TRACESAMORS: TRACE element SAMplers and sensORS

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Proposal for a SCOR Working Group: TRACE element SAMplers and sensORS (TRACESAMORS) – A step change to observing and understanding trace metal biogeochemistry in the ocean

1- Abstract (251/250 words)

The availability of essential trace metals (Fe, Zn, Co, Cu, Mn...) controls primary productivity in up to half of the world oceans and modulates the ecological framework of different ocean biomes. One of the biggest remaining challenges to improving our understanding of ocean biogeochemistry is the availability of accurate *in situ* techniques for the determination of the concentration and speciation of these essential trace metals. Our present understanding is severely constrained by the lack of high temporal and spatial resolution observations during critical seasonal and event-driven transitions in remote areas of the oceans. This is due to the absence of sensors that are suitably sensitive, selective and robust to determine elements at extremely low concentrations. Hence, the proposed topic is to initiate international collaborations to foster the application and development of new samplers and sensors, for the determination of trace metal concentrations and speciation in specific parts of the ocean. It builds upon Grand et al. (2019) OceanObs'19 paper recommendations on the creation of an international working group of trace metal sensor developers. This working group will focus on evaluating key analytical issues with existing oceanographic sensors for trace metal analysis, review emerging sensing technologies in other disciplines and their potential for oceanographic use, and provide recommendations for inter-comparison with current remote samplers. The aim is to promote collaborative research to instigate a step change in our ability to monitor trace metal dynamics.

2- Scientific Background and Rationale (1251/1250 words)

Understanding the role of trace elements and how their supply, abundance and speciation will change with projected global environmental forcings (e.g. increased aridity, ocean acidification, warming, global circulation, and expanding oxygen minimum zones, Turner and Hunter 2001, Bruland and Lohan, 2004, Birchill et al. 2017) is a pressing research need. The international GEOTRACES program (https://www.geotraces.org) has provided a snapshot of the distributions of trace elements and their isotopes using ocean section cruises through all the ocean basins. This has led to significant paradigm shifts, particularly with regards to the micronutrient iron (Fe). For example, discrete sampling in the south Pacific Ocean has shown that hydrothermal inputs of Fe can be detected many thousands of kilometers away from their source (Resing et al., 2015) and recent observational evidence in the Southern Ocean suggests that hydrothermal Fe could trigger massive phytoplankton blooms (Ardyna et al., 2019).

The 'tool box' of methods available to chemical oceanographers to constrain the sources, sinks, transport, residence time and internal cycling of micronutrient trace metals is limited to discrete sampling onboard ships (which has been the cornerstone of GEOTRACES observations). A limited number of autonomous systems capable of observing trace metals at subnanomolar concentrations have been deployed (Bell et al. 2002, van der Merwe et al. 2019) but these require some degree of regular turnaround and maintenance (van der Merwe et al., 2019). Overall, these observational constraints hamper the development of a mechanistic understanding of trace metal cycling, which can then be fed into global ocean biogeochemical models. Micronutrient metals are characterized with short residence times, highly variable source terms, and sub-nanomolar concentrations in open ocean settings. Thus, the development of *in situ* sampling and sensing technologies necessary to capture the spatial and temporal variabilities will undoubtedly induce a step change in our understanding of the biogeochemical cycling of essential trace elements and their role in modulating biological productivity and carbon export.

The international research community now has the capacity and infrastructure needed for this next phase. This includes: (i) enhanced and novel analytical chemistry capabilities (ii) expertise for development of *in situ* sensors for macronutrients and physical parameters (iii) marine platforms (floats, moorings, gliders, submarines, satellite telemetry) for testing and use of sensors including float networks and observations within GOOS and AtlantOS programmes.

This idea of working towards novel sensors for micronutrients combining analytical advances with the gaps in marine biogeochemistry observing techniques was put forward at a Town Hall Meeting at the AGU Ocean Science meeting in Salt Lake City 2012 and ultimately led to the Collaborative on Ocean Chemistry and Analysis (COCA) meeting (http://media.journals.elsevier.com/content/files/cocameeting-30202026.pdf). While the COCA meeting was well received by the community, few sustained collaborations emerged from it, presumably because there was little long-term community or programmatic structure bridging the distinct disciplinary fields of oceanography, analytical chemistry and engineering that is necessary to make trace metal sensors a reality. This is a drawback that TRACESAMORS proposes to address.

Which processes and specific regions of the ocean would benefit the most of remote samplers and trace metal sensors ? Capturing seasonal and short-term variability of trace metals as well as the variability from specific processes, such as hydrothermal dispersal, dust deposition and shelf transport, are essential to determine their (i) supply to the euphotic zone linked to primary production, (ii) residence time and (iii) inventory in various oceanographic regimes. Repeated transects and international programmes (such as GEOTRACES) will help identify 'target zones' where biogeochemical changes and ecological sensitivity which need high frequency monitoring of trace elements.

The objectives pursued by the Working Group (WG) will focus on assessing target zones that are the most appropriate for trace metal sensor deployment, taking into account location, facility of maintenance and maximum value of observed data.

How can we incorporate in situ trace metals sampling and measurements into observational networks and models? To successfully develop trace metal sampling and sensors that are *fit for purpose* for observational networks, will require prior knowledge of the challenges of doing this in remote environments. This includes having a practical knowledge of requirements such as power consumption, automation, signal-to-noise control and calibration. Similarly, contributing the right data at the right resolution requires knowledge of the requirements of modelling regional and global oceanic trace metal distributions by the scientific community. Biogeochemical cycling models often have to make broad assumptions because of poor knowledge about temporal trace element observations used to inform any simulation. Furthermore, information on the speciation of essential elements, such as Fe, are often missing (Boyd *et al*. 2010, Parekh et al. 2005).

To address this, a project should include direct, structured discussion and dissemination at meetings and workshops between marine analysts and those involved in (i) oceanographic biogeochemical modelling, (ii) ocean observational networks (iii) deployment of sensor platforms. It is also important that lessons learnt from previous programmes and current projects relating to trace element measurements (e.g. CLIVAR, GEOTRACES) are considered. This includes the importance of metadata and recording of measurement uncertainty, but further that we move forward with sensor and sampling development with an understanding of the limitations in model parameterizations and identify what measurements (location, sampling resolution) would critically improve these models.

What are the most promising techniques for remote sampling of important trace elements? What intercalibration and metrics are important to evaluate and to determine if remote samplers are fit for purpose? The extremely low natural concentrations of metals and their ubiquity in traditional sampling equipment (ships, frames, bottles, chemicals) have led trace metal geochemists to develop extreme methodologies to avoid contamination during all phases of sampling and analysis. Taking care of our future choices of materials so that they have less impact on the environment is also essential. Improving the level of interoperability for *in situ* trace metal sampling and analysis via intercomparison and harmonisation of operational technologies as performed for *in situ* macronutrients analysis (GOSHIP manual, Becker et al., (2019) SCOR#147, Daniel et al. (2020)), would be off great benefit to the marine community.

We propose in this WG to bring together the oceanographic community to provide recommendations for inter-comparison of remote samplers as well as consideration on the type and nature of platform on which they can be deployed keeping in mind sustainability goals.

What are the most promising techniques and limitations for in situ sensors of trace elements? Are chemical oceanographers "missing out" on recent developments in other fields? State-of-the-art analytical detection methods and technologies (e.g., 3D printing, nanotechnologies, novel fluorescent probes) are emerging in multiple scientific fields. Therefore, it has become challenging for chemical oceanographers to keep up with all these analytical and technological developments and to anticipate potential application to oceanography, alongside delivering pioneering basin scale ocean observations with high spatial and temporal resolution. The latest trends and developments in analytical chemistry (novel ligands, fluorophores, ionophores, biosensors, miniaturized methods) should be evaluated for their oceanographic potential. Adopting new strategies among other branches of knowledge could help create the synergies that would facilitate new sensor development research in oceanography.

We propose to review and evaluate recent techniques of in situ sensors used in oceanography and to identify new promising technologies in other disciplines through identification of additional associated SCOR workgroup members from the medical, engineering and other environmental research areas. In order to do this we propose a strategy to leave 5 associate member positions open in order to target and recruit key members from these different disciplines (See empty associate members position in table below).

3- Terms of Reference (245/250 words)

Objective 1: To critically evaluate key analytical issues with currently employed methodologies (samplers and sensors) to establish whether they can be improved, supplemented or eventually replaced.

Objective 2: To define the requirements for measurement conditions and ideal analytical properties of sensors and sampling devices; depending on the context of analysis in different ocean regimes (concentration, pressure…) and the provenance, fate, distribution and biochemical functions of trace elements.

Objective 3: To provide recommendations for controlled inter-comparison of remote samplers and potential in situ sensors on various deployed platforms.

Objective 4: To review published results and identify individuals and communities working on all aspects of trace metal sensors in industry, medicine and other environmental fields (3D printing, nanotechnologies, ligands), to generate a critical review of promising technologies for automated remote marine biogeochemical measurements.

Objective 5: To recommend approaches for future analytical development and deployment of different types of trace metal sensors and samplers (including ongoing GEOTRACES transects and process studies), to identify target zones (with the help of modellers) and techniques suited to extreme environments (e.g. deep sea, sub-zero temperatures).

Objective 6: To develop capacity and disseminate information resulting from the WG outcome in the form of (i) Website (hosted at the University of Plymouth) to share results, reports (Ocean best practices, IOC), tutorials and software, (ii) open access journal special issue (e.g. Limnology and Oceanography-Methods) (iii) platform for partnership collaborative proposals to generate sustained collaboration (*Capacity Building*) and (iv) a final report to SCOR.

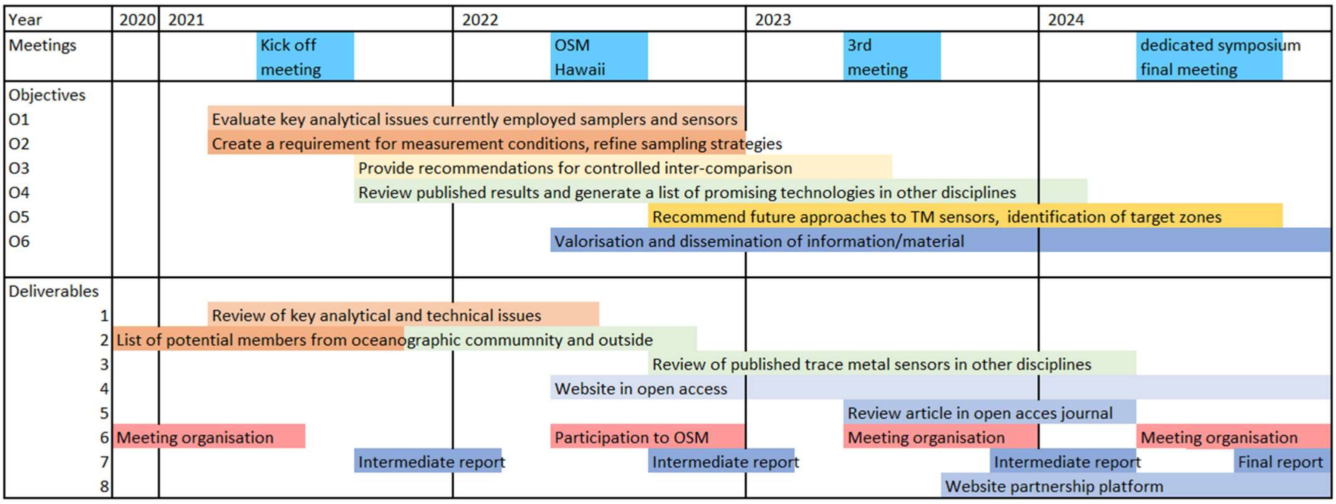
4- Working plan (608/1000 words)

2021: We will first inform the oceanographic and analytical community of this WG via a short summary in AGU Eos, national and international society and research funding newsletters (e.g. GEOTRACES network, chemical societies), publicize this working group through existing international and European observational programs such as GOOS, AtlantOS, Jerico, EMSO, POGO, and french CNRS INSU professional network. Preliminary communications leading up to this meeting will take place during the preceding year and will lead to planning a focused agenda for the meeting, identification of additional Associate Members (**O4**), discussions of plans to address the Terms of Reference. Scheduled video conferences will be 3 monthly amongst members and start immediately leading up to the kick off meeting in 2021 (***Meeting 1***). The WG members will attend the kick off meeting, and set up a framework for investigating a broad variety of analytical technologies and sensor chemistry (**O1, O2**). A reporting database and web page will be formulated ready for implementation, which will also act as a forum for information exchange and details of new meetings and targets (**O6**). Other funding sources for the travel and meeting expenses and final publications will be determined. We will also aim to involve members from the POGO office to help plan capacity building from the start.

2022: Approximately one year after the kick off meeting, an intermediate townhall meeting (***Meeting 2***) with the WG and selected key members of the oceanographic, analytical and engineering communities in the form of an international workshop on marine trace metal sensors will be held. **O3** and **O5** will be discussed then with the feedback from initial work on **O1** and **O2**. One session will be entirely dedicated to new technologies from other disciplines (**O4**). This will allow a nominal one-year period over which to structure and plan the final workshop agendas, issue announcements and invitations, secure needed funds, and make other necessary preparations. To reduce individual costs by sharing funding from other oceanographic research projects, Meeting 2 would occur in combination with the Ocean Sciences Meeting (Hawaii 2022). The workshop will provide the opportunity for all Full and Associate members of the WG to discuss all points of the terms of references and to develop capacity building (**O6**). Groups will be formed and tasks assigned to work on projects and prepare material to be presented at *Meeting 3* and in the special issue or separate book chapter (**O6**).

2023: In year 3 of the project all WG members and associate members will meet again (***Meeting 3***) to record and assess the progress made by different groups and discuss necessary actions to successfully present at a dedicated symposium in year 4 during 2024. It would also set the date for the final meeting during which the WG will be rounding off the results and outcomes and finalize the publications (**O6**).

2024: The final meeting (***Meeting 4***) and conference will be planned to take place in an emerging country in order to generate new interest, contribute to the local economy, and capacity by sharing and exchange expert knowledge in various science fields by opening sessions to students from local universities. It is anticipated that the major part of the funding from SCOR will be utilised to disseminate the findings, build networks, hold meetings and pay for travel to those meetings. Separate funding will be sought from ISBLUE LabexMer (Fr), California State University (USA), US NSF and Ifremer international organization (France), NERC (UK), the Australian Research Council (ARC) and other sources, such as local universities and institutes. At this meeting we will also hold a training workshop and engage the POGO programme to help advertise and support this (see *6. Capacity Building*). We will also endeavour to invite members of international ocean observational networks (e.g. GOOS and AtlantOS representatives) and key members of the modelling community to disseminate results and engage them in discussion of future work.



5- **Deliverables (227/250 words).**

1. **Review of key analytical and technical issues** using currently employed methodologies to establish whether they need to be improved, supplemented or eventually replaced. (**O1, O2, O3**)
2. **Select a list of interested researchers** in the oceanographic community (GEOTRACES, modellers, physical oceanographers), identify members from other disciplines (**O1, O2, O3**). Invite 5 associate members from communities outside of chemical oceanography to join the group. (**O4**)
3. **Review of published techniques** on all aspects of trace metal sensors used in industry, medicine and environmental (3D printing, nanotechnologies, novel ligands, fluorophore…), and generate a list of promising technologies for automated remote marine biogeochemical measurements (make this information publicly available, **O4, O5**)
4. **Produce a Website** (at the University of Plymouth) to share results, reports, tutorials and software in open access format (**O6**)
5. **Publish a review article** in an open access journal special issue (e,g. Limnology and Oceanography-Methods) combining the currently employed methods and the **future promising technologies** with optimised location and platforms required to easily deploy them (**O2, O3, O6**)
6. **Participation at international ocean science meetings** to present the general objectives and progress of the TRACEAMORS WG (**O6**) and organisation of one conference in an emerging country with participation of university students and lecturers
7. **Organize a final meeting and deliver a final report to SCOR** (**O6**)
8. **Generate new sustained collaborations and capacity** from the various meetings through a **website and partnership platform** (**O6**)

6- **Capacity Building (713/1500 words)**

The lack of robust and accurate sensors and reliable remote sampling platforms for observing event driven and seasonal biogeochemical changes in the oceans, inhibits scientists, governments and non-governmental organizations from effectively monitoring and managing the marine environment. The targeted, interdisciplinary nature of the TRACESAMORS project will enable individuals and research groups from across the world to obtain new knowledge and advanced analytical skills, develop new marine sensors and equipment urgently needed to advance marine global networks.

The success of the aims of this proposal will undoubtedly lead to a step change in approaching in situ sampling and analysis of trace elements by:

(i) involving **international experts in other fields** and disciplines external to marine biogeochemistry through **collective intelligence**

(ii) encouraging a **cultural change** of marine analysts and engineers creating a **learning community** who share analytical ideas and develop a united strategic global effort rather than isolated individuals working on method development

(iii) encouraging **involvement of graduate students and junior researchers** in meetings and interlaboratory collaborative work.

To provide **opportunity for associated members and early-career scientists** who are not members of the WGs to attend the SCOR workshop, the second year meeting will occur in combination with the Ocean Sciences Meeting (Hawaii 2022). TRACESAMORS will apply for travel funds from SCOR and the AGU, for the travel and subsistence of students and scientists from developing countries to the third year meeting. Moreover, the final meeting (Meeting 4) will be planned to take place in an **emerging / developing country** to contribute to the local economy, allow networking and to **share and exchange** expert knowledge.

One of our objectives is also to develop **soft-skills** and **pedagogical innovation** in various science fields by **opening sessions to students** from local universities (Walder, 2014) and enhancing interaction and interactivity between the expert and the graduate communities by performing **a training workshop** in the final meeting and explore ways to generate sustained collaboration in networks including involvement of the POGO programme and its network. In order to optimize the use of the SCOR fundings, extra funding will be requested from ISBLUE LabexMer (Fr) through Permanent call for invited professors and researchers and through a second call for projects workshops, seminars, thematic schools, open to Isblue students and international students.

We promote a project that is more **stimulating** and **enjoyable** to engage with because it carries meaning to the trace metal community and a realistic future vision. The dissemination and **sharing of information** through a website and a platform for partnership collaborative proposals will be built up by **partners co-responsible** for the production, ambition and impacts of the project. Live and recorded Powerpoint-type presentations from the meetings, videos showing innovative technologies selected for the future sensors, recommendations for the use of remote samplers will be part of the website content in order to facilitate productive, effective and stimulating face-to-face or remote knowledge exchange.

Beyond the scope of the SCOR funding, successful ideas and collaboration will ultimately lead to major infrastructure development for the oceanographic community. The latter will help strengthen the skill base of marine biogeochemistry and engineering communities to achieve global future goals towards understanding marine elemental cycles and ecological controls.

Why a SCOR working group ?

A SCOR working group is the best way to create a coordinated approach by assembling an international team from various disciplines and expertise (analytical chemistry, biomedical field, space engineering, other environmental fields and chemical oceanography) from different countries. This will permit the identification of priority areas and research questions that would immediately benefit from in situ sampling/analysis, a review of existing technologies, the identification of promising technologies from diverse fields as well as the adoption of best practices for trace metal sensing and autonomous sampling. Importantly, a coordinated international approach, avoids duplication of efforts by individual groups.

The opportunity of this international SCOR WG is timely as the international state-of-the-art technology observation networks and platforms are well developed. Other organizations cannot ensure that the activity is suitably interdisciplinary, involving scientists from a wide range of fields, countries and developing nations, while helping train young scientists. We aim to highlight community or programmatic structure on an international scale and with emerging countries combining senior and young scientists in order to bridge the distinct disciplinary fields of oceanography, analytical chemistry and engineering.

7- **Working Group Membership (149/500 words)**

TRACESAMORS is composed of 10 full members and currently 5 associated members with expertise in chemical oceanography, including nutrient and metal *in situ* analysis, remote sampling and analysis via flow injection techniques, and electrochemical methods. The 5 associate members are experts in atmospheric chemistry, ice core sciences, analytical development, nanotechnology, electronic instrumentation and microfluidics. Several associated positions were not yet allocated *intentionally*, because one deliverable of the working plan of the SCOR WG TRACEAMORS is to identify and invite new collaborators from other disciplines in order to adopt innovative strategies among other branches of knowledge. The 10 full members are from 9 different nations including 4 emerging/developing nations (South Africa, China, India and Chile) and they represent 5 women and 1 early career researcher (Max Grand). The full members are responsible for the delivery of our objectives, while the associated members provide important input from other fields (nanotechnology and modelling).

7.1 Full members

	Name	**Affiliation**	**Gender**	**Specialty within the field of trace metal, analysis and speciation in seawater**
1	Simon Ussher (proposed co-chair)	University of Plymouth, United Kingdom	M	Flow injection techniques (FIA), fluorescence and chemiluminescence detection. simon.ussher@plymouth.ac.uk
2	Agathe Laës-Huon (proposed co-chair)	IFREMER, Brest, France	F	Nutrients, trace metal analysis and deep sea automated analysers Agathe.Laes@ifremer.fr
3	Maxime Grand	Moss Landing Marine Laboratories, USA	M	Application of Flow injection techniques and microfluidics to chemical oceanography (trace metals, nutrients) mgrand@mlml.calstate.edu
4	Andrew Bowie	University of Tasmania, Australia	M	Chemical oceanographer and analytical chemist andrew.bowie@utas.edu.au
5	Maija Iris Heller	Pontificia Universidad Católica de Valparaíso | PUCV · Facultad de Ciencias del Mar y Geografía, Chile	F	Trace metal, analysis and speciation in seawater maija.heller@pucv.cl
6	Susanne Fietz	Department of Earth Sciences, Stellenbosch University, Stellenbosch, South Africa	F	Biogeochemist, focusing on links between phytoplankton and trace metals sfietz@sun.ac.za
7	Mariko Hatta	Institute of Arctic Climate and Environment Research (IACE), JAMSTEC, Japan	F	Chemical oceanographer for shipboard flow injection analysis for trace metals, and analytical chemist adapting microfluidics techniques to determination of nutrients. (Currently at Department of Oceanography, University of Hawaii). mhatta@hawaii.edu
8	Sunil Kumar	CSIR, National Institute Of Oceanography, Goa, India	M	Geochemistry & Isotope Chemistry, Nutrient Cycling & Biogeochemistry sunil@nio.org
9	Maeve Lohan	University of Southampton, UK	F	Expert in electrochemical methods, organic complexation, Flow injection analysis M.Lohan@soton.ac.uk

10	Jian Ma	Xiamen University, China	M	Expert in field nutrient and metal analysis, flow analysis and automatic instrumentation jma@xmu.edu.cn

7.2 Associate

	Name	**Affiliation**	**Gender**	**Specialty within the field of analytical chemistry, engineering, nanofrabrication…**
1	Joe Resing	University of Washington, USA	M	Instrument automation and data acquisition, flow injection analysis.
2	Vincent Raimbault	Laboratory for analysis and architecture of systems, Toulouse, France	M	Nanotechnology, nanofabrication, electronic instrumentation, sensor development, microfluidics
3	Manuel Miro	Universitat de les Illes Balears, Spain	M	Automatisation of analytical methods based on the new generations of flow analysis and 3D-printed mesofluidic platforms
4	Roberto Grilli	Institut des Géosciences de l'environnement, Grenoble, France	M	Laser spectroscopy, Atmospheric chemistry, Ice core sciences, Trace gas analysis, Isotope geochemistry
5	Geng Leng	University of Electronic Science and Technology of China	M	Development of analytical techniques including microextraction, spectrophotometry chemiluminescence, atomic fluorescence, gas and liquid chromatography.
6-10	**Positions left to make strategic recruitment of international experts engineers, analysts, chemists, modellers when funded.**			

8- Working Group contribution (496/500 words)

Agathe Laës-Huon is involved in analytical chemistry dedicated to seawater analysis and development of in situ instrumentation for monitoring marine chemicals and pollutants in coastal and deep-sea waters (FIA, electrochemistry, extraction and water sampling). She is in charge of the in situ chemical analyzers CHEMINI project.

Simon Ussher has >20 years of research experience as an analytical chemist and marine biogeochemist. His research has advanced our understanding of trace metal biogeochemistry in the Atlantic Ocean, including basin scale processes of iron (Fe) biogeochemistry from the atmosphere to the deep ocean. He employs expertise in techniques including FIA and ICP-MS to analyse Fe and trace elements in aerosol and marine samples.

Maxime Grand has pioneered the application of micro-Sequential Lab-On-Valve techniques to trace metal analysis at the sub-nanomolar level and worked on the development of the first generation in situ Lab-On-Chip phosphate analyzers at the NOC, UK. His research interests are focused on the biogeochemical cycling of Fe and Al in open-ocean settings such as the Indian Ocean.

Andrew Bowie is a chemical oceanographer and analytical chemist whose research investigates the biogeochemistry of trace elements in Southern Ocean and Antarctic environments. He has developed novel analytical techniques and instrumentation to probe trace element cycling in remote marine environments. He is currently co-chair of the GEOTRACES program.

Maija Heller is an analytical chemist and chemical oceanographer working in the global oceans on GEOTRACES, SOLAS and GO-SHIP related topics. In 2019 she started a position in Chile and she is currently building analytical and human capacity for the analysis of trace metals in seawater.

Susanne Fietz is a biogeochemist studying the dust deposition and the links between trace metals and phytoplankton in the Atlantic sector of the Southern Ocean. She is a current national representative of the GEOTRACES programme.

Mariko Hatta is a chemical oceanographer and analytical chemist, conducting shipboard determination of dissolved metals using flow injection analytical methodologies during CLIVAR, GEOTRACES, and Southern Ocean projects. She has developed a novel programmable flow injection technique for nutrient determination using a microfluidic platform, and planning to participate in the international nutrient inter-calibration cruise.

Maeve Lohan is Professor of Marine Chemistry at the National Oceanography Centre Southampton and an internationally recognised trace metal biogeochemist specialising in voltammetric and flow injection techniques. Maeve is the GEOTRACES co-chair of Standards and Intercalibration Committee and GEOTRACES Scientific Steering Committee member.

Jian Ma is an environmental analytical chemist dedicated to trace analysis using flow techniques. He has developed a robust integrated Syringe-pump-based Environmental-water Analyzer (*i*SEA) for real-time analyzing the nutrients, metals and carbonate ion in seawater.

Sunil Kumar Singh is Professor at the Physical Research Laboratory and the director of the National Institute of Oceanography (India). He is specialised in the biogeochemistry of Trace Elements and Isotopes (TEIs) in the Indian and Southern Oceans and in the Indian Estuaries and in micro-nutrient cycling, erosion and weathering studies in the Indian River System. He is a past member of the GEOTRACES Scientific Steering Committee.

9- Relationships to Other Programmes and SCOR Working Groups (198/500 words)

TRACESAMORS will be closely linked to a broad variety of programmes and networks:
Biogeochemical modeling: The SCOR working group FeMIP on iron model intercomparison aiming to produce guidelines for how models can best represent the iron cycle and develop tools for objective interpretations of models skill relative to observations.
Methods and best practice: We will also take advantages of the recent SCOR International Nutrient Working Group #147 who delivered the GOSHIP manual for best practice in performing nutrient measurements at sea. Both chairs (Laes-Huon and Ussher) are funded investigators and partners in the AtlantOS programme and the best practice workgroup (https://www.atlantos-h2020.eu/project-information/best-practices). WG member Lohan is also a leader in the GEOTRACES Standards and Intercalibration Committee.
GEOTRACES: A close link with GEOTRACES programmes and planned follow-up programme BioGeoSCAPES will also be maintained as some of the full members are already leaders in this trace metal community (Bowie, Lohan, Kumar Singh, Fietz)

Capacity building: we would like to link up with the POGO programme and in particular the NANO alumni programme (NF-POGO Alumni Network for Oceanspast networks of students).
International observational programs: through membership of members in GOOS, AtlantOS (Ussher), Jerico (Laes-Huon) and EMSO (Laes-Huon).

10- Key References (499/500 words)

Ardyna, M., Lacour, L., Sergi, S. *et al.* (2019). Hydrothermal vents trigger massive phytoplankton blooms in the Southern Ocean. Nat. Commun. *10*, 2451 . doi: 10.1038/s41467-019-09973-6

Becker, S., Aoyama, M., Woodward, E.M.S., *et al.* (2019). GO-SHIP Repeat Hydrography Nutrient Manual: The precise and accurate determination of dissolved inorganic nutrients in seawater, using Continuous Flow Analysis methods. In: The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. Available online at: http://www.go-ship.org/HydroMan.html. DOI: 10.25607/OBP-555

Bell, J., J. Betts, E. Boyle. (2002). Mitess: A moored in situ trace element serial sampler for deep-sea moorings. Deep-Sea Res. Part I 49: 2103–2118. doi:10.1016/S0967-0637(02)00126-7

Birchill, A. , et al. (2017). Seasonal iron depletion in temperate shelf seas, Geophys. Res. Lett., 44, 8987–8996, doi:10.1002/2017GL073881.

Boyd, P., Ibisanmi, E. *et al*. (2010). Remineralization of upper ocean particles: Implications for iron biogeochemistry. *Limnol. Oceanogr*., 55**:** 1271-1288, doi: 10.4319/lo.2010.55.3.1271

Bruland, K., Lohan M. (2004). “Controls of trace metals in seawater”, *Treatise on Geochemistry*, vol. 6, pp. 23–47.

Elrod, V., Johnson, K., Fitzwater, S. , Plant, J., (2008). A long-term, high-resolution record of surface water iron concentrations in the upwelling-driven central California region, Journal of Geophysical Research Atmospheres 113 (C11), DOI: 10.1029/2007JC004610

GEOTRACES (www.geotraces.org)

Grand, M., Laes-Huon, A., Fietz, S., Resing, J. , Obata, H., Luther, G., *et al*. (2019). Developing autonomous observing systems for micronutrient trace metals. *Frontiers in Marine Science*, *6* , 35. doi: 10.3389/FMARS.2019.00035

Resing J.A., Sedwick P.N., German C.R. , *et al*. (2015). Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean, Nature 523, doi: 10.1038/nature14577

Lohan, M, Tagliabue, A. (2018). Oceanic micronutrients: trace metals that are essential for marine life. Elements 14 (6):385, doi: 10.2138/gselements.14.6.

Parekh, P., Follows, M. *et al*. (2005). Modelling the global iron cycle. *Glob. Biogeochem. Cycles*, **18:** GB1002, doi:10.1029/ 2003GB002061.

Peers, G., Quesnel, S. *et al.* (2005). Copper requirements for iron acquisition and growth of coastal and oceanic diatoms. *Limnol. Oceanogr*., 50**:** 1149-1158.

SCOR WG 109**:** http://www.scor-int.org/Working_Groups/wg109front.htm

Tagliabue, A., Bopp, L. *et al*. (2010). Hydrothermal contribution to the oceanic dissolved iron inventory. *Nature Geoscience***.**

Turner, D., Hunter, K. (2001). The Biogeochemistry of Iron in Seawater. IUPAC Series on Analytical and Physical Chemistry vol 7. John Wiley & Sons, Chichester 396pp.

van der Merwe, P., T. Trull, T. Goodwin, P. Jansen, A. Bowie, (2019) The autonomous clean environmental (ACE) sampler: A trace-metal clean seawater sampler suitable for open-ocean time-series applications, , Limnol and oceanography methods, 17 (9), doi: 10.1002/lom3.10327

Walder, A. (2014) The Concept of Pedagogical Innovation in Higher Education. Education Journal. Vol. 3, No. 3, 2014, pp. 195-202., doi: 10.11648/j.edu.20140303.22

Appendix

Agathe Laës-Huon

1- Daniel, A., Laës-huon, A., Barus, C., Beaton, A. D., Blandfort, D., Guigues, N., … Muraron, D. (2020). *Toward a Harmonization for Using in situ Nutrient Sensors in the Marine Environment*. *6* (January), 1–22. doi: 10.3389/fmars.2019.00773

2- Grand, M. M., Laes-Huon, A., Fietz, S., Resing, J. A., Obata, H., Luther, G. W., … Tovar-Sanchez, A. (2019). Developing autonomous observing systems for micronutrient trace metals. *Frontiers in Marine Science*, *6*(February), 35. doi: 10.3389/FMARS.2019.00035

3- Laes-Huon, A., Cathalot, C., Legrand, J., Tanguy, V., & Sarradin, P. M. (2016). Long-Term in situ survey of reactive iron concentrations at the Emso-Azores observatory. *IEEE Journal of Oceanic Engineering*, *41*(4), 744–752. doi: 10.1109/JOE.2016.2552779

4- Cuvelier, D., Legendre, P., Laës-Huon, A., Sarradin, P.-M., & Sarrazin, J. (2017). Biological and environmental rhythms in (dark) deep-sea hydrothermal ecosystems. *Biogeosciences*, *14*(12). doi: 10.5194/bg-14-2955-2017

5- Laës, A., Vuillemin, R., Leilde, B., Sarthou, G., Bournot-Marec, C., & Blain, S. (2005). Impact of environmental factors on in situ determination of iron in seawater by flow injection analysis. *Marine Chemistry*, *97*(3–4), 347–356.

Simon Ussher

1- Birchill, A., N. Hartner, K. Kunde, B. Siemering, C. Daniels, D. González-Santana, A. Milne, S.J. Ussher, P. Worsfold, K. Leopold, S. Painter, M. Lohan,*The eastern extent of seasonal iron limitation in the high latitude North Atlantic Ocean, Scientific Reports* (2019) , 9. doi:10.1038/s41598-018-37436-3

2- Ussher S.J., EP. Achterberg, C. Powell, AR. Baker, TD, Jickells, R. Torres, PJ. Worsfold, 2. *Impact of atmospheric deposition on the contrasting iron biogeochemistry of the North and South Atlantic Ocean*, *Global Biogeochemical Cycles*, 27(1), (2013), 1096–1107.

3- Moore,C.M. M.M. Mills, E.P. Achterberg, R.J. Geider, J. LaRoche, M.I. Lucas, E.L. McDonagh, X. Pan, A.J. Poulton, Micha J.A. Rijkenberg, D.J. Suggett, S.J. Ussher & E.M.S. Woodward, *Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability.* , *Nature Geoscience*, 2, (2009), 867–871.

4- Mawji, E., M. Gledhill, J. A. Milton, G. A. Tarran, S. Ussher, A. Thompson, G. A. Wolff, P. J. Worsfold and E. P. Achterberg, *Hydroxamate siderophores: occurrence and importance in the Atlantic Ocean*, *Environmental Science and Technology*, 42 (23), (2008), 8675–8680.

5- Ussher, S.J., M. Yaqoob, E.P. Achterberg, A. Nabi and P. J. Worsfold, *Effect of Model Ligands on the determination of Fe(II) in Natural Waters Using Flow Injection with Luminol Chemiluminescence Detection*, *Analytical Chemistry*, 77 (7), (2005), 1971-1978.

Maxime M Grand

1 - Grand, M.M., A. Laes-Huon, S. Fietz, J.A. Resing, H. Obata, G.W. Luther III, A. Tagliabue, E.P., Achterberg, Middag, R., A. Tovar-Sanchez and A.R. Bowie (2019). Developing autonomous observing systems for micronutrient trace metals. *Frontiers in Marine Science,* doi: 10.3389/fmars.2019.00035

2 - Grand, M.M., G.T. Clinton-Bailey, A.D. Beaton, A.M. Schaap, T.H. Johengen, M. Tamburri, D.P. Connelly, M.C. Mowlem and E.A. Achterberg (2017). A Lab-On-Chip Phosphate Analyzer for Long-Term in Situ Monitoring at Fixed Observatories: Optimization and Performance Evaluation in Estuarine and Oligotrophic Coastal Waters. *Frontiers in Marine Science,* doi: 10.3389/fmars.2017.00255

3 - Grand, M.M., P. Chocholous, J. Ruzicka, P. Solich and C.I. Measures (2016). Determination of trace Zn in seawater by coupling solid phase extraction and fluorescence detection in the Lab-On-Valve format. *Analytica Chimica Acta*, 923: 45-54. doi: 10.1016/j.aca.2016.03.056

4 - Oliveira, H.M., M.M. Grand, J.Ruzicka and C.I. Measures (2015). Towards chemiluminescence detection in micro-sequential injection lab-on-valve format: A proof of concept based on the reaction between Fe(II) and luminol in seawater. *Talanta*, 133: 107-111. doi: 10.1016/j.talanta.2014.06.076

5 - Grand, M.M, C.I. Measures, M. Hatta, P.L. Morton, P.M. Barrett, A. Milne, J.A. Resing and W.M. Landing (2015). The impact of circulation and dust deposition in controlling the distributions of dissolved Fe and Al in the South Indian subtropical gyre. *Marine Chemistry,* 176: 110-125 doi: 10.1016/j.marchem.2015.08.002

Andrew Bowie

1 - Perron MMG, Strzelec M, Gault-Ringold M, Proemse BC, Boyd PW, et al., 'Assessment of leaching protocols to determine the solubility of trace metals in aerosols', Talanta, 208 Article 120377. ISSN 0039-9140 (2020) DOI: 10.1016/j.talanta.2019.120377

2 - Tagliabue A, Bowie AR, DeVries T, Ellwood MJ, Landing WM, et al., 'The interplay between regeneration and scavenging fluxes drives ocean iron cycling', Nature Communications, 10, (1) Article 4960. ISSN 2041-1723 (2019) DOI: 10.1038/s41467-019-12775-5

3 - Wuttig K, Townsend AT, van der Merwe P, Gault-Ringold M, Holmes T, et al., 'Critical evaluation of a seaFAST system for the analysis of trace metals in marine samples', Talanta, 197 pp. 653-668. ISSN 0039-9140 (2019) DOI: 10.1016/j.talanta.2019.01.047

4 - van der Merwe P, Trull TW, Goodwin T, Jansen P, Bowie A, 'The autonomous clean environmental (ACE) sampler: a trace-metal-clean seawater sampler suitable for open-oceantime-series applications', Limnology and Oceanography: Methods, 17, (9) pp. 490-504. ISSN 1541-5856 (2019) DOI: 10.1002/lom3.10327

5 - Bowie A, Tagliabue A, 'GEOTRACES data products: standardising and linking ocean trace element and isotope data at a global scale', Elements (Quebec), December pp. 436-437. ISSN 1811-5209 (2018) DOI: 10.2113/gselements.14.6.436

Maija Iris Heller

1- Heller, M.I. and P.L. Croot, Superoxide Decay Kinetics in the Southern Ocean. Environmental Science & Technology, (2010). 44(1): p. 191-196.

2- Heller, M.I. and P.L. Croot, Application of a superoxide (O-2(-)) thermal source (SOTS-1) for the determination and calibration of O-2(-) fluxes in seawater. Analytica Chimica Acta, (2010). 667(1-2): p. 1-13.

3- Wuttig, K., M.I. Heller, and P.L. Croot, Reactivity of Inorganic Mn and Mn Desferrioxamine B with O-2, O-2(-), and H2O2 in Seawater. Environmental Science & Technology, (2013). 47(18): p. 10257-10265.

4- Heller, M.I., et al., Accumulation of Fe oxyhydroxides in the Peruvian oxygen deficient zone implies non-oxygen dependent Fe oxidation. Geochimica et Cosmochimica Acta, (2017). 211: p. 174-193.

5- Ho, P., et al., The distribution of dissolved and particulate Mo and V along the U.S. GEOTRACES East Pacific Zonal Transect (GP16): The roles of oxides and biogenic particles in their distributions in the oxygen deficient zone and the hydrothermal plume. Marine Chemistry, (2018). 201: p. 242-255.

Susanne Fietz

1- Viljoen J, Weir I, Fietz S*, Cloete R, Loock J, Philibert R, Roychoudhury AN. (2019) Links between phytoplankton community composition and trace metal distribution in the surface waters of the Atlantic Southern Ocean. Frontiers in Marine Science, 6:295, doi: 10.3389/fmars.2019.00295

2- Grand MM, Laes-Huon A, Fietz S, Resing JA, Obata H, Luther GW, Tagliabue A, Achterberg EP, Middag R, Tovar-Sanchez A, Bowie A (2019) Developing autonomous observing systems for micronutrient trace metals. Frontiers in Marine Science 6:35, doi: 10.3389/fmars.2019.00035

3- Cloete R, Loock JC, Mtshali TN, Fietz S, Roychoudhury AN. (2019) Winter and summer distributions of Copper, Zinc and Nickel along the International GEOTRACES section GIPY05: Insights into deep winter mixing. Chemical Geology 511, 342-357. doi: 10.1016/j.chemgeo.2018.10.023

4- Viljoen JJ, Philibert R, van Horsten N, Mtshali TN, Roychoudhury A, Thomalla S, Fietz S* (2018) Response of phytoplankton in growth, community structure and photophysiology to iron and light addition in the Polar Frontal and Antarctic Waters of the Southern Ocean. Deep Sea research I, 141, 118-129 https://www.sciencedirect.com/science/article/pii/S0967063718301420

5- Weir I, Fawcett S, Smith S, Walker D, Bornman T, Fietz S*. Winter biogenic silica and diatom distributions in the Indian Sector of the Southern Ocean. in review.

Mariko Hatta

1- Hatta, M., Measures, C.I., Ruzicka, J.J. (2019). Determination of traces of phosphate in sea water is automated by programmable flow injection, and optimized by means of novel information on kinetics of formation and spectra of phosphomolybdenum blue. Talanta. 191. 333-341.

2-Hatta, M., Measures, C.I., Ruzicka, J. J. (2018). Programmable Flow Injection. Principle, methodology and application for trace analysis of iron in a sea water matrix. Talanta 178. 698-703. 2018. doi: 10.1016/j.talanta.2017.10.007.

3- Jenkins, W.J., Hatta, M., Fitzsimmons, J.N., Schlitzer, R., Lanning, N.T., Shiller, A., Buckley, N.R., German, C.R., Lott III, D.E., Weiss, G., Whitmore, L., Casciotti, K., Lam, P.J., Cutter, G.A., Cahill, K.L. (2020). An intermediate-depth source of hydrothermal 3He and dissolved iron in the North Pacific. Earth and Planetary Science Letters 539. 116223.

4-Hatta, M., Measures, C.I., Wu, J., Fitzsimmons, J., Sedwick, P., Morton, P. (2015). Overview: Dissolved Fe and Mn concentrations in the North Atlantic Ocean during GEOTRACES 2010/2011 cruises. *Deep-Sea Res. II.* 116.117-129.

5- Hatta, M., Measures, C.I., Lam, P.J., Ohnemus, D.C., Auro, M.E., Grand, M.M., Selph, K.E. (2017). The relative roles of modified circumpolar deep water and benthic sources in supplying iron to the recurrent phytoplankton blooms above Pennell and Mawson Banks, Ross Sea, Antarctica, Journal of Marine Systems. 166, 61-72.

Jian Ma

1- Martiny, A.C., Lomas, M.W., Fu, W., Boyd, P.W., Chen, Y.L., Cutter, G.A., Ellwood, M.J., Furuya, K., Hashihama, F., Kanda, J., Karl, D.M., Kodama, T., Li, Q.P., Ma, J., Moutin, T., Woodward, E.M.S., Moore, J.K., Biogeochemical controls of surface ocean phosphate, Science Advances, 2019, 5, eaax0341, 9 pages.

2- Ma, J., Li, P., Chen, Z., Lin, K., Chen, N., Jiang, Y., Chen, J., Huang, B., Yuan, D., Development of an integrated syringe-pump-based environmental-water analyzer (*i*SEA) and application of it for fully automated real-time determination of ammonium in fresh water, Analytical Chemistry, 2018, 90(11), 6431-6434

3- Ma, J., Yuan, Y., Yuan, D., Underway analysis of nanomolar dissolved reactive phosphorus in oligotrophic seawater with automated on-line solid phase extraction and spectrophotometric system, Analytica Chimica Acta, 2017, 950, 80-87

4- Ma, J., Yuan, D., Lin, K., Feng, S., Zhou, T., Li, Q., Applications of flow techniques in seawater analysis: A review, Trends in Environmental Analytical Chemistry, 2016, 10, 1-10

5- Ma, J., Adornato, L., Byrne, R.H., Yuan, D., Determination of nanomolar levels of nutrients in seawater, Trends in Analytical Chemistry, 2014, 60, 1-15

Maeve Lohan

1- Sedwick, P. N., Bowie, A. R., Church, T. M., Cullen, J. T., Johnson, R. J., Lohan, M. C., ... Ussher, S. J. (2020). Dissolved iron in the Bermuda region of the subtropical North Atlantic Ocean: Seasonal dynamics, mesoscale variability, and physicochemical speciation. *Marine Chemistry*, *219*, 103748. DOI: 10.1016/j.marchem.2019.103748

2- Artigue, L., Lacan, F., Van Gennip, S., Lohan, M. C., Wyatt, N. J., Woodward, E. M. S., ... Drillet, Y. (2020). Water mass analysis along 22 °N in the subtropical North Atlantic for the JC150 cruise (GEOTRACES, GApr08). *Deep Sea Research Part I: Oceanographic Research Papers*, [103230]. DOI: 10.1016/j.dsr.2020.103230

3- Kunde, K., Wyatt, N. J., González-Santana, D., Tagliabue, A., Mahaffey, C., & Lohan, M. C. (2019). Iron distribution in the subtropical North Atlantic: the pivotal role of colloidal iron. *Global Biogeochemical Cycles*, *33*(12), 1532-1547. DOI: 10.1029/2019GB006326

4- Birchill, A. J., Hartner, N. T., Kunde, K., Siemering, B., Daniels, C., González-Santana, D., ... Lohan, M. C. (2019). The eastern extent of seasonal iron limitation in the high latitude North Atlantic Ocean. *Scientific Reports*, *9*(1), 1-12. [1435]. DOI: 10.1038/s41598-018-37436-3

5- Shelley, R. U., Zachhuber, B., Sedwick, P. N., Worsfold, P. J., & Lohan, M. C. (2010). Determination of total dissolved cobalt in UV-irradiated seawater using flow injection with chemiluminescence detection. *Limnology and Oceanography: Methods*, *8*(7), 352-362. DOI: 10.4319/lom.2010.8.352

Sunil Kumar Singh

1- Singh S.P., Singh S.K., Goswami V., Bhushan R., Rai V.K., Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and mixing of water masses, *Geochimica et Cosmochimica Acta*, 94, 2012, 38–56, doi: http://dx.doi.org/10.1016/j.gca.2012.07.017.

2- Rahaman W., Singh S.K. and Rai V.K., Molybdenum isotopes in two Indian estuaries: Mixing characteristics and input to oceans *Geochim. Cosmochim. Acta,*141, 2014, 407–422, doi: 10.1016/j.gca.2014.06.027*2014.*

3- Singh S.P., Singh S.K.,Bhushan R. and Rai V.K. Dissolved silicon and its isotopes in water column of the Bay of Bengal: Internal cycling versus lateral transport,*Geochim. Cosmochim. Acta,* 151, 2015, 172–191.

4- Chinni V., Singh S. K., Bhushan R., Rengarajan R. and Sarma V.V.S.S., Spatial variability in dissolved iron concentrations in the marginal and open waters of the Indian Ocean, *Marine Chemistry* 208, 11-28 2019,

5- Singh Naman Deep, Chinni Venkatesh and Singh S. K., Dissolved aluminium cycling in the northern, equatorial and subtropical gyre region of the Indian Ocean, *Geochim. Cosmochim. Acta, Geochim. Cosmochim. Acta,* 268, 160-185, 220.

ACRONYM:

GOOS: Global Ocean Observing System
AtlantOS: Optimizing and Enhancing the Integrated Atlantic Ocean Observing Systems
AGU: American Geophysical Union
CLIVAR : Climate and Ocean -Variability, Predictability, and Change
GOSHIP: Global Ocean SHIP based hydrographic investigation program
EMSO: European Multidisciplinary Seafloor and water column Observatory
POGO: Partnership for the Observation of the Global Ocean
CNRS: Centre National de la Recherche Scientifique
ICP-MS Inductively coupled mass spectrometry
INSU: Institut National des Science de l'Univers
ISblue : Interdisciplinary School for the blue planet
LABEX-Mer: LABoratoire d'EXcellence Mer
US NSF: National Science Foundation
NERC: Natural Environment Research Council
CHEMINI: Chemical MINIaturised analyser
NOC: National Oceanography Center
SOLAS: Surface Ocean - Lower Atmosphere Study
IOC: Intergovernmental Oceanographic Commission
FIA: Flow Injection Analysis