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Tinel, Liselotte Leona Georgette orcid.org/0000-0003-1742-2755 (2019) Investigating ozone deposition at the sea-surface: the interplay of iodide and organics. In: Influence of coastal pollution on marine atmospheric chemistry: effects on climate and human health., 27-28 Nov 2018, National Research Council.

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Figure 1: Presentation in the plenary room at the Italian National Research Council. © Jessica Gier

dealt with “Interactions between aerosols, clouds and marine ecosystems in contrasting environments”.

Workshop I focused on the importance of the coastal environment from the air-sea interaction point of view and on the different aspects of coastal pollution (air and water), with two main objectives:

- 1) discussing how coastal pollution affects gas and particles emitted over the coasts, and
- 2) understanding the effects of coastal pollution on the air quality-climate system and human health.

Presentations addressed various topics but with a clear focus on the peculiarities of atmospheric chemistry and air quality in coastal regions, with an emphasis on radical/halogen chemistry and on the oxidative properties of the coastal atmosphere. The role of sea-spray as a vehicle for transferring a variety of seawater components (biogenic organic matter, pollutants, bacteria, viruses and toxins) from the sea surface to the atmosphere has been intensively treated, evidencing a fundamental lack of knowledge on such processes and associated

impacts. Emerging themes of crucial importance for the coastal environment were also identified and discussed, such as the environmental and human health impacts of micro-plastics pollution and the increased occurrence of toxic (red) tides.

The discussion sections led to the definition of two major research areas for a better understanding of coastal air-sea interactions. The first need comes with the understanding of processes of sea-air exchange in the coastal environment, which in many cases are

scarcely characterised. For instance, the exchange of particles, toxins, pollutants (including newly developed materials, such as engineered nano-particles and graphene) are scarcely understood in general and in the coastal context in particular. Moreover, the role of the sea surface microlayer in this process has been pointed out as potentially important and warrants more detailed investigations. The second research area addresses the forcing and feedbacks between the sea and the atmosphere in the coastal environment. The importance of non-linear interactions between water biology, water and air composition, meteorology, human health, ecosys-



Figure 2: Plenary presentation of Spyros Pandis. © Jessica Gier

tems, economy, etc. was pointed out during the discussion, with a particular stress for the necessity of understanding these topics in a changing climate perspective.

Finally, the participants expressed a series of research needs for air-sea exchange investigation in the coastal environment. The necessity of linking different scientific communities (atmosphere, ocean, toxicology, and social) was considered of paramount importance in order to produce a significant advancement of science, through the development of a multidisciplinary investigation approach. The necessity of integrating laboratory and field observations, remote sensing and modelling was also highlighted, together with the importance of implementing integrated sea-atmosphere long-term observations in the coastal environment, which are almost non-existent at present.

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The outcomes of the workshop contribute to advance our knowledge of the Core Theme 5 "Ocean biogeochemical controls on atmospheric chemistry" of the SOLAS 2015-2025 Science Plan and Organisation.



Figure 3: Joint group picture of the workshops participants.

Front row left to right: Lin Du, Chiara Santinelli, Jurgita Ovadnevaite, Cristina Facchini, Michel Flores, Manuela van Pinxteren, Tiera-Brandy Robinson, Tim Bates, Francesca Malfatti, Karine Sellegri, Trish Quinn, Rafel Simó, and Karam Mansour.

Middle row left to right: Stefano Decesari, Emmanuel Boss, Kimberly Prather, Graham Jones, Ilan Koren, Maurice Lévassieur, Aurelia Tubaro, Theresa Barthelmess, and Frédéric Gazeau.

Back row left to right: Manuel Dall'Osto, Jon Abbatt, Alfonso Saiz-Lopez, Matteo Rinaldi, Eric Saltzman, Christian Stolle, Richard Moore, Yinon Rudich, Oliver Wurl, Erik Hoffmann, Alcide Di Sarra, Karine Desbeoufs, Cliff Law, Thipsukon Khumsaeng, and Paquita Zuidema. , Kohei Sakata

Missing: Weidong Chen, Cécile Coeur, Erik van Doorn, Christian George, Roy Harrison, Monica Mårtensson, Michela Maione, Helge Niemann, Spyros Pandis, and Liselotte Tinel. © Jessica Gier

Workshop II was dedicated to bringing together scientists participating in eleven recent and current field programs that are addressing at least a part of the science of the ocean ecosystem-aerosol-cloud linkage, which is one of the key elements in the Surface Ocean - Lower Atmosphere Study (SOLAS) sciences. The aim of the workshops was that participants will:

1. be aware of what other programs are doing;
2. reach out to others to initiate cross-cutting studies.

SOLAS invited ten scientists to present eleven programs and the meeting was open to all interested scientists.

To set the stage, the first half-a-day of the workshop was dedicated to perspective talks associated with each program. We then moved to discuss cross-cutting themes on the second day. The meeting started with a quick introduction of all present. Maurice Levasseur then provided a short overview of SOLAS, its objectives, and the meeting objectives. He was followed by Rafael Simó who presented two relevant projects, the “Antarctic Circumnavigation Expedition” ([ACE](#)) and the “Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean” ([PEGASO](#)), the first, circumnavigating the Southern Ocean sampling the oceans and a rela-

tively pristine atmosphere and the second focused on Lagrangian following of high phytoplankton biomass patch and measuring their emissions. Karine Desboeufs discussed the “Process studies at the air-sea interface after dust deposition in the Mediterranean Sea” ([PEACETIME](#)), which focused on the Western Mediterranean sampling ocean/aerosols and interaction between the two using, among others, on-ship experimental chambers. Jon Abbatt presented the “Network on Climate and Aerosols: Addressing Key Uncertainties in Remote Canadian Environments” ([NETCARE](#)) project, focused on aerosol dynamics in the arctic and how they may be changing as a result of climate change. Study approach involved two cruises, airplane samplings, as well as a large modelling component. Manuela van Pinxteren presented the “Marine biological production, organic aerosol particles and marine clouds: a Process Chain” ([MarParCloud](#)) program that focused on organic matter originating in the ocean and its tracing in the micro-layer, aerosols, and cloud near Cape Verde (sampling on land as well as ocean). Cliff Law presented the “Surface Ocean Aerosol Production” ([SOAP](#)) project, which sampled ocean-aerosol relevant parameters near New Zealand in the fall of 2011 and 2012, and included sampling a variety of different oceanic blooms. He also mentioned an upcoming campaign called Sea2Cloud, a collaboration between New Zealand and France and which is planned for September-October 2019. Richard Moore presented the “North Atlantic Aerosols and Marine Ecosystems Study” ([NAAMES](#)), a four-cruise program to study the annual cycle of phytoplankton in the North



Figure 4: Maurice Levasseur is providing a short overview of SOLAS. © Jessica Gier

Atlantic and its linkages to aerosols and clouds, sampling with ship, airplane and a variety of in-situ and remote-sensing tools. Graham Jones presented the program “Reef to Rain Forest” (R2R) which focuses on the role of the Great Barrier Reef in aerosol and precursor production, sampling both water and overlying atmosphere at high temporal resolution. Michel Flores introduced the TARA Pacific

project, covering the tropical and subtropical Pacific and associated ocean/aerosol sampling. Jurgita Ovadnevaite introduced the “Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic Understanding” (BACCHUS) synthesis project, a comprehensive program designed to understand the impacts of biogenic and anthropogenic emissions on clouds. The project involved process studies as well as compilation of a database of relevant measurements to improve parametrization in models. Finally, Paquita Zuidema presented “Variability of the American Monsoon Systems Ocean-Cloud-Atmosphere-Land Study” (VOCALS), a project focused on aerosols-clouds interaction in the Eastern South Pacific using ships and airplanes for sampling.

On the 2nd day, we reconvened as a group and each scientist discussed what they hoped to achieve on that day based on what they heard on the 1st day and stating common themes that were observed in many of the project presented. We then broke into two groups whose themes were:

- 1) What are the cross-cutting SOLAS science questions that are common to many of the presented projects - headed by Ilan Koren and Maurice Levasseur, and
- 2) What are the measurements necessary to study the ocean ecosystem-aerosol-cloud linkage and which require community effort to estab-



Figure 5: Breakout group discussion on “What are the cross-cutting SOLAS science questions that are common to many of the presented projects”, headed by Ilan Koren and Maurice Levasseur. © Jessica Gier

lish common practices - headed by Emmanuel Boss.

The two groups regrouped after lunch and several action items were decided on:

1. All the projects presented should be linked to the SOLAS website (some are, but not all).
2. A need was identified for method homogenisation and cross-comparison among SOLAS researchers to insure the inter-comparability between measurements and results conducted during different campaigns. The SOLAS website was suggested as a clearing house for community documents addressing SOLAS sampling issues (e.g. the SCOR working group report on how to sample the surface micro layer). The aerosol community has addressed this need with “Global Aerosol Synthesis and Science Project” (GASSP, Reddington *et al.*, 2017) but this effort does not reach to clouds and ocean variables.
3. The necessity to compile a table of measurements (and instruments) necessary to study the ocean ecosystem-aerosol-cloud linkage that will reside on the SOLAS website. The table will also include a wish list of measurements that are not essential (due to the significant efforts of costs associated) but that are encouraged. Such a table could be used to encourage global sampling programs (e.g. Global Ocean Ship-based Hydrographic

Investigations Program (GO-SHIP)) to add such measurements to increase systematic global sampling of ocean, aerosol, and clouds. This table will also reside on the SOLAS website and will be a living document that will be revisited every few years (perhaps in association with the SOLAS summer school).

4. Participants showed a clear interest to maintain contact and to exchange ideas on cross-cutting methodological and science topics.

We thank all the participants, the organisers as well as our funders, who supported this activity by funds and actions.

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The outcomes of the workshops contribute to advance our knowledge of the Core Theme 4 “Interconnections between aerosols, clouds, and marine ecosystems” of the SOLAS 2015-2025 Science Plan and Organisation.

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Kohei Sakata completed a PhD degree in geochemistry at Hiroshima University, Japan, in 2017. He started a postdoctoral position at the National Institute for Environmental Studies in 2017. His topic is chemical speciation of organic matter and their complexes in sea spray aerosol by X-ray spectroscopy.

Organic matters in sea spray aerosol: their role as a driving force of atmospheric chemistry in the marine boundary layer

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Great attention has been paid to organic matters (OM) in sea spray aerosol (SSA) as one of the factors controlling cloud condensation nuclei (CCN) and ice nuclei (IN) activities (Quinn *et al.*, 2015). Furthermore, OMs in SSA are related to various chemical reactions with oxidants and pre-existing particles (Figure 6). These reactions impact ozone formation/depletion, oxidation of methane and dimethylsulfide (DMS) and the promotion of primary production in the surface ocean by bioactive trace metals (BTM including iron (Fe)), and they are also important factors to regulate the marine climate and to control the biogeochemical cycle in the marine boundary layer (Mahowald *et al.*, 2016). Therefore, a better understanding of the reaction processes of OMs in SSA is an indispensable task for further development of air-sea interaction research.

One of the challenges in improving knowledge about the atmospheric chemistry of OMs in SSA is the complexity of OM species in nascent SSA. Much effort has been made to clarify OMs in SSA based on mesocosm studies (Prather *et al.*, 2013; Quinn *et al.*, 2015) but field observations are still insufficient. Online analysis (e.g. aerosol

mass spectrometry: AMS) has an excellent time resolution for chemical composition measurements in aerosol. However, accurate chemical speciation and morphological analyses are difficult to make due to fragmentation during ionization. By contrast, filter-based observation is suitable for OM speciation in SSA, even if the time resolution is inferior to online analysis, because various speciation techniques including X-ray spectroscopy can be applied. In addition, we recently developed a method for high time-resolution filter-based sampling of marine aerosols by dramatic decrease of the background of targeted elements in the filter (Sakata *et al.*, 2018).

X-ray absorption fine structure (XAFS) spectroscopy, a non-destructive speciation method, can analyse bulk species in aerosol regardless of their physical state, and determine species on aerosol surface by combining the method with electron yield. Comparison of chemical species between bulk and surface species is useful for clarifying heterogeneous reactions on aerosol surface. Furthermore, micrometer/nanometer X-ray spectroscopy (e.g., scanning transmission X-

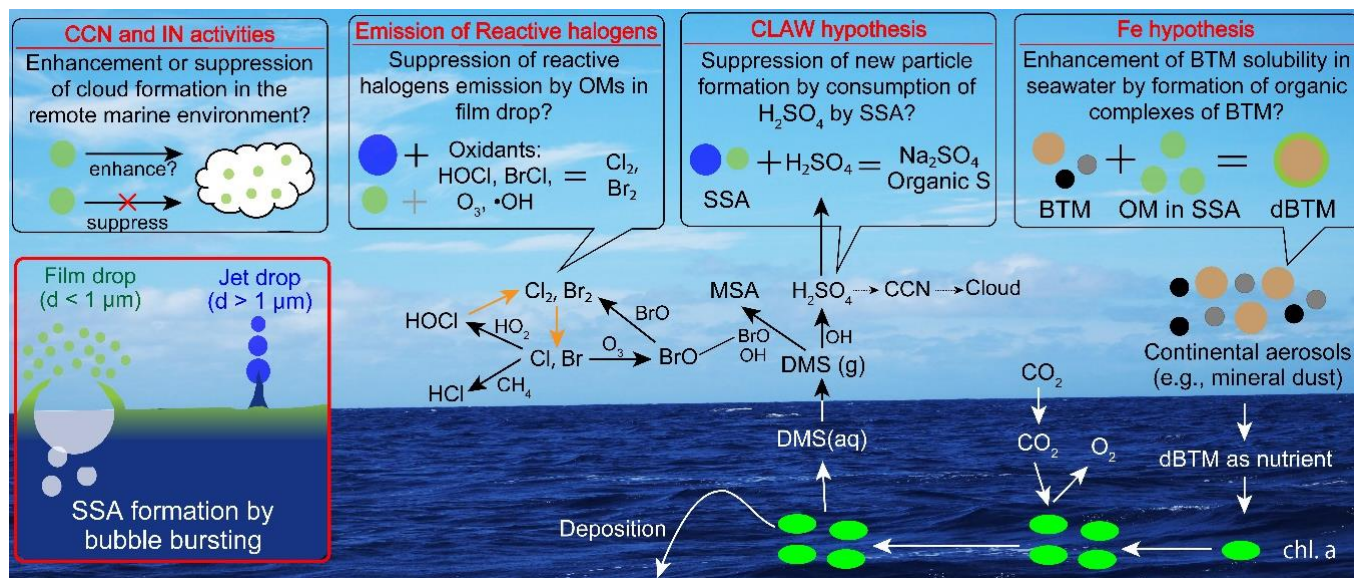


Figure 6: Schematic illustration of atmospheric chemistry related to sea spray aerosol (SSA). Abbreviations: cloud condensation nuclei (CCN), ice nuclei (IN), iron (Fe), organic matter (OM), dimethylsulfide (DMS), bioactive trace metals (BTM), methane sulfonate (MSA).

ray microscope: STXM) reveals chemical species with morphology in a single particle. However, there are only few cases where XAFS and STXM have been applied to marine aerosol. In our research, comprehensive analyses of chemical species of OMs and metals in size-fractionated marine aerosol collected in the Pacific Ocean were conducted.

We found (i) enhancement of atmospheric Fe solubility by complexation with OC in SSA, (ii) suppression effects of organic films on SSA for reactive halogen emission and oxidation reactions of reduced S including DMS, and (iii) formation of organic sulfates by reaction of organic films on SSA with H_2SO_4 . In addition, we will optimize quantitative methods for water-soluble organic sulfur and semivolatile organic carbon by triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ-MS) and proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS). We believe that these novel data will lead to gaining new perspectives about the biogeochemical cycle and marine climate related to OMs in SSA, which in turn produces further development of air-sea interaction research through refinement of the experimental conditions for laboratory experiments and model calculation.

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Acknowledgements

This study was supported by the JSPS Research Fellowships for Young Scientists and Research Institute for Oceanography Foundation.



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After a master in linguistics, **Liselotte Tinel** discovered her love for science during a master in Environmental Chemistry in Marseille, France, followed by a PhD at the University of Lyon, France. Currently, as post-doc at the University of York, United Kingdom, she continues to work on interfacial reactions at the surface of the ocean.

Investigating ozone deposition at the sea-surface: the interplay of iodide and organics

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Oceans cover more than 70% of the surface of our planet; hence reactions at the sea-surface can have a significant effect on the atmospheric and oceanic chemical composition. The oceans can be a sink or a source for atmospheric gases. For ozone, a greenhouse gas influencing also air quality and human health, dry deposition at the surface of the ocean is an important removal route over the open ocean, and responsible for about a third of total global ozone deposition (Ganzeveld *et al.*, 2009). One of the major loss paths for ozone over the ocean is its reaction with iodide (I^-) at the sea-surface. Iodide is a naturally occurring sea salt and an essential element for many metabolisms, e.g. humans. It's the more reactive form of iodine present at low concentrations (10^{-7} - 10^{-9} M) alongside the more thermodynamically stable iodate (IO_3^-) (Chance *et al.*, 2014). Ozone is very reactive towards iodide ($k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 8, Magi *et al.*, 1997), and leads to the release of inorganic iodine into the atmosphere, mainly as hypoiodous acid (HOI) and iodine (I_2) (Carpenter *et al.*, 2013), where gas phase reactions of these species can lead to further ozone depletion and participate in particle nucleation (Figure 7). Recent

modelling studies have shown that the iodine chemistry decreases the ozone burden in the marine troposphere by approx. 20%, thereby reducing ozone's radiative forcing (Sherwen *et al.*, 2016, 2017). However, the I_2 climatology used in these models is based on rather sparse measurements of iodide concentrations in the surface waters (<20m depth). A part of my work has therefore aimed at improving the global coverage of sea surface iodide concentrations through

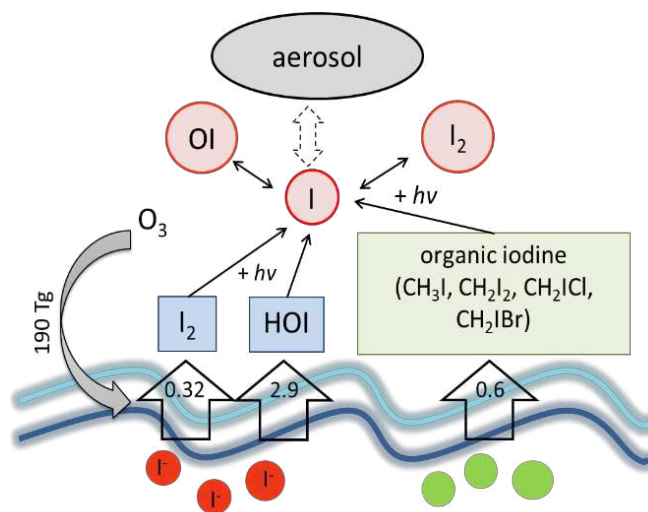


Figure 7: Simplified representation of iodine (I_2) chemistry at the sea-surface, with iodite (OI), ozone (O_3), hypoiodous acid (HOI), I iodide (I^-), $h\nu$ Modelled fluxes from Sherwen *et al.*, 2016 (in $Tg \text{ I yr}^{-1}$).

participation in a research cruise, the Indian Southern Ocean Expedition 9, in 2017 where I^- and IO_3^- concentrations were measured in the under sampled region of the Indian & Southern Ocean (Figure 8). This data combined with simultaneous atmospheric observations of ozone and IO (performed by our project partner Dr. Anoop S. Mahajan, Indian Institute of Tropical Meteorology, India) should provide a better insight in the I_2 chemistry in that region and will be incorporated into a new I_2 climatology for atmospheric and oceanic modelling.

The interaction with dissolved organic carbon (DOC) is another major process believed to contribute to the dry deposition of ozone over the ocean. However, the nature of direct reactions of ozone with DOC at the sea surface is unknown, mainly due to the complexity of the nature of DOC. Emissions driven by the reaction of ozone with DOC at the sea surface are less well characterised, although potentially a significant source of functionalised and/or halogenated organic volatile compounds. By comparison, the reaction of I^- and ozone is relatively well characterised, but uncertainties remain and in particular the influence of natural DOC at the sea-surface on this reaction is not entirely understood. Therefore, a series of laboratory experiments were performed aimed at refining the estimate of the rate constant for the reaction of ozone with I^- at ambient or near ambient concentrations and at evaluating the influence of organics on this reaction. Emission fluxes of I_2 were measured using both organic-free artificial I^- solutions and natural seawater. Inorganic I_2 fluxes were measured using a Broadband Cavity Enhanced Absorption Spectrometer (BBCEAS) and organic halogenated species by Thermo-Desorption Gas Chromatography Mass Spectrometry (TD-GC-MS). The first results from these studies indicate a significant suppression of inorganic I_2 emission in the presence of organics. Using real seawater samples, the fluxes of I_2 were 70-85% lower compared to artificial seawater with similar I^- concentrations and even less I_2 was observed above



Figure 8: Images of the Indian Southern Ocean Expedition in January - March 2017 to sample the Indian and Southern Ocean from Mauritius to Prydz Bay (Antarctica).

samples of the surface microlayer. These results underline the importance of DOC in air-sea gas exchanges. Our observations will be used to refine the I_2 flux model proposed in Carpenter *et al.*, 2013.

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Acknowledgements

I acknowledge the Natural Environment Research Council (NERC) in the UK (grant NE/N009983/1) for funding this research project and the Ministry of Earth Science in India for providing a berth on the SOE9 cruise. Acknowledgments to all partners at IITM, Pune, India & NCPOR, Goa, India for support during the cruise and Dr. Thomas Adams and Dr. Lloyd Hollis from the University of Leicester, UK for the BBCEAS experiments.

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Tiera-Brandy Robinson studied marine biology in Alaska, USA, and then completed a Master of Research degree in Ocean Science at the University of Southampton, United Kingdom. In 2016 she moved to Germany to start a PhD with the University of Oldenburg in Oliver Wurl's sea surface group, investigating the role of transparent extracellular particles (TEP) in the formation and characterisation of the sea surface microlayer.

New depth profiles to understand biochemical parameters in the upper 1m of the ocean

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At the surface of the ocean, with a thickness between 1 μm and 1 mm, lies the sea surface microlayer. This layer is easily distinguished from the underlying water by its unique chemical, biological, and physical properties (Wurl *et al.* 2011) and has a large role to play as the boundary layer between the ocean and atmosphere. We understand this layer to be highly gelatinous, permeated with transparent extracellular particles (TEP) which hold the biological and chemical components together (Wurl *et al.* 2008). At high concentrations these can form biofilms at the sea surface (Wurl *et al.* 2016a) which affect air-sea exchanges and have been hypothesised to reduce gas exchange rates by 15% (Wurl *et al.* 2016b). For this reason, my PhD has three main focuses; 1, the effect of breaking waves and bubble scavenging on the enrichment and transport of TEP in the sea surface microlayer; 2, vertical and horizontal transport of TEP in the ocean; and 3, the relationship between primary production, TEP concentrations, and sea surface microlayer properties. Until now, the standard measuring procedure was to collect samples from the sea surface microlayer and 1 m depth

as a reference. However, here I would like to introduce new techniques we have used to investigate what happens between the sea surface microlayer and 1 m.

We use a catamaran (Figure 9) for *in situ* measurements of the sea surface microlayer and underlying water at 1 m (Ribas-Ribas *et al.* 2017).



Figure 9: Our Catamaran "Sea Surface Scanner" which can collect *in situ* data on the SML and ULW at 1 m and can collect discreet water samples. Featured being deployed in the Baltic Sea. © Oliver Wurl

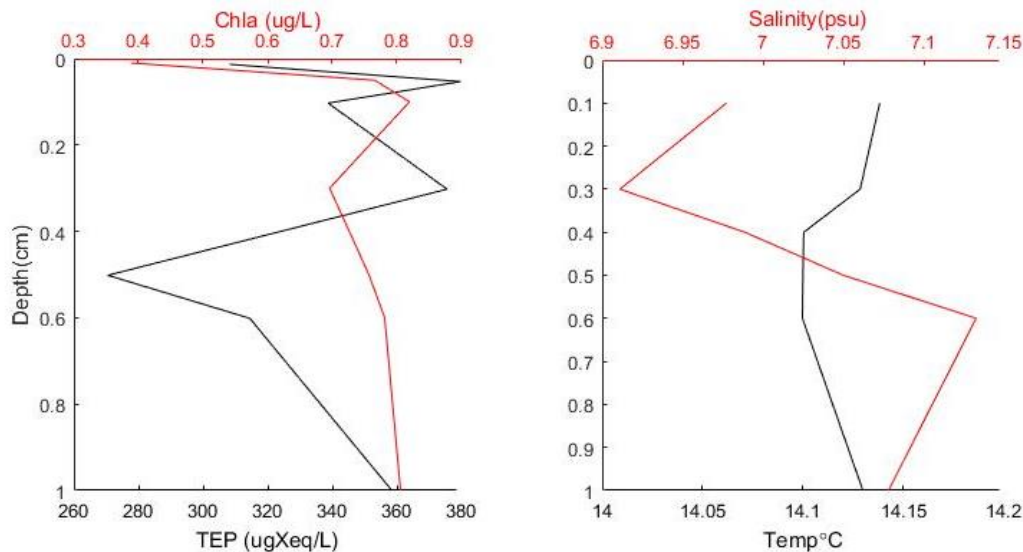


Figure 10: Data from a campaign in the Baltic Sea in July 2018, showing changes with depth of a) transparent extracellular particles (TEP), b) Chlorophyll (Chl) a, c) Temperature (°C), and d) Salinity (psu).

The catamaran uses 6 rotating glass plates to collect the sea surface microlayer and peristaltic pumps to collect underlying water from 1m depth. Recently we have attached multiparameter probes (Aqua TROLL) which measure *in situ* data at 5 depths between the sea surface microlayer and 1 m depth, in order to enhance the resolution of observed changes in the upper 1m. Additionally, we deploy a “vertical water sampler” which uses peristaltic pumps to collect discreet water samples from the same 5 depths as the probes.

Figure 10 shows data from a research cruise in the Baltic Sea in July 2018. There are noticeable changes in both biological and chemical properties within the upper 1m of the water. TEP and Chlorophyll (Chl) a show a negative enrichment with the highest concentrations in the underlying water rather than the sea surface microlayer. This finding is opposite to what is normally found in the ocean. There is a rapid increase for both TEP and Chl a at 5 and 10 cm below the surface, with concentrations increasing from 0.8 to 1.5 $\mu\text{g}/\text{m}^3$ for Chl a and 1400 to 4000 $\mu\text{gXeq}/\text{L}$ (expressed as a standardised Xanthan equivalent in microgram (μg) per litre (L)) for TEP. Meanwhile temperature showed minimal changes of <0.05 °C and salinity rapidly increased >0.2 psu below 30 cm.

Only one station is shown here but multiple sta-

tions showed changes in biological and chemical parameters over both time and depth, while other stations showed minimal changes. Future analysis will be looking at the effect of wind speed on the homogeneity of parameters in the top 1 m. My hypothesis is that with higher wind speeds (>8 m/s) higher mixing will be seen, resulting in homogenous layers and lower wind speed (<8 m/s) will result in less mixed layers and higher influence of physical parameters on biological ones. While negative enrichment is likely a result of sinking TEP/organic matter (OM) aggregates, photodegradation is a possible explanation for the observed rapid increase of TEP and Chl a just below the surface at 5 and 10 cm.

Within the air-sea interaction community, the role of the sea surface microlayer has slowly gained recognition as an important boundary layer, influencing all interactions. This new approach aims to further understand the formation of the sea surface microlayer and the role of biochemical processes not only at the sea surface microlayer and 1 m below but what is happening between, which is proving to be a dynamic environment that can no longer be considered homogenous. This type of high-resolution depth data will improve our understanding of process trends in the surface ocean and can help to explain effects like photodegradation or bubble scavenging on the sea surface microlayer.

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Acknowledgements

I thank the European Research Council for funding this study under the European Union's Framework Program (FP/2007-2013)/ERC Grant Agreement 290852-AIRSEA. The European Union's Horizon 2020 research and innovation programme EUROCHAMP-2020 and MARSU.

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