating materials for Swiss Polar Class, an educational outreach programme (in German and French) for school-going students (ages 8-12). These can be found at https://polar-class.ch/de/arctic-century-expedition/

New GEOTRACES or GEOTRACES-relevant publications (*Researchers at Swiss institutions in bold*)

- Brzezinski, M. A., I. Closset, J. L. Jones, G. F. de Souza, C. Maden (2022). New constraints on the physical and biological controls on the silicon isotopic composition of the Arctic Ocean. Frontiers in Marine Science 8, Article 699762.
- **de Souza, G. F., D. Vance, M**. Sieber, T. M. Conway and S. H. Little (2022). Re-assessing the influence of particle-hosted sulphide formation on the marine cadmium cycle. Geochimica et Cosmochimica Acta 322, 274-296. Invited review article.
- Farmer, J. R., J. E. Hertzberg, D. Cardinal, S. Fietz, K. Hendry, S. L. Jaccard, A. Paytan, P. A. Rafter, H. Ren, C. J. Somes, J. N. Sutton, GEOTRACES–PAGES Biological Productivity Working Group Members (2021). Assessment of C, N and Si isotopes as tracers of past ocean nutrient and carbon cycling. Global Biogeochemical Cycles 35, doi: 10.1029/2020GB006775.
- Giesbrecht, K. E., D. E. Varela, **G. F. de Souza, C. Maden** (2022). Natural variations in dissolved silicon isotopes across the Arctic Ocean from the Pacific to the Atlantic. Global Biogeochemical Cycles 36, doi: 10.1029/2021GB007107.
- Hayes, C. T. and 28 co-authors including **S. L. Jaccard** (2021). Global ocean sediment composition and burial flux in the deep sea. Global Biogeochemical Cycles 35, doi: 10.1029/2020GB006769.
- He, Z., M. O. Clarkson, M. B. Andersen, C. Archer, T. C. Sweere, P. Kraal, A. Guthauser, F. Huang, D. Vance (2021). Temporally and spatially dynamic redox conditions on an upwelling margin: the impact on coupled sedimentary Mo and U isotope systematics, and implications for the Mo-U paleoredox proxy. Geochimica et Cosmochimica Acta 309, 251-271.
- Horner, T. J., S. H. Little, T. M. Conway, J. R. Farmer, J. E. Hertzberg, D. J. Janssen, A. J. M. Lough, J. McKay, A. Tessin, S. J. G. Galer, S. L. Jaccard, F. Lacan, A. Paytan, K. Wuttig, GEOTRACES–PAGES Biological Productivity Working Group Members (2021). Bioactive trace metals and their isotopes as paleoproductivity proxies: An assessment using GEOTRACES-era data. Global Biogeochemical Cycles 35, Article 2020GB006814.
- Janssen, D. J., J. Rickli, A. N. Abbott, M. J. Ellwod, B. S. Twining, D. C. Ohnemus, P. Nasemann, D. Gilliard, S. L. Jaccard (2021). Release from biogenic particles, benthic fluxes, and deep water circulation control Cr and ⁵³Cr distributions in the ocean interior. Earth and Planetary Science Letters 574, Article 117163.
- Kurzweil, F., C. Archer, M. Wille, R. Schoenberg, C. Münker, O. Dellwig (2021). Redox control on the tungsten isotope composition of seawater. PNAS 118, Article 2023544118.
- Lemaitre, N., J. Du, G. F. de Souza, C. Archer, D. Vance (2022). The essential bioactive role of nickel in the oceans: evidence from nickel isotopes. Earth and Planetary Science Letters 584, Article 117513, doi: 10.1016/j.epsl.2022.117513.
- Nixon, R. L., M. A. Peña, R. Taves, **D. J. Janssen**, J. T. Cullen, A. R. Ross (2021). Evidence for the production of copper-complexing ligands by marine phytoplankton in the subarctic northeast Pacific. Marine Chemistry 237, Article 104034.
- **Pöppelmeier, F., D. J. Janssen, S. L. Jaccard, T. F. Stocker** (2021). Modeling the marine chromium cycle: New constraints on global-scale processes. Biogeosciences 18, 5447–5463.

- **Revels, B. N., J. Rickli,** C. A. V. Moura, **D. Vance** (2021). Nickel and its isotopes in the Amazon Basin: The impact of the weathering regime and delivery to the oceans. Geochimica et Cosmochimica Acta 293, 344-364.
- Schwab, M. S., J. D. Rickli, R. W. Macdonald, H. R. Harvey, N. Haghipour, T. I. Eglinton (2021). Detrital neodymium and (radio)carbon as complementary sedimentary bedfellows? The Western Arctic Ocean as a testbed. Geochimica et Cosmochimica Acta 315, 101-126.
- Sherwood, O. A., S. H. Davin, N. Lehmann, C. Buchwald, E. N. Edinger, M. F. Lehmann, M. Kienast (2021). Stable isotope ratios in seawater nitrate reflect the influence of Pacific water along the northwest Atlantic margin. Biogeosciences 18, 4491-4510.
- Sieber, M., T. M. Conway, G. F. de Souza, C. S. Hassler, M. J. Ellwood, D. Vance (2021). Isotopic fingerprinting of biogeochemical processes and iron sources in the iron-limited surface Southern Ocean. Earth and Planetary Science Letters 567, Article 116967.
- Taves, R. C., D. J. Janssen, M. A. Peña, A. R. S. Ross, K. G. Simpson, W. R. Crawford, J. T. Cullen (2022). Relationship between surface dissolved iron inventories and net community production during a marine heatwave in the subarctic northeast Pacific. Environmental Science: Processes and Impacts, doi: 10.1039/D2EM00021K.

Completed GEOTRACES PhD or Master theses

• Delphine Gilliard (2021). Dissolved chromium concentration and ⁵³Cr: a tool to quantify the strength of the biological pump in the South Pacific Ocean. M.Sc. thesis, University of Bern.

GEOTRACES presentations in international conferences (Researchers at Swiss institutions in bold)

- Conway, T. M., J. B. Palter and **G. F. de Souza** (2021). Gulf Stream eddies as an important transfer of high-Fe slope water across the Gulf Stream into the North Atlantic Subtropical Gyre. Poster presentation at the International Workshop on Western Boundary Current-Subtropical Continental Shelf Interactions (Savannah GA, USA).
- Deng, K., J. Du, J. Rickli, T. J. Suhrhoff, D. Vance (2021). Preconcentration and determination of beryllium and rare earth elements in small volumes of marine pore-water. Poster presentation at the 2021 Goldschmidt Conference (virtual).
- **de Souza, G. F., D. Vance,** M. Sieber, T. M. Conway, S. H. Little (2021). Re-assessing the role of water-column sulphide formation in the marine Cd cycle. Oral presentation at the 2021 Goldschmidt Conference (virtual).
- **Du, J.,** B. A. Haley, A. C. Mix, **D. Vance** (2021). Studying the cycles of trace elements and isotopes at the sediment-water interface using a diagenetic model with automatic code generation for user defined problems. Oral presentation at the 2021 Goldschmidt Conference (virtual).
- **Eisenring, C., G. F. de Souza,** S. E. Oliver, S. Khatiwala, **D. Vance** (2021). The potential of GEOTRACES Zn data for constraining biogeochemical model behaviour. Oral presentation at the 2021 Goldschmidt Conference (virtual).
- Fleischmann, S., A. Chatterjee, J. McManus, D. Vance (2021). The oceanic budget of nickel: new concentration and isotope data from Mn-rich pelagic sediments. Poster presentation at the 2021 Goldschmidt Conference (virtual).

- Janssen, D.J., J. Rickli, M. Wille, C. S. Hassler, H. Vogel, S. L. Jaccard (2022). Chromium cycling in euxinic basins: Implications for the δ53Cr paleoredox proxy from modern systems. Oral presentation at the 2022 Ocean Sciences Meeting (Hawai'i and virtual).
- Janssen, D.J., J. Rickli, A. N. Abbott, M. J. Ellwood, P. Nasemann, B. S. Twining, D. C. Ohnemus, D. Gilliard, S. L. Jaccard (2021). Elucidating biogenic components of the δ53Cr cycle in the modern ocean. Oral presentation at the 2021 Goldschmidt Conference (virtual).
- Lemaitre, N., C. Archer, G. F. de Souza, J. Du, D. Vance (2021). The oceanic biogeochemistry of nickel and its isotopes. Oral presentation at the 2021 Goldschmidt Conference (virtual).
- **Pöppelmeier, F., D. J. Janssen, S. L. Jaccard, T. F. Stocker** (2021). Modeling the marine chromium cycle with an EMIC: constraining global-scale processes. Oral presentation at the 2021 Goldschmidt Conference (virtual).
- Sweere, T., K. A. Ungerhofer, N. Lemaitre, P. Kraal, D. Vance (2021). Nickel-isotope cycling on the Namibian margin. Oral presentation at the 2021 Goldschmidt Conference (virtual).

Compiled and submitted by Gregory de Souza, ETH Zurich (desouza@erdw.ethz.ch).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN TURKEY

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

Turkish oceanographic teams mostly turned their attention to the Black Sea - Marmara Sea system in much of 2021 and up until mid-2022. New GEOTRACES relevant results include new findings on the seasonal dynamics of hypoxia in the Sea of Marmara and how this modulates benthic fluxes of iron and manganese. Also, on-board measured vertical profiles of iron and manganese have also been produced from the suboxic and anoxic part of the water columns

GEOTRACES or GEOTRACES relevant cruises

Three expeditions, with the R/V Bilim of the Institute of Marine Sciences, Middle East Technical University of Turkey, was held in the Black Sea, Bosporus Strait and the Sea of Marmara in June 2021, September 2021 and March 2022. Access to Black Sea was not possible in March 2022 due to the risk with the sea mines released into the Black Sea as a result of Russia's aggression on Ukraine. For the chemical oceanographic community this will pose a major risk in the next months.

New projects and/or funding

Most important development of the report term was the acceptance of Dr Mustafa Yücel's (METU-IMS) proposal for EU Horizon Europe, European Research Council ERC Consolidator Grant in the call ERC-CoG-2021. The project, DeepTrace has been accepted for funding and will start in January 2023, to run until December 2027. This 5-year, 2.4 M Euro prestigious European project advance a ground-breaking mechanistic, analytical and predictive understanding of how the life-supporting metals cycle across Earth's deep-sea ecosystems such as the Black Sea and hydrothermal vents, developing the application of metal nanoparticles as tracers of planetary redox habitability and bridging together the study of Earth's Oceans with the Ocean Worlds of the Solar system. A web site for the project is under cosntruction.

Several PhD and postdoc openings are available and details can be found at:

https://ims.metu.edu.tr/announcement/erc-deeptrace-project-seeking-phd-candidates

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

Yücel M, Sevgen S and Le Bris N (2021). Soluble, Colloidal, and Particulate Iron Across the Hydrothermal Vent Mixing Zones in Broken Spur and Rainbow, Mid-Atlantic Ridge. Front. Microbiol. 12:631885. doi: 10.3389/fmicb.2021.6318852022

Alimli N and Yücel M (2022). Seafloor iron mobilization across the deep-water redox gradients of the Black Sea and the Sea of Marmara. EGU22-9601 https://doi.org/10.5194/egusphere-egu22-9601 EGU General Assembly 2022

Submitted by Dr. Mustafa Yucel (myucel@ims.metu.edu.tr).

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN UNITED KINGDOM

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

Bridgestock and co-authors investigated the transport of barium into the ocean from rivers. Combining data on barium and barium isotopes across a set of river / estuarine systems, the underlying processes and an estimate of the net barium flux is derived. Desorption of barium from particles in estuaries emerged as the major driver of the changes in barium isotope changes. This then modifies the isotope composition of net riverine dissolved Ba fluxes that reach the ocean. River dissolved loads are also systematically offset to higher barium isotope values than the major oceanic sink: via burial of BaSO4 in marine sediments, which represents an apparent imbalance in the modern marine Ba isotope budget. Accounting for modification of the $\delta^{138/134}$ Ba of net riverine Ba fluxes to the ocean by estuarine processes is likely to play a key role towards balancing the modern marine Ba isotope budget and that river barium isotope values do not represent the net inputs to the ocean.

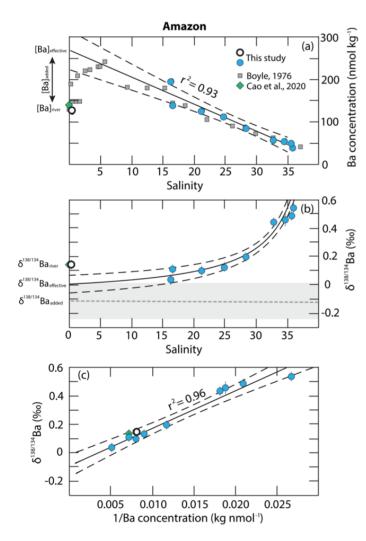


Fig. 2. Relationships between salinity, Ba concentrations and $\delta^{138/13^4}$ Ba values in the Amazon River estuary. Solid black lines represent conservative mixing relationships, defined by linear regressions between Ba concentration (and salinity (panel a) and $\delta^{138/134}$ Ba and 1/Ba concentration (panel c) with dashed lines showing 95% confidence intervals. The mixing relationship in panel (b) is defined by combining the linear regressions in panels (a) and (c). Open circle denotes the Amazon River water endmember, which is omitted from regressions to define mixing relationships. Literature data are displayed by grey squares (Boyle, 1976) and the green diamond (Cao et al., 2020). In panel (b) the horizontal grey dashed lines show the $\delta^{138/134}$ Ba value estimated for the Ba added to the dissolved riverine flux by estuarine processe, with uncertainties shown by the grey shaded intervals.

Paper: L. Bridgestock, Nathan, J., Paver, R., Hsieh, Y-T. Porcelli, D., Tanzil, J., Holdship, P., Carrasco, G., Annammala, K. V., Swarzenski[,] P. W., and Henderson, G. M., 2021, Estuarine processes modify the isotope composition of dissolved riverine barium fluxes to the ocean, *Chemical Geology*, 579, doi:10.1016/j.chemgeo.2021.120340

PhD student Daniela Koenig (supervised by Alessandro Tagliabue) published the first ever global iron isotope model in collaboration with Tim Conway, Michael Ellwood and Will Homoky. In this work, the relative contribution of external inputs and internal cycling to the distribution of iron isotopes was determined for the first time using models and observations. Overall, both distinct external source endmembers and fractionation during organic complexation and phytoplankton uptake are required to reproduce δ^{56} Fediss observations along GEOTRACES transects., with the δ^{56} Fediss distributions through the water column resulting from regional imbalances of remineralization and abiotic removal processes. δ^{56} Fediss signals from hydrothermal or sediment sources could not be reproduced by adjusting δ^{56} Fe endmember values., which highlights the importance of additional processes governing the exchange and/or speciation of Fe supplied by these sources to the ocean.

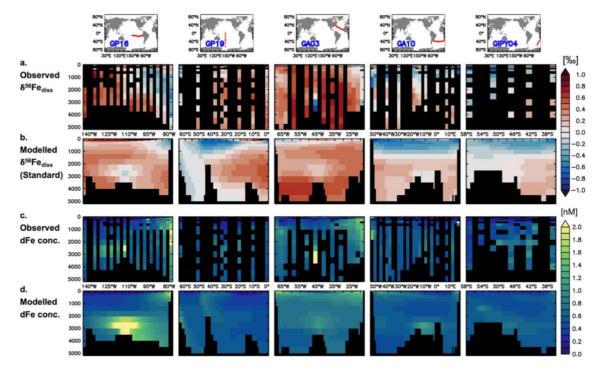


Figure 4. Observed (a, c) and standard experiment (b, d) $\delta^{56}Fe_{diss}$ (a, b; %) and dFe concentration (c, d; μ mol m⁻³) for five GEOTRACES sections. Data are binned at model depths; model output is extracted at the same coordinates as observations, and on interpolated coordinates in between.

Paper: König, D., T. M. Conway, M. J. Ellwood, W. B. Homoky, and A. Tagliabue, Constraints on the Cycling of Iron Isotopes From a Global Ocean Model, *Global Biogeochemical Cycles*, *35*(9), doi:10.1029/2021gb006968. 2021.

GEOTRACES or GEOTRACES relevant cruises

Homoky (Leeds) obtained new porewater and sediment samples collected for TEI analyses from RV Pelagia in July 2021 in support of the GEOTRACES process cruise, MetalGate (Lead PI R. Middag, NIOZ)

Annett (Southampton) participated (along with PhD student) in the MetalGate process study

New projects and/or funding

- Royal Society funded workshop on Marine Microbes in a Changing Climate organised by A Tagliabue, with T Mock, J Robidart and P Sanchez-Baracaldo 12-13 September 2022 with links to Biogeotraces and new BioGeoSCAPES programme
- NERC funded project: A new perspective on ocean photosynthesis (N-POP) Lohan, Bibby & Mark (Southampton)
- Annett (Southampton) obtained funding as CoI for beamtime at the European Synchrotron Research Facility to analyse samples from the MetalGate GEOTRACES process study

Outreach activities conducted (please list any outreach/educational material available that could be shared through the GEOTRACES web site)

Luke Bridgestock gave an online symposium talk and a tutorial on the importance of marine trace metal cycles and the GEOTRACES Program to students participating in the African Regional Graduate Network in Oceanography Academy, hosted in Namibia. The tutorial involved the students interpreting data from the GEOTRACES data product using webODV to answer questions about sources of Fe to the ocean, and human perturbation to the marine Pb cycle.

Other GEOTRACES activities

- Maeve Lohan (University of Southampton, co-chair) and Tina van de Flierdt (Imperial College London, committee member) attended 6 x virtual Standards & Intercalibration (S&I) meetings
- Maeve Lohan (University of Southampton, co-chair), Tina van de Flierdt (Imperial College London) and Alessandro Tagliabue (University of Liverpool) attended the virtual annual SSC meeting.
- Alessandro Tagliabue (University of Liverpool, co-chair) and Maeve Lohan attended 4 x virtual DMC meetings

Data Products

New iron climatology data product: Nicolas Cassar, Yibin Huang, & Alessandro Tagliabue. (2022). Data-driven modeling of dissolved iron in the global ocean., https://doi.org/10.5281/zenodo.6385044

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

- Gregory F.de Souza, Derek Vance, Matthias Sieber, Tim M. Conway, Susan H. Little (2022) Re-assessing the influence of particle-hosted sulphide precipitation on the marine cadmium cycle, Geochimica et Cosmochimica Acta 322, Pages 274-296
- Igor Živković, Matthew P. Humphreys, Eric P. Achterberg, Cynthia Dumousseaud, E. Malcolm S. Woodward, Natalia Bojanić, Mladen Šolić, Arne Bratkič, Jože Kotnik, Mitja Vahčič, Kristina Obu Vazner, Ermira Begu, Vesna Fajon, Yaroslav Shlyapnikov, and Milena Horvat. (2022). Enhanced mercury reduction in the South Atlantic Ocean during carbon remineralization. Marine Pollution Bulletin, Volume 178, May 2022, https://doi.org/10.1016/j.marpolbul.2022.113644.

- Sofen, L.E., Antipova, O.A., Ellwood, M.J., Gilbert, N.E., Gilbert, N.E., LeClier, G.R., Lohan, M.C., Mahaffey, C., Mann, E.L., Ohnemus, D.C., Wilhelm, S.W. & Twining (2022) Trace metal contents of autotrophic flagellates from contrasting open-ocean ecosystems. Limnology & Oceanography Letters doi.org/10.1002/lol2.10258
- Wang, W., Lough, A., Loahn, M.C., Connelly, D.P., Cooper, M.J., Milton, A., Chavagnac, V., Castillo, A. & James, R.H (2021) Behavior of iron isotopes in hydrothermal systems: Beebe and Von Damm vent fields on the Mid-Cayman ultraslow-spreading ridge. EPSL doi.org/10.1016/j.epsl.2021.117200
- Artigue, L., Wyatt, N.J., Lacan, F., Mahaffey, C. & Lohan, M.C. (2021) The importance of water mass transport and dissolved-particulate interactions on the aluminium cycle in the subtropical North Atlantic. GBC doi.org/10.1029/2020GB006569
- Zhu, K., Birchill, A.J., Milne, A., Ussher, S., Humphreys, M.P., Carr, N., Mahaffey, C.Lohan, M.C., Achterberg, E.P. & Gledhill (20210 Equilibrium calculations of iron speciation and apparent iron solubility in the Celtic Sea at ambient seawater pH using the NICA-Donnan model. Mar. Chem 237 doi.org/10.1016/j.marchem.2021.104038
- Cerdan-Garcia, E., Baylay A., Polyviou D., Woodward E.M.S., Wrightson L., Mahaffey C., Lohan M.C., Moore C.M., Bibby T.S., Robidart J.C. (2021). Transcriptional responses of Trichodesmium to natural inverse gradients of Fe and P availability. ISME Journal. https://doi.org/10.1038/s41396-021-01151-1
- Delvigne, C., Guihou, A., Schuessler, J. A., Savage, P., Poitrasson, F., Fischer, S., ... & Basile-Doelsch, I. (2021). Silicon Isotope Analyses of Soil and Plant Reference Materials: An Inter-Comparison of Seven Laboratories. Geostandards and Geoanalytical Research, 45(3), 525-538.
- Sean Selzer, Amber L. Annett, William B. Homoky, RaDeCC Reader: Fast, accurate and automated data processing for Radium Delayed Coincidence Counting systems, Computers & Geosciences, https://doi.org/10.1016/j.cageo.2021.104699.
- Farmer, J. R., Hertzberg, J. E., Cardinal, D., Fietz, S., Hendry, K., Jaccard, S. L., ... & GEOTRACES-PAGES Biological Productivity Working Group Members. (2021). Assessment of C, N, and Si isotopes as tracers of past ocean nutrient and carbon cycling.
- Ward, J., Hendry, K., Arndt, S., Faust, J. C., Freitas, F. S., Henley, S. F., ... & Pickering, R. A. (accepted). Stable silicon isotopes uncover a mineralogical control on the benthic silicon cycle in the Arctic Barents Sea. Geochim. Cosmochim. Acta.
- Hatton, J. E., Hendry, K. R., Hawkings, J., Wadham, J. L., Benning, L. G., Blukis, R., ... & Wang, T. (2021). Physical weathering by glaciers enhances silicon mobilisation and isotopic fractionation. Geochemical Perspectives Letters, 19, 7-12.
- Cassarino, L., Curnow, P., & Hendry, K. R. (2021). A biomimetic peptide has no effect on the isotopic fractionation during in vitro silica precipitation. Scientific reports, 11(1), 1-10.
- Murphy, M. J., Hendry, K., & Opfergelt, S. (2021). Novel Isotope Systems and Biogeochemical Cycling During Cryospheric Weathering in Polar Environments. Frontiers in Earth Science, 9, 88.
- L. Bridgestock, J. Nathan, Y-T. Hsieh, P. Holdship, D. Porcelli, P. S. Andersson and G. M. Henderson, 2021, Assessing the utility of barium isotopes to trace Eurasian riverine freshwater inputs to the Arctic Ocean, Marine Chemistry, 236, doi:10.1016/j.marchem.2021.104029

- L. Bridgestock, Nathan, J., Paver, R., Hsieh, Y-T. Porcelli, D., Tanzil, J., Holdship, P., Carrasco, G., Annammala, K. V., Swarzenski, P. W., and Henderson, G. M., 2021, Estuarine processes modify the isotope composition of dissolved riverine barium fluxes to the ocean, Chemical Geology, 579, doi:10.1016/j.chemgeo.2021.120340
- Hsieh, Y.-T., R. Paver, J. T. I. Tanzil, L. Bridgestock, J. N. Lee, and G. M. Henderson (2022), Multi-colony calibration of barium isotopes between shallow-water coral skeletons and in-situ seawater: Implications for paleo proxies, Earth and Planetary Science Letters, 580, doi:10.1016/j.epsl.2022.117369.
- Tagliabue, A, A. R. Bowie, T. Holmes, P. Latour, P. van der Merwe, M. Gault-Ringold, K. Wuttig, and J. A. Resing (2022), Constraining the Contribution of Hydrothermal Iron to Southern Ocean Export Production Using Deep Ocean Iron Observations, Frontiers in Marine Science, 9, doi:10.3389/fmars.2022.754517.
- Medieu, A., et al. (incl. A Tagliabue), Evidence that Pacific tuna mercury levels are driven by marine methylmercury production and anthropogenic inputs, Proceedings of the National Academy of Sciences of the United States of America, 119(2), doi:10.1073/pnas.2113032119. 2022
- König, D., T. M. Conway, M. J. Ellwood, W. B. Homoky, and A Tagliabue, Constraints on the Cycling of Iron Isotopes From a Global Ocean Model, Global Biogeochemical Cycles, 35(9), doi:10.1029/2021gb006968. 2021.
- Hamilton, D. S., et al. (incl. A Tagliabue), Earth, Wind, Fire, and Pollution: Aerosol Nutrient Sources and Impacts on Ocean Biogeochemistry, Annual review of marine science, doi:10.1146/annurev-marine-031921-013612. 2021
- Shaked, Y., B. S. Twining, A Tagliabue, and M. T. Maldonado, Probing the Bioavailability of Dissolved Iron to Marine Eukaryotic Phytoplankton Using In Situ Single Cell Iron Quotas, Global Biogeochemical Cycles, 35(8), doi:10.1029/2021gb006979. 2021
- Homoky, W. B., T. M. Conway, S. G. John, D. Konig, F. Deng, A Tagliabue, and R. A. Mills, Iron colloids dominate sedimentary supply to the ocean interior, Proceedings of the National Academy of Sciences of the United States of America, 118(13), doi:10.1073/pnas.2016078118.2021
- González-Santana, D., M. González-Dávila, M. C. Lohan, L. Artigue, H. Planquette, G. Sarthou, A Tagliabue, and J. M. Santana-Casiano, Variability in iron (II) oxidation kinetics across diverse hydrothermal sites on the northern Mid Atlantic Ridge, Geochimica et Cosmochimica Acta, 297, 143-157, doi:10.1016/j.gca.2021.01.013. 2021
- Huang, Y., Tagliabue, A., & Cassar, N. (2022). Data-driven modeling of dissolved iron in the global ocean. Frontiers in Marine Science. doi:10.3389/fmars.2022.837183

Completed GEOTRACES PhD or Master theses

- Hollie Packman, PhD thesis, Imperial College London, "Stable isotope tracing of trace metals from anthropogenic and natural sources to the ocean". Completed April 2022.
- Mr Sean Selzer, University of Oxford, submitted a D.Phil thesis developed from the GA13 FRidge transect, entitled "Behaviour of Radium, Barium and the Rare Earth Elements in Mid-Atlantic Ridge Hydrothermal Plumes".

GEOTRACES presentations in international conferences

- Goldschmidt conference; keynote: The unreconciled significance of terrigenous iron supply for the ocean carbon cycle, William B. Homoky, University of Leeds
- Hoffman, C., Toner, B., Lough, A., Lohan, M.C., Lang, S., Moore, L., Monreal, P., Tagliabue, A., Resing, J., Bundy, R. (2022) Important role for microbially produced siderophores in the cycling of hydrothermal iron. Ocean Sciences
- Jones, R., Meredith, M., Lohan, M.C, Flanagan, O., Vora, M. Sourse, J., Annett, A. (2022) Tracing the impact of glacial meltwater upon fjord macronutrients at the West Antarctic Peninsula using stable oxygen isotopes and short-lived radium isotopes. Ocean Sciences
- Twining, B., Sofen, L.E., Antipova, O.A., Ellwood, M.J., Gilbert, N.E., Gilbert, N.E., LeClier, G.R., Lohan, M.C., Mahaffey, C., Mann, E.L., Ohnemus, D.C., Wilhelm, S.W (2022). Metal contents of autotrophic flagellates from contrasting open-ocean ecosystems
- Flanagan, O., Annett, A., Sherrell, R.M., Fitzsimmons, J., Ohnemus, D.C, & Lohan, M.C. (2021) Controls on the distribution of particulate trace metals accoss the Western Antarctic Peninsula Shelf. Goldschmidt
- González-Santana, D., González-Dávila, M., Lohan, M.C., Artigue, L., Planquette, H., Sarthou, G., Tagliabue, A., Santana-Casiano J.M. (2021), Variability in iron (II) oxidation kinetics across diverse hydrothermal sites on the northern Mid Atlantic Ridge. Goldschmidt

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ANNUAL REPORT ON GEOTRACES ACTIVITIES IN UNITED STATES

May 1st, 2021 to April 30th, 2022

New GEOTRACES or GEOTRACES relevant scientific results

With 70 peer-reviewed publications in the past year (see attached list) there are too many results to describe them all. Therefore, the approach here is to begin by listing the projects from US GEOTRACES that were featured as GEOTRACES science highlights during the reporting period. See: < <u>https://www.geotraces.org/category/science/newsflash/</u>>. Following that we will report briefly on the status of GEOTRACES section GP15, completed in 2018, and planning for GEOTRACES section GP17.

Science highlights, in reverse chronological order, with the name of the lead investigator, include:

Highlight Date	Lead P.I.	Synopsis
05 Apr. 2022	L. Whitmore	Investigated barium (Ba) cycle in the Arctic Ocean through a unique data set containing dissolved (dBa), particulate (pBa), and stable isotope Ba ratio (δ^{138} Ba) data from four Arctic GEOTRACES expeditions in 2015. Determined that the distribution of dissolved Ba in the upper 500 m of the Arctic Ocean is largely set by a shelf sediment source.
17 Mar. 2022	C. Marsay	Trace element (TE) atmospheric deposition fluxes were assessed during the U.S GEOTRACES GP15 transect by measuring bulk aerosol trace element concentrations and deposition during the low dust season. TE concentrations were the lowest measured during GEOTRACES sections. Deposition rates of TEs on particles to the ocean were calculated from the activity of beryllium-7 (⁷ Be) measured in the same aerosol samples as the TM and in the upper 200 m of the water column.
4 Mar. 2022	J. Bishop	Developed optical sensors for collecting real-time particulate inorganic carbon (PIC) concentration and composition data. The system can be deployed from CTDs and ARGO-style Carbon Flux floats providing PIC concentration vertical profiles. Two prototype sensors had been CTD-deployed during GEOTRACES GP15. After PIC comparison and validation retrieved by other methods, the results show that the sensors can detect PIC concentration variability from 0.01 to >1 μ M in the water column (except in nepheloid layers).
28 Jan. 2022	H. Xu	A data-assimilation model of the dissolved aluminum (Al) cycle was developed using data measured along 11 sections and extracted from the GEOTRACES Intermediate Data Product (IDP2017). The model considers all the processes that might affect the oceanic Al distribution. They determined that 37.2 ± 11.0 Gmol/yr of soluble Al is added to the global ocean, predominantly

		in the Atlantic Ocean, and that Al fractional solubility varies strongly as a function of atmospheric dust concentration. Based on the soluble Fe:Al ratio of dust, the æolian Fe inputs lie between 3.82 and 9.25 Gmol/yr globally.
28 Jan. 2022	SY. S. Chen	Explore the behavior of thorium-230 (²³⁰ Th) and
		protactinium-231 (²³¹ Pa) in the benthic nepheloid layers
		(BNLs) by using hydrographic, optical, and radionuclide data from the western segment of GA03 and a simplified
		model of particle and radionuclide cycling. Results
		suggest that the processes of sediment resuspension and
		lateral transport likely play a significant role in the cycling
		of ²³⁰ Th and ²³¹ Pa in BNLs near oceanic margins. The study also highlights potential biases introduced by
		sediment redistribution in regions near oceanic margins
		where benthic nepheloid layers may be present,
		complicating the application of ²³⁰ Th normalization and
		the interpretation of sediment ²³¹ Pa/ ²³⁰ Th records for deep-ocean cores raised from near continental rises and
		similar reliefs.
10 Nov. 2021	C. Measures	An examination of the vertical profiles of aluminum (Al),
		silicic acid (Si), and the Si:Al ratio from the 2015 U.S.
		Arctic GEOTRACES section (GN01), indicates that the enrichment of dissolved Al in the bottom waters of the
		Arctic basins can result from the dissolution of amorphous
		aluminosilicates that are produced within the sedimentary
		pore waters by reverse weathering processes. The
		conclusions challenge the paradigm that dissolved Al in bottom waters of the Arctic basins could result from top-
		down process, i.e. the water column remineralization of
		vertically transported biological material.
14 Sep. 2021	M.	Report on a comprehensive study of the Arctic Ocean
	Brzezinski	silicic acid (Si(OH) ₄) concentrations and silicon (Si) isotopic composition based on the analysis of a large set
		of GEOTRACES GN01 cruise samples together with
		previous data sets. Anomalously heavy isotopes
		$(d^{30}Si(OH)_4 \text{ up to } +3.2 \%)$ together with high Si(OH) ₄
		concentrations characterize the surface waters along the transpolar drift. This reflects the influence of the high
		silicate content of riverine source waters and the strong
		biological Si(OH) ₄ consumption on the Eurasian shelves.
23 Jul. 2021	Y. Shaked	From the analysis of large datasets collected during 3
		GEOTRACES and other research cruises, a new approach for quantifying the availability of dissolved iron (dFe) in
		natural seawater was established. This approach, based on
		its uptake kinetics by Fe-limited cultured phytoplankton
		establishes a standardized proxy for dFe bioavailability in
		low-Fe oceanic regions. The data suggest that dFe species
		are highly available in low-Fe settings, likely due to photochemical reactions in sunlit waters.
L	1	

19 Jul. 2021	L. Zheng	Reports basin-scale sectional distributions of cadmium (Cd), nickel (Ni), zinc (Zn), and copper (Cu) in the North Pacific Ocean along three GEOTRACES transects. Based on the analysis of mole ratios of dissolved metal (dM) to phosphate (dM/PO ₄) and the enrichment factor of dM, it is proposed that scavenging influences the distribution of these recycled-type metals in the stagnant Pacific Deep Water (PWD). Cu is the most affected by scavenging, while Cd is the least affected, and scavenging plays a significant role on Zn and Ni.
1 Jul. 2021	J. Farmer	Review of geochemical proxies based upon sedimentary isotope ratios of three abundant biologically mediated elements: carbon (C), nitrogen (N), and silicon (Si), commonly used as productivity tracers. Based on GEOTRACES-era data in four key ocean regions there is an evaluation of the processes that lead to changes in the concentration of these elements and their isotopes in the ocean. The study includes a discussion of the uncertainty on interpreting past sedimentary records by these isotopes and examples of representative geochemical reconstructions using sediment records from the last ice age and over the last 70 million years. This paper was a product of the GEOTRACES-PAGES synthesis workshop held in December 2018.
30 Jun. 2021	T. Horner	Review of oceanic distributions, driving processes, and depositional archives of iron, zinc, copper, cadmium, molybdenum, barium, nickel, chromium, and silver based on GEOTRACES-era datasets. The assessment of the overall maturity of each isotope system as a proxy for past ocean productivity reveals that cadmium, barium, nickel and chromium isotopes offer the most promise as tracers of paleoproductivity, whereas iron, zinc, copper, and molybdenum do not. This paper was a product of the GEOTRACES-PAGES synthesis workshop held in December 2018.
23 Jun. 2021	S. Roshan	Used Artificial Neural Network (ANN) mapping to derive a global 3-dimensional climatology of dissolved Cadmium (Cd). Coupled the climatological maps to an Ocean Circulation Inverse Model to diagnose the biogeochemical sources and sinks of Cd and nutrient phosphate (PO4 ³⁻). The dissolved Cd climatology is downloadable and can benefit the calibration of seawater dissolved Cd concentration against core-top foraminiferal Cd/Ca ratio for paleoceanographic applications.
21 May 2021	C. Hayes	Employ a recently compiled global data set of Thorium- normalized fluxes with an updated database of seafloor surface sediment composition to derive atlases of the deep-sea burial flux of calcium carbonate, biogenic opal, total organic carbon (TOC), nonbiogenic material, iron,

We reiterate that the papers by Hayes, Horner and Farmer are products of the GEOTRACES-PAGES synthesis workshop held in December 2018.

The US GEOTRACES project office paid the open access fees to increase the visibility and availability of the following GEOTRACES synthesis papers:

- Costa, K. M., et al (2020), 230Th Normalization: New Insights on an Essential Tool for Quantifying Sedimentary Fluxes in the Modern and Quaternary Ocean, Paleoceanography and Paleoclimatology, 35(2), e2019PA003820, doi:10.1029/2019PA003820.
- Charette, M. A., et al (2020), The Transpolar Drift as a Source of Riverine and Shelf-Derived Trace Elements to the Central Arctic Ocean, Journal of Geophysical Research: Oceans, 125(5), e2019JC015920, doi:10.1029/2019JC015920.
- Black, E. E., et al (2020), Ironing Out Fe Residence Time in the Dynamic Upper Ocean, Global Biogeochemical Cycles, 34(9), e2020GB006592, doi:10.1029/2020GB006592.
- Hayes, C. T., et al (2021), Global Ocean Sediment Composition and Burial Flux in the Deep Sea, Global Biogeochemical Cycles, 35(4), e2020GB006769, doi:https://doi.org/10.1029/2020GB006769.
- Horner, T. J., et al (2021), Bioactive Trace Metals and Their Isotopes as Paleoproductivity Proxies: An Assessment Using GEOTRACES-Era Data, Global Biogeochemical Cycles, 35(11), e2020GB006814, doi:https://doi.org/10.1029/2020GB006814.
- Shaked, Y., et al (2021), Probing the Bioavailability of Dissolved Iron to Marine Eukaryotic Phytoplankton Using In Situ Single Cell Iron Quotas, GLOBAL BIOGEOCHEMICAL CYCLES, 35(8), doi:10.1029/2021GB006979.
- Whitmore, et al (2022), Strong Margin Influence on the Arctic Ocean Barium Cycle Revealed by Pan-Arctic Synthesis, Journal of Geophysical Research: Oceans, 127(4), e2021JC017417, doi:https://doi.org/10.1029/2021JC017417.
- Rahman, S., et al (2022), Dissolved and particulate barium distributions along the US GEOTRACES North Atlantic and East Pacific Zonal Transects (GA03 and GP16): Global implications for the marine barium cycle, Global Biogeochemical Cycles, n/a(n/a), e2022GB007330, doi:https://doi.org/10.1029/2022GB007330.

GP15

Papers are starting to be published in greater numbers for GP15, the meridional transect from Alaska to Tahiti, while publication of results continues for GA03, GP16 and GN01 (See the

science highlights table above and the appended publication list). Here we highlight two publications presenting results from GP15.

Marsay et al. (2022; see publication list for the complete reference) measured trace element (TE) concentrations in aerosols. Combining these TE data with results from the measurement of ⁷Be in the same aerosol samples, and in the upper ~200 m of seawater, these authors were able to compute atmospheric deposition fluxes of TE along the full extent of the GP15 transect during the low dust season (Figure 1).

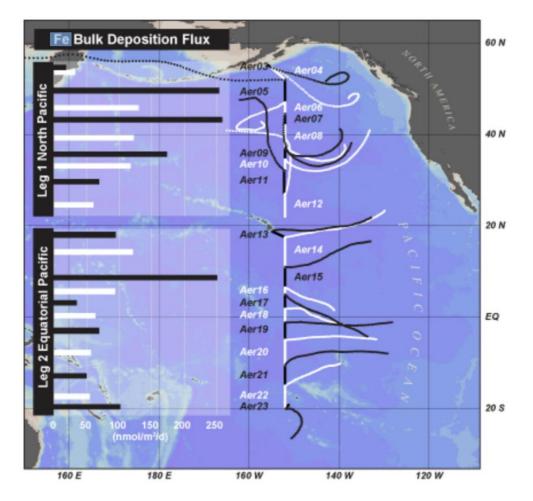


Figure 1. Map of the GP15 transect with aerosol sampling represented by black (odd number deployments) and white (even deployments) lines spanning between sample deployment and recovery positions. Also shown are 3-day back-trajectories for air masses reaching the start point of each aerosol deployment, and bulk deposition fluxes of Fe for each deployment, based on aerosol Fe concentrations and deposition velocities from ⁷Be measurements. Figure from the GEOTRACES website < https://www.geotraces.org/from-alaska-to-tahiti/>.

Along the GP15 transect Chmiel et al. (2022 see publication list for the complete reference) measured dissolved Co (dCo) concentrations, including total dissolved and labile Co. In the upper-ocean (sigma-zero <26) dCo was linearly correlated with dissolved phosphate (dPO₄) due to phytoplankton uptake and remineralization (Figure 2). As depth increased, dCo concentrations became increasingly decoupled from dPO₄ due to co-scavenging with Mn oxide particles. Elevated concentrations of dCo within oxygen minimum zones (OMZs) in the equatorial North and South Pacific were consistent with the suppression of oxidative scavenging. In Pacific Deep Water (PDW), a fraction of elevated ligand-bound dCo appeared

protected from scavenging by the high biogenic particle flux in the North Pacific basin. This finding is counter to previous expectations of low dCo concentrations in the deep Pacific due to scavenging along the path of thermohaline circulation.

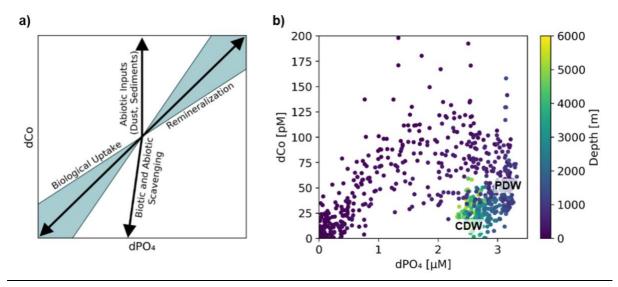


Figure 2. (a) A vector schematic showing the relationship between dCo and dPO₄ concentrations and the effects of major oceanic processes on nutrient distribution. Biological uptake and remineralization can exhibit a range of stoichiometric relationships, depicted here by the blue shaded region. (b) Observed dCo vs. dPO₄ along the GP15 transect. Approximate positions of Circumpolar Deep Water (CDW) and Pacific Deep Water (PDW) are marked. Figure from Chmiel et al. (2022).

GEOTRACES or GEOTRACES relevant cruises

There were no US GEOTRACES cruises during the reporting year.

Cruise preparation continues for the two expeditions contributing to GP17: GP17-OCE and GP17-ANT.

US GEOTRACES was originally scheduled to undertake both expeditions (Figure 3) during the current reporting period, but the expeditions were delayed for a year (GP17-OCE) or 2 years (GP17-ANT). The original schedule called for back-to-back cruises with a global class research vessel leaving Tahiti in November 2021 and arriving in Punta Arenas in January 2022. Gear would be immediately transferred to the RVIB Nathaniel B. Palmer and the second cruise would take place from January to March 2022. Currently, the best estimates are that the first cruise will sail from Tahiti at the end of November 2022 while the second cruise will depart from Punta Arenas in late November of 2023. These dates, though recommended, are still subject to change.

The proposed cruise track for each ship is shown below in Figure 3, but as discussed at the GP17-OCE cruise logistics meeting in Norfolk (see below), and subsequently via email, actual planned station locations are still subject to fine tuning. Figure 3 shows the desired station locations for GP17-ANT, with the expectation that actual station locations will be determined by ice conditions at the time of the cruise.

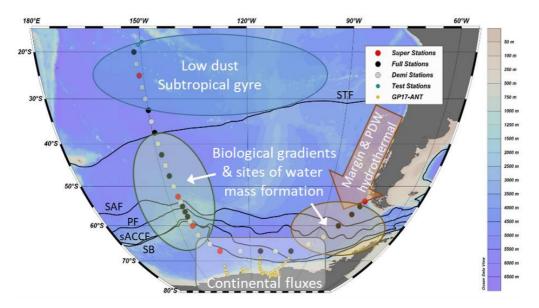


Figure 3. Station locations for the proposed two-ship operation constituting GEOTRACES section GP17. The legend shows the different types of stations to be sampled from the global class research vessel. In yellow near the coast of Antarctica are the proposed stations for the icebreaker. The principal oceanographic features targeted for study are also indicated. The transits to and from the Amundsen Sea on the icebreaker are not shown in this map.

Principal investigators for the voyage from Tahiti to Antarctica and then to Chile are Ben Twining (chief scientist), Jessica Fitzsimmons, and Greg Cutter. Principal investigators for the cruise into the Amundsen Sea are Pete Sedwick (chief scientist), Phoebe Lam, and Rob Sherrell.

New projects and/or funding

As of the close of this reporting period, 11 research projects have been funded to participate in GP17-OCE, 3 projects to participate in GP17-ANT, and 11 projects to participate in both. Funding decisions for some proposals are still pending at the time this report was written.

GEOTRACES workshops and meetings organized

<u>US GEOTRACES SSC</u> held a virtual meeting on 7 June 2021. The 8-hour meeting included news from the US NSF, which funds US GEOTRACES research, status reports on GN01 (Arctic Ocean) and GP15 (northern Pacific meridional transect), and the status of plans for GP17-OCE (Tahiti to Antarctica and then to Chile) and GP17-ANT (coastal Antarctica in the Amundsen Sea). There was also a discussion of GEOTRACES data management, of the use of ROMS models in GEOTRACES, and of the need to replace/renew GEOTRACES seawater standards. The meeting concluded with a discussion of priorities for GEOTRACES after completion of GP17, anticipating that this would be the primary topic of discussion at the annual SSC meeting in 2022.

<u>A synthesis workshop for GEOTRACES Section GP15</u> was held in Norfolk Virginia, 14-16 March 2022, at Old Dominion University. Greg Cutter served as the local host. The meeting was held in a hybrid format with approximately 70 total participants. This was the first opportunity for US GEOTRACES investigators to see each other in person since the beginning of the pandemic in early 2020. The meeting began with a plenary review and discussion of 6 existing synthesis topics (Alaskan Margin Processes; Hydrothermal Sources; Near-bottom features in TEIs; Atmospheric inputs; Biological uptake, particle flux, regeneration, scavenging; and Water masses, end member composition, circulation). Workshop participants then broke into working groups to flesh out these topics and to identify new ones. The workshop concluded with a list of potential publications that would pursue these synthesis topics.

<u>A cruise logistics meeting for GEOTRACES Section GP17-OCE</u> was held immediately following the GP15 workshop, 17-18 March 2022, also at Old Dominion University. Holding these meetings back to back saved on the transportation cost because many investigators are involved in both sections. The meeting was held in a hybrid format with approximately 70 total participants. With more than 20 funded individual projects, involving a much larger number of investigators to the extent possible given the constraints of the cruise logistics. The cruise track and station locations were discussed in plenary after which participants met in breakout groups to sort out the sample requirements for the three principle sampling systems: the standard rosette, used for parameters not prone to contamination; the trace metal-clean rosette, used for parameters and samples for selected radionuclides that are recovered from large volumes of seawater by sorption onto cartridges.

<u>Early career presence</u>: There were no early career participants at the SSC meeting. There were about 70 participants attending each the Norfolk meetings. Neither meeting compiled a participant list; although there were a number of early career scientists involved in each meeting, it is impossible to determine the number of early career investigators that participated online.

Outreach activities conducted

Outreach activities during the past year were impeded by the pandemic and by the focus on completing GP15. Nevertheless, US GEOTRACES has several outreach activities to report.

Alan Shiller gave a keynote talk at the Research Day of the University of Southern Mississippi in November 2021. The talk was titled "Trace Elements Dissolved in Natural Waters: How the small picture matters for the big picture" and highlighted aspects of GEOTRACES work. The talk was designed for a general audience.

Jennifer Kenyon (WHOI) combined her PhD thesis research that included ²³⁴Th on GEOTRACES sections with artwork to help produce a graphic comic book designed to explain through art some of the key scientific concepts featured in GEOTRACES. She helped run a program while still in graduate school called "Synergy II," which is the host name of the website below. Students and scientists at WHOI were partnered with artists who were affiliated with Art League Rhode Island. Kenyon paired up with artist Laurie Kaplowitz, a Boston-based artist and formerly a professor of fine arts at the University of Massachusetts Dartmouth, to produce the comic. The program participation was all voluntary, and Kenyon wrote the proposals to fund the production of the artwork. One can learn more about the comic book here: https://www.synergyexperience.org/pursuit-and-decay.

Investigators at US institutions contributed to several activities related to the release of IDP2021 that were designed to make GEOTRACES data more accessible to users. The principal example is the video of the launch of IDP2021:

https://www.geotraces.org/geotraces-intermediate-data-product-2021-launch-webinar-event-videos/

Phoebe Lam (University of California at Santa Cruz) described the GEOTRACES program in a US-NSF sponsored video/webinar on NSF-supported programs that observe the ocean:

 $\underline{https://www.geotraces.org/webinar-recording-available-learn-about-geotraces-and-other-nsf-funded-projects/}$

or

https://www.nsf.gov/geo/oce/ocean-obs/ocean-observing-webinar-video.mp4

A related post, written by Chris Parsons and edited by Elena Masferrer and Bob Anderson, can be found on the NSF "Science Matters" website:

https://beta.nsf.gov/science-matters/geotraces-research-voyages-studying-rare-substancesoceans

Other GEOTRACES activities

US GEOTRACES has a new website <https://usgeotraces.ldeo.columbia.edu>. Among the new features that will make this website a valuable resource to the oceanographic community are numerous links to relevant information on the international GEOTRACES website and a searchable database of US GEOTRACES publications. Cruise leaders identified as their first priority for the new website that it contains the publications associated with each US GEOTRACES section. This priority has been incorporated into the search features, along with the ability to search by keyword or by each of the following categories: Synthesis, Methods (including intercalibration), International efforts, and Related publications. Work on the website is currently ongoing, but it is sufficiently complete that the website has been opened to public access.

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

A list of 70 US GEOTRACES peer-reviewed papers that were published during the 12 month reporting period is appended at the end of this report.

The number of publications and the number of authors is so large that it is impossible to track all of the early career investigators involved in these publications, or to check each publication to see if it acknowledges SCOR support. However, US GEOTRACES investigators have been asked to include SCOR support in their acknowledgements.

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

A list of dissertations is included in the list of publications appended at the end of this report.

GEOTRACES presentations in international conferences

The number of US GEOTRACES presentations at international meetings and conferences is too large to track.

Closing Remark

We close this annual report by remembering David Kadko, Chief Scientist of GN01, who passed away during the current reporting period. The original plan of US GEOTRACES field activities did not include work in the Arctic Ocean. David led the charge to insert an Arctic expedition into the US GEOTRACES cruise schedule. He organized and led the expedition as well as research that combined data from different investigators to derive fluxes and residence times of trace elements in the surface waters of the Arctic Ocean. He led similar synthesis research in the southern Equatorial Pacific Ocean and one of his last efforts was to derive a method of estimating aerosol settling rates globally from satellite data. His research was a model for GEOTRACES and he will be sorely missed.

A tribute to Dr. David Kadko is posted on the GEOTRACES website:

https://www.geotraces.org/a-tribute-to-dr-david-kadko/

Submitted by

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Publication appendix follows.

2021-2022 US GEOTRACES and GEOTRACES-related Publications and other products

References 1 May 2021 – 30 April 2022 plus papers missed in previous reports

70 publications, 6 Dissertations and one Data Product (listed after journal publications)

US GEOTRACES and Related Publications

Related Publications include:

- 1) US GEOTRACES PIs publishing results that support the GEOTRACES mission but the results are not from GEOTRACES cruises,
- 2) Papers that use data from US GEOTRACES cruises but do not include US GEOTRACES PIs as co-authors, and
- 3) Papers describing international collaboration on which US GEOTRACES PIs appear as co-authors.
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Dissertations

PhD Dissertations

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- Kelly, Rachel (2022). Investigations on marine metal cycling through a global expedition, a wildfire survey, and a viral infection. PhD dissertation. University of Southern California.

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Other Products

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ANNUAL REPORT ON BIOGEOTRACES ACTIVITIES

July 2021 to June 2022

by Maite Maldonado & all co-authors mentioned below

1. Promoting internationally BioGEOTRACES and the GEOTRACES IDP2021

M. Maldonado & R. Schiltzer. GEOTRACES: Sharing marine geochemical data. "An Accessible Ocean" May 10, 2022, Ocean Decade Laboratory, United Nations Decade of Ocean Science for Sustainable Development 2021-2030.

W. Landing, C. Jeandel, R. Schlitzer, P. Lam, M.T. Maldonado. Townhall 33. Accessing and utilizing the GEOTRACES 2021 Intermediate Data Product (IDP2021). Ocean Science Meeting 2022; February 25 (<u>https://www.geotraces.org/updated-programme-geotraces-town-hall-sessions-and-booth-osm2022/</u>)

R. Schlitzer et al., GEOTRACES IDP 2021 Launch What does it include; how can it be accessed, November 17, 2021(<u>https://www.geotraces.org/register-on-line-launch-of-geotraces-idp2021/</u>)

M. Maldonado. BioGeoSCAPES community building in other countries. A US National Biogeoscapes Workshop supported by OCB November 10-12, 2021 (https://www.us-ocb.org/ocb-scoping-workshop-laying-the-foundation-for-a-potential-future-biogeoscapes-program/)

Maldonado, M.T. (Invited Talk). BioGeoSCAPES Ocean metabolism and nutrient cycles on a changing planet. CSIR – National Institute of Oceanography, Goa, India. July 15, 2021

2. Sallie W. Chisholm GROUP (Massachusetts Institute of Technology, Boston, MA, USA)
Jed Fuhrman (University of Southern California)
Paul M. Berube (Massachusetts Institute of Technology)
Jesse McNichol (University of Southern California)

GEOTRACES IDP 2021 & CMAP

To facilitate co-localization of GEOTRACES chemical and physical data sets with biological data sets generated by the broader biological oceanography research community, the Simons CMAP team has begun ingestion of a portion of the IDP2021. The Simons Collaborative Marine Atlas Project (CMAP; (Ashkezari et al., 2021, <u>https://simonscmap.com/</u>) was built with the intent of making oceanographic data (biological, chemical, or physical) more easily accessible to diverse users and intercomparable by having each measurement indexed by explicit space/time coordinates. For example, an investigator interested in complementary measurements taken near one of the GEOTRACES sections could input the latitude / longitude / depth / time information from the cruise path to CMAP and retrieve any other data sources matching those spatiotemporal coordinates.

The developers of CMAP (Ashkezari and Armbrust, University of Washington; Ashkezari et al., 2021) reached out to the GEOTRACES Data Management Committee in the spring of 2022 in order to improve cross-platform access to diverse GEOTRACES data sets, including the BioGEOTRACES 'omics data. Members of the GEOTRACES DMC have had several meetings with Dr. Diana Haring, a Data Engineer at the University of Washington, School of Oceanography. So far, the GEOTRACES IDP2021 CTD sensor data have been ingested (inclusive data 2007-01-19 through 2018-11-23) in CMAP, can be found at the following URL: <u>https://simonscmap.com/catalog/datasets/GEOTRACES_Sensor;</u> and can be easily downloaded at CMAP website.

Information on the Fair Use Agreement is prominently displayed for each GEOTRACES data product on CMAP to ensure compliance with GEOTRACES' policies on data use and reuse. Further information on data sources, data distribution centers, and the IDP2021 is further referenced on each GEOTRACES data product page within CMAP.

Dr. Diana Haring and team are also working on adding links to detailed cruise documents, such as the cruise report or (in the GEOTRACES example) to dedicated cruise pages maintained by BODC.

Datasets in the GEOTRACES IDP 2021

The BioGEOTRACES data sets from Chisholm Laboratory (MIT) that were incorporated in the GEOTRACES IDP2021 include data from GA02, GA03, GA10, and GP13 sections: a) metagenomic data (Biller et al., 2018), b) 16S/18S rRNA gene amplicon sequences to facilitate high resolution taxonomy (McNichol et al., 2021), and c) single cell genomes (Berube et al., 2018; Pachiadaki et al., 2019).

One single cell genomics data set is focused on cyanobacterial genomes (Berube et al., 2018). The other single cell genomics data set (Pachiadaki et al., 2019) – generated by the Stepanauskas group at the Bigelow Laboratory for Ocean Sciences, in collaboration with the Chisholm group at MIT – aimed to capture a wide breadth of the microbial diversity in the epipelagic zone of both the Pacific and Atlantic basins. Multiple downstream papers have resulted from further analysis of these data sets (Becker et al., 2019; Berube et al., 2019; Acker et al., 2020; Hackl et al., 2020; among others). Additionally, a newly released data set compilation (Martiny group at UC-Irvine) combines metagenomic data from BioGEOTRACES, Tara Oceans, and Bio-GO-SHIP (Larkin et al., 2021).

A major challenge while incorporating the omics data in the GEOTRACES IDP2021 was that the omics data are dynamic (changes depending on ever-growing genome reference databases) while the TEI data is static.

The solution was to provide linkages between the omics data in NCBI (i.e., 480 Metagenomes; 14 Single-Cell genomes; and 273 16S-18S-rRNA gene analyses) and EMBL-EBI (480 16S/18S amplicons for microbial community taxonomic & functional structure and abundance) websites and the GEOTRACES IDP 2021 data. Thus, in the GEOTRACES IDP 2021, one can find 4 types of sample descriptors for omics data in the Metadata variables (which are associated with specific GEOTRACES bottle numbers): accession numbers at NCBI or EMBL-EBI; or links to functional and taxonomic analyses webpages.

Therefore, the OMICs linkages in GEOTRACES IDP 2021 Metadata VARIABLES # are:

Variable # 11. NCBI_Metagenome_BioSample accession #: Variable #13. NCBI_16S-18S-rRNA-gene_BioSample accession #: @ https://www.ncbi.nlm.nih.gov/biosample/

Variable #12. NCBI_Single_cell_genome_BioProject accession #: @ https://www.ncbi.nlm.nih.gov/bioproject/

Variable #14. EMBL_EBI_Metagenome_MGNIFY_Analysis_Accession #: @https://www.ebi.ac.uk/metagenomics/analyses/MGYA

For the next IDP

The generation of additional datasets for the GP15 section are planned, but have been delayed due to the COVID-19 health emergency. These data sets include 16S/18S amplicons and cyanobacterial 16S-23S rRNA gene internal transcribed spacer sequence amplicons (generated by Paul Berube and Dreux Chappell for GP15). Jed Fuhrman and Jesse McNichol are also currently working up data for GA02 and GA10, in addition to the published data for GA03 and GP13 (McNichol et al., 2021).

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3. Ben Twining GROUP (Bigelow Laboratory for Ocean Sciences, East Boothbay, ME, USA)

Several papers have been published or submitted with GEOTRACES (section or process cruise) cellular metal quota data:

- Shaked, Y., B.S. Twining (co first author), A. Tagliabue, and M.T. Maldonado. 2021. Probing the bioavailability of dissolved iron to marine eukaryotic phytoplankton using *in situ* single cell iron quotas. *Global Biogeochemical Cycles*. doi: 10.1029/2021GB006979.
- Sofen, L., O. Antipova, M.J. Ellwood, N.E. Gilbert, G. LeCleir, M.C. Lohan, C. Mahaffey, E.L. Mann, D.C. Ohnemus, S.W. Wilhelm, and B.S. Twining. 2022. Metal contents of autotrophic flagellates from contrasting open-ocean ecosystems. *Limnology and Oceanography Letters*. In press.
- Hawco, N.J., A. Tagliabue, and B.S. Twining. 2022. Biogeochemical controls on manganese limitation of phytoplankton physiology in the Southern Ocean. *Global Biogeochemical Cycles*. In revision.
- Kunde, K., N.A. Held, C.E. Davis, N.J. Wyatt, E.L. Mann, E.M.S. Woodward, M. McIlvin, A. Tagliabue, B.S. Twining, C. Mahaffey, M. Saito, and M.C. Lohan. 2022. Trace metal effects on cyanobacterial alkaline phosphatase concentrations in the subtropical North Atlantic. *Nature Communications*. Submitted.
- Wiseman, N.A., J.K. Moore, B.S. Twining, D. Hamilton, and N. Mahowald. 2022. Variable phytoplankton iron quotas modify marine biogeochemistry and dampen the response to varying atmospheric deposition. *Global Biogeochemical Cycles*. Submitted.

Twining is leading the upcoming GP17-OCE section cruise across the South Pacific Gyre and Southern Ocean. Samples will be collected for several BioGEOTRACES parameters, including cellular metal quotas (Twining), proteins (Saito), 16s/18s amplicon sequencing and some eukaryote metatranscriptomics (2 depths: Dreux Chappell and Sophie Clayton), photosynthetic pigments (Twining), particulate ATP (Alexander Bochdansky), phytoplankton community composition (via Imaging FlowCytobot; Twining).

4. Mak Saito GROUP (Woods Hole Oceanographic Institution, MA, USA)

NSF AccelNet Grant

An **NSF AccelNet grant** was recently funded for the development of BioGeoSCAPES "AccelNet -Implementation: Development of an International Network for the Study of Ocean Metabolism and Nutrient Cycles on a Changing Planet (Biogeoscapes)". The Accel-Net program (Accelerating Research through International Network-to-Network Collaborations program) is designed to accelerate the process of scientific discovery and prepare the next generation of U.S. researchers for multiteam international collaborations. This grant will fund international workshops on science integration and planning, informatics and data management, intercalibration review and assessment, and science implementation and infrastructure, and modeling and data integration. In addition, there are significant educational components including a BioGeoSCAPES summer school and a partnership with the Coastal Ocean Environment Summer School in Ghana. While this grant does not fund science directly, it is hoped to catalyze the international coordination needed to launch the BioGeoSCAPES program. Numerous US and international researchers have contributed to the ongoing BioGeoSCAPES effort through participation in workshops and conference sessions as well as in letters of support and contributing to the writing of this grant.

Graduate student Riss Kellogg published a study identifying novel Zinc and cobalt responsive proteins in diatoms that can be used as Zn biomarkers and observed their presence in the South Pacific Ocean. Kellogg, R.M., Moosburner, M.A., Cohen, N.R., Hawco, N.J., McIlvin, M.R., Moran, D.M., DiTullio, G.R., Subhas, A.V., Allen, A.E. and Saito, M.A., 2022. Adaptive responses of marine diatoms to zinc scarcity and ecological implications. *Nature* https://www.nature.com/articles/s41467-022-29603-y

Communications, *13*(1), pp.1-13.

Metaproteomic intercomparison project supported by OCB, led by Saito and McIlvin, is ongoing. BATS protein filter samples have been distributed to 10 labs, 9 have submitted data, a data workshop was conducted in September of 2021 and a manuscript has been drafted (edits recently received from co-authors) and is being prepared for submission to ISME in the coming months. <u>https://www.us-ocb.org/intercomparison-and-intercalibration-metaproteomics/</u>

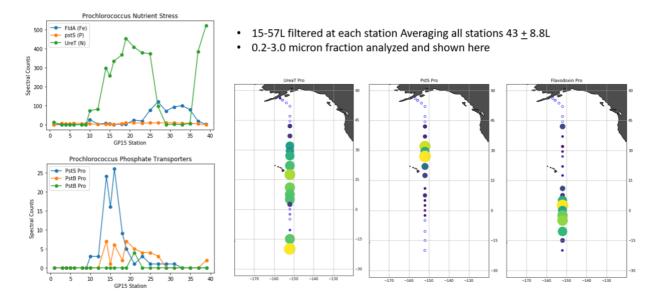
The Ocean Protein Portal

The Ocean Protein Portal (<u>www.oceanproteinportal.org</u>) received renewed NSF funding to develop Version 2.0 for enhanced capabilities and sustainability in 2020.

Surface protein transect from US GEOTRACES track GP15 have been completed, showing Fe, N, P stresses occurring along the transect, which can be compared other cruise data. The results were shared at a US GEOTRACES GP15 seminar. The data will be uploaded to the Ocean Protein Portal when QC is complete for public access. A python Jupyter notebook version of the data is available as well upon request and will be submitted to BCO-DMO. See figure below. These GP15 protein datasets will be submitted to the next IDP, and a manuscript is in preparation by graduate student Becca Chmiel.

Proteins on GEOTRACES GP15

N, P, and Fe limitation signals in Prochlorococcus vary by latitude



Former postdoc Mike Mazzotta published two studies on the use of metals within marine heterotrophic bacteria using metalloproteomics, and comparing it to metaproteomic sections from the METYZME and ProteOMZ expeditions.

Mazzotta, M.G., McIlvin, M.R. and Saito, M.A., 2020. Characterization of the Fe metalloproteome of a ubiquitous marine heterotroph, Pseudoalteromonas (BB2-AT2): multiple bacterioferritin copies enable significant Fe storage. *Metallomics*, *12*(5), pp.654-667. <u>https://doi.org/10.1039/d0mt00034e</u>

Mazzotta, M.G., McIlvin, M.R., Moran, D.M., Wang, D.T., Bidle, K.D., Lamborg, C.H. and Saito, M.A., 2021. Characterization of the metalloproteome of Pseudoalteromonas (BB2-AT2):

Biogeochemical underpinnings for zinc, manganese, cobalt, and nickel cycling in a ubiquitous marine heterotroph. *Metallomics*, *13*(12), p.mfab060. <u>https://pubmed.ncbi.nlm.nih.gov/34694406/</u>

Clio: a vehicle for BioGeotraces sampling

First manuscript describing BATS science validation and Bermuda-Woods Hole section described: Breier, J.A., Jakuba, M.V., Saito, M.A., Dick, G.J., Grim, S.L., Chan, E.W., McIlvin, M.R., Moran, D.M., Alanis, B.A., Allen, A.E. and Dupont, C.L., 2020. Revealing ocean-scale biochemical structure with a deep-diving vertical profiling autonomous vehicle. *Science Robotics*, *5*(48). https://robotics.sciencemag.org/content/5/48/eabc7104.abstract

- Awaiting scheduling for Clio expedition in the Pacific OMZ (delayed due to COVID)
- Short Atlantic Continental shelf Clio expedition planned for November 2021, could follow up on the study of nepheloid layers characterized during the GEOTRACES North Atlantic expeditions. Clio will conduct high-resolution sampling near the seafloor.

5. Julie LaRoche GROUP (Dalhousie University, Halifax, NS, Canada)

Abstracts submitted to the Ocean Sciences meeting in Feb 2022:

Particulate trace element dynamics in the Canadian Arctic Ocean by Manuel Colombo, Jingxuan Lim Birgit Rogalla Dhwani Desai, Julie LaRoche, Susan Allen and Maria T. Maldonado

Marine particles play a key role in the biogeochemistry of many dissolved trace elements, isotopes and nutrients in the ocean, and therefore, understanding the processes that control particulate trace element dynamics is of primary importance for the oceanographic community. Results from the 2015 Canadian GEOTRACES cruise across the Canada Basin (CB), the Canadian Arctic Archipelago (CAA), Baffin Bay (BB) and the Labrador Sea (LS) shed light on the distributions of total particulate trace elements (Al, V, Fe, Mn and P). Lateral transport of lithogenic-derived particles shapes pAl, pV and pFe distributions in the deep CB, BB and LS basins, where these particulate trace elements display higher concentrations along the flow path of boundary currents and in near-bottom waters. Unlike pAl, pV and pFe, primarily controlled by lithogenic sources, pMn distributions in our study regions (with the exception of LS) are dominated by authigenic Mn^{+3/4} oxides, with distinctively high concentrations in CB and BB subsurface halocline waters, as well as in the deepest samples in BB. This phenomenon is likely explained by enhanced bacterially-mediated Mn oxide formation in these waters which have the potential to sustain large populations of Mn oxidizing bacteria as result of the close sediment-water interactions and distinct environmental conditions.

In addition, there are 2 papers published that include some molecular data from the French Geovide GEOTRACES cruise:

Louropoulou et al. 2019 <u>https://www.frontiersin.org/articles/10.3389/fmicb.2019.01566/full</u> Fonseca-Batista et al. 2019 <u>https://www.biogeosciences.net/16/999/2019/</u>

The data submitted for the IDP2021 includes:

GA03 (USA) Southern North Atlantic transect (KN204 and KN199)

- DNA samples/nifH qPCR
- Published (Ratten et al. 2015 Deep-Sea Research special issue)

GN01 (Canada) Canadian Arctic cruise

- DNA samples/flow cytometry/16S rRNA, 18S rRNA, nifH genes amplicon sequencing. qPCR for some diazotrophs
- Manuscripts submitted:
 - Colombo M, LaRoche J, Desai D, Li J, Maldonado MT. Particulate manganese (Mn) cycling in the Canadian Arctic Ocean controlled by putative Mn-oxidizing bacteria dynamics. Submitted to L&O in June 2022.
 - Robicheau et al. *Diazotrophs and phytoplankton community structure in the Canadian Arctic Ocean* (in prep.)

Submitted by Maite Maldonado (mmaldonado@eoas.ubc.ca).

ANNUAL REPORT ON BIOGEOSCAPES ACTIVITIES

July 2021 to June 2022

BioGeoSCAPES Newsletter #4 (March, 2022)

Dear BioGeoSCAPES community,

We hope everyone continues to be safe during the pandemic and that we will all be able to meet in the near future at international meetings. There continues to be strong interest and activity in developing an international BioGeo SCAPES program. Most recently there was an excellent series of BioGeoSCAPES sessions at the Ocean Sciences Meeting as described below.

- There were well-attended BioGeoSCAPES sessions with great interdisciplinary talks with many early career researchers at the virtual Ocean Sciences Meeting in February. The session was entitled: "Towards BioGeoSCAPES: Linking cellular metabolism with ocean biogeochemistry (OB20)" and consisted of five oral presentation blocks and one poster presentation block and were divided into research themes as listed below and there were 80-100 audience members in each of the sessions.
 - Session 1: Global Scale Processes (Mon. Feb. 28, 9AM)
 - Session 2: Southern Ocean Dynamics (Mon. Feb. 28, 10AM)
 - Session 3: Cyanobacteria and bacteria (Mon. Feb, 28, 11:30AM)
 - Session 4: Phosphorus and DOM (Fri. March 4, 11:30AM)
 - Session 5: Protists (Fri. March 4, 12:30PM)
 - BioGeoSCAPES posters were presented on Wed. March 2: the 7-9pm EST poster session.
- US national BioGeoSCAPES scoping workshop occurred virtually in November 10-12, 2021. The meeting had broad interdisciplinary interest with over 160 registrations from the US community over the three-day meeting. Recordings of presentations are available online, and a summary report has just been released.
- The 2nd French BioGeoSCAPES workshop occurred in December 8-9th, 2021 organized by C. Jeandel, I. Obernosterer, and D. Cardinal.
- The workshop report from the OCB Ocean Nucleic Acids 'Omics Intercalibration and Standardization workshop held in 2020 has been completed and is now <u>posted</u>. The report provides an overview of the current status of nucleic acid 'omics approaches and proposes future activities towards community intercalibration and standardization efforts.
- An Ocean Metaproteomic Intercomparison Workshop occurred in September 16-17 (2021), sponsored by the US Ocean Carbon and Biogeochemistry office. The workshop examined the results of the first ocean metaproteomic intercomparison, using samples from the North Atlantic. A total of 16 laboratories participated in the study: 9 in the wet-lab component and 9 in the informatic component, with some labs participating in both activities. The results demonstrated reproducible protein identifications and quantitation, and a manuscript of the results is being prepared for publication. Future metaproteomic intercalibration efforts will be planned as a follow-up.
- The first legs of the AtlantECO Mission Microbiomes project involving the Tara schooner are underway in the Atlantic Ocean and Antarctica
- The US, Canadian, and EU BioGeoSCAPES communities have been submitting grant proposals aimed at building international networks to foster the development of the BioGeoSCAPES program.

Future Events:

- EU 2022 Euromarine (Dates TBD 2022; Zagreb, Croatia) A Pan-European workshop to further foster BioGeoSCAPES collaborations and to support their COST application. Martha Gledhill (GEOMAR Helmholtz Centre for Ocean Research) and Sandi Orlic (Institut Ruđer Bošković, Zagreb, Croatia). For further details see the <u>website</u> or contact Martha Gledhill; mgledhill@geomar.de
- Expeditions are being planned in the Indian Ocean from March to May with a BioGeoSCAPES component.
- UK Two events to look forward to in the UK during 2022:
 - 12-13 Sept 2022, London International Royal Society meeting on Marine Microbes in a Changing Climate (organized by A. Tagliabue, T. Mock, J.Robidart, P. Sanchez-Baracaldo),
 - 6-8 Sept 2022, <u>Challenger 150: The Challenger Society Conference 2022</u> in London. More info will be forthcoming.

In addition to the website (<u>www.biogeoscapes.org</u>), BioGeoSCAPES related science is being promoted on social media through the Twitter account "@BioGeoSCAPES". If you have any highlights for the Twitter feed, please share them with us.

If you would like to get involved in BioGeoSCAPES activities, please contact your country's representative listed at the link above, or one of us. If your country is not listed and you wish to be added as a representative, please contact us (Mak, Al, Adrian or Maite).

Thanks for showing interest in BioGeoSCAPES!

Sincerely, Mak Saito, Alessandro Tagliabue, Adrian Marchetti, and Maite Maldonado.

We would also like to take the opportunity to encourage you to organize your own national meeting to continue gauging interest and brainstorming your national scientific goals. During these national meetings we would like to suggest discussing/addressing the following questions:

1) What science questions do we see as the most important within the broad scope of BioGeoSCAPES on a 10 year timeframe?

2) How would your nation best contribute to BioGeoSCAPES efforts – e.g. fieldwork, laboratory work, modelling, intercalibration efforts, project coordination, data management, bioinformatics?

3) Are there any impediments within your nation that the International program could seek to mitigate via training or collaboration?

4) What productive strategies can you undertake to secure funding for a BioGeoSCAPES program in your nation?

The answers to these questions by each nation will be invaluable in guiding the write up of the international BioGeoSCAPES science plan in the next couple of years. We will also like to start populating the website with 2-page National Scoping Documents summarizing the Planning Workshop outcomes, using the answers to these 4 questions as a starting template.

BioGeoSCAPES related science is being promoted on social media through the Twitter account "@BioGeoSCAPES". If you have any highlights for the Twitter feed, please share them with us.

Thanks for showing interest in BioGeoSCAPES!

For those who are new to this initiative, here is a bit of history

In an effort to explore and develop international community interest for a potential future "Biogeotraces-like" program to study the microbial biological and chemical oceanography of the oceans, a working group of 28 scientists from 9 nations met in Woods Hole in November 2018. There was strong interest in continuing this effort among the international participants, who agreed to act as ambassadors to communicate these discussions to their respective national communities. Please join us in building community support for this effort.

General Information

- Join the email list for updates and information. Send BioGeoSCAPES subscribe request here
- 2018 Workshop report
- 2022 BioGeoSCAPES Ocean Sciences Meeting Overview Poster
- List of current national <u>ambassadors</u> and contact information
- For further BioGeoSCAPES information contact: <u>info@biogeoscapes.org</u>

Submitted by Maite Maldonado (mmaldonado@eoas.ubc.ca).