

Report for the year 2018 and future activities

SOLAS France
compiled by: Rémi Losno



This report has two parts:

- **Part 1:** reporting of activities in the period of January 2018 – Jan-Feb 2019
- **Part 2:** reporting on planned activities for 2019/2020 and 2021.

The information provided will be used for reporting, fundraising, networking, strategic development and updating of the live web-based implementation plan. As much as possible, please indicate the specific SOLAS 2015-2025 Science Plan Themes addressed by each activity or specify an overlap between Themes or Cross-Cutting Themes.

- 1 Greenhouse gases and the oceans;
 - 2 Air-sea interfaces and fluxes of mass and energy;
 - 3 Atmospheric deposition and ocean biogeochemistry;
 - 4 Interconnections between aerosols, clouds, and marine ecosystems;
 - 5 Ocean biogeochemical control on atmospheric chemistry;
- Integrated studies;
 Environmental impacts of geoengineering;
 Science and society.

IMPORTANT: *This report should reflect the efforts of the SOLAS community in the entire country you are representing (all universities, institutes, lab, units, groups, cities).*

PART 1 - Activities from January 2018 to Jan/Feb 2019

1. Scientific highlight

Biogeochemical response of the Mediterranean Sea to the transient SRES–A2 climate change scenario (Camille Richon, Jean-Claude Dutay, François Dulac), Richon et al. 2019 paper.

The Mediterranean region is a climate change hotspot. Increasing greenhouse gas emissions are projected to lead to a substantial warming of the Mediterranean Sea as well as major changes in its circulation, but the subsequent effects of such changes on marine biogeochemistry are poorly understood. Here, our aim is to investigate how climate change will affect nutrient concentrations and biological productivity in the Mediterranean Sea. To do so, we perform transient simulations with the coupled high-resolution model NEMOMED8-PISCES using the high-emission IPCC Special Report on Emissions Scenarios (SRES) A2 socio-economic scenario and corresponding Atlantic, Black Sea, and riverine nutrient inputs. Our results indicate that nitrate is accumulating in the Mediterranean Sea over the 21st century, while phosphorus shows no tendency. These contrasting changes result from an unbalanced nitrogen-to-phosphorus input from riverine discharge and fluxes via the Strait of Gibraltar, which lead to an expansion of phosphorus-limited regions across the Mediterranean. In addition, phytoplankton net primary productivity is reduced by 10 % in the 2090s in comparison to the present state, with reductions of up to 50 % in some

regions such as the Aegean Sea as a result of nutrient limitation and vertical stratification. We also perform sensitivity tests to separately study the effects of climate and bio-geochemical input changes on the future state of the Mediterranean Sea. Our results show that changes in nutrient supply from the Strait of Gibraltar and from rivers and circulation changes linked to climate change may have antagonistic or synergistic effects on nutrient concentrations and surface primary productivity. In some regions such as the Adriatic Sea, half of the biogeochemical changes simulated during the 21st century are linked with external changes in nutrient input, while the other half are linked to climate change. This study is the first to simulate future transient climate change effects on Mediterranean Sea biogeochemistry but calls for further work to characterize effects from atmospheric deposition and to assess the various sources of uncertainty.

This article simulates for the first time the response of the Mediterranean biogeochemistry to a transient severe (SRES-A2) climate change scenario. This study shows that the effects of changing biogeochemical forcings (river discharge and nutrient exchanges through the Strait of Gibraltar) may have important effects on the future biogeochemistry of the Mediterranean Sea. Moreover, the study shows that the nutrient limitations in the surface Mediterranean may change by the end of the 21st century as a result of climate and biogeochemical changes. These changes in limiting nutrient may modify the sensitivity of the surface Mediterranean to aerosol deposition (See figure 1).

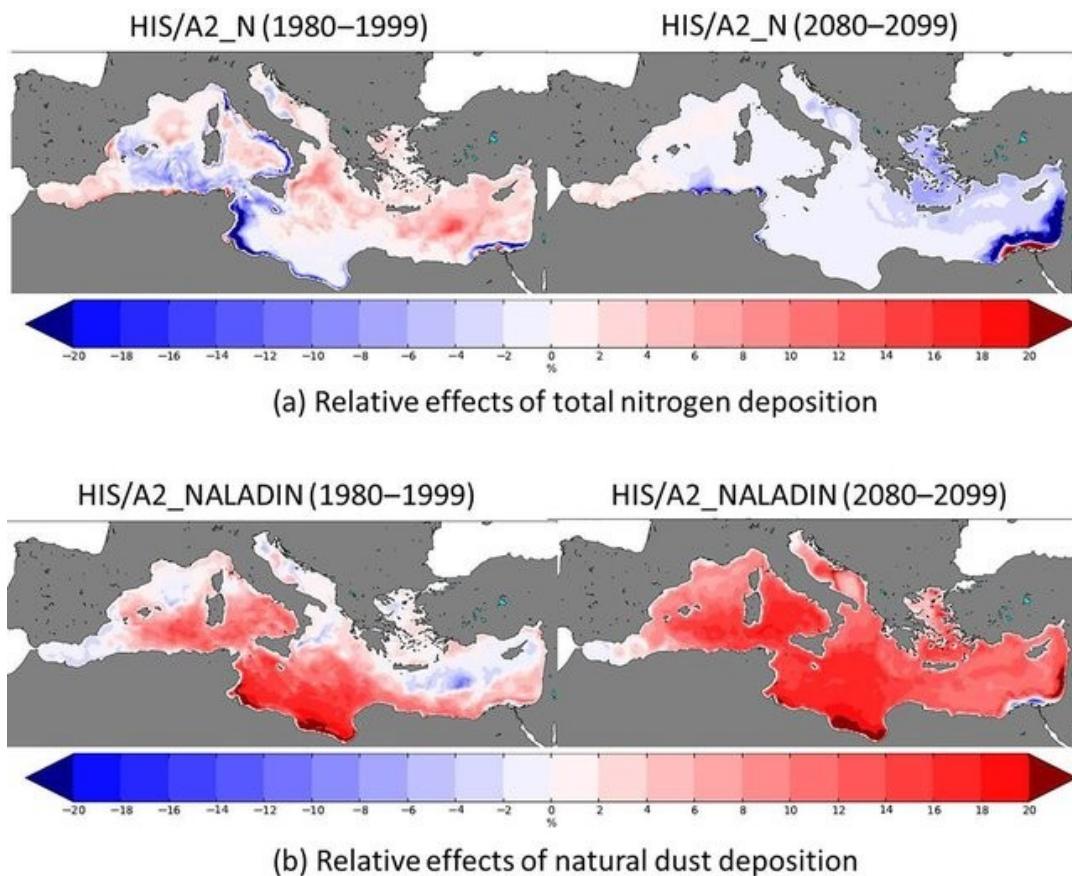


Figure 1: Present (1980-1999, left) and future (2080-2099, right) relative effects (in %) of atmospheric deposition of total nitrogen (top) and of both total nitrogen and of P from desert dust (bottom), on surface (0-10 m) total primary production.

As a result of the SRES-A2 climate change scenario and associated changes in riverine and Gibraltar nutrient discharge, the surface Mediterranean may become almost entirely P-limited by the end of the 21st century. As a consequence, nitrogen atmospheric deposition from anthropogenic and natural sources will have little effect on the sea surface primary productivity whereas natural dust deposition, bringing phosphate to the surface Mediterranean, may relieve the surface P-limitation and increase primary productivity in the entire basin.

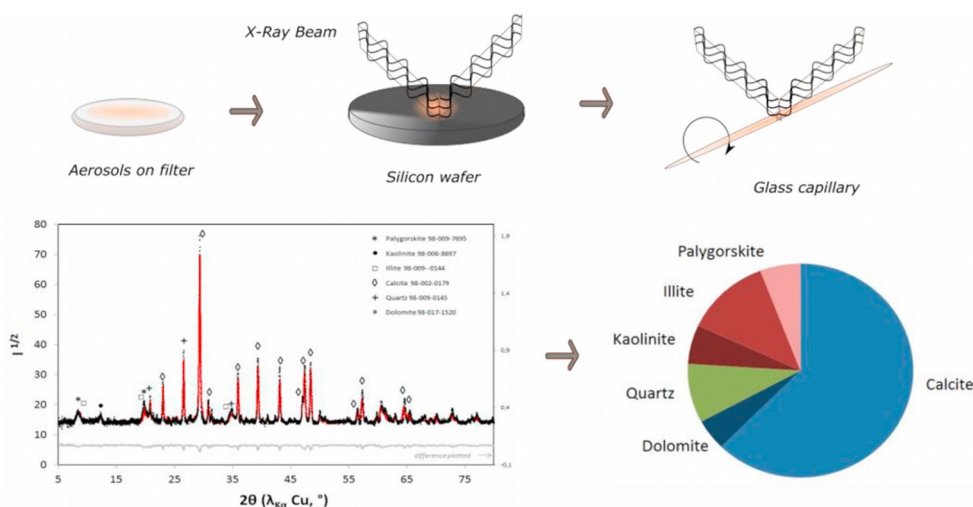
This is the first study simulating transient climate change scenarios in the Mediterranean basin. Multiple scenarios should be used for climate change, nutrient discharges and atmospheric

deposition in order to evaluate the response of the Mediterranean biogeochemistry to different scenarios.

Reference: Richon, C., Dutay, J.-C., Bopp, L., Le Vu, B., Orr, J. C., Somot, S., and Dulac, F.: Biogeochemical response of the Mediterranean Sea to the transient SRES-A2 climate change scenario, *Biogeosciences*, 16, 135-165, doi:10.5194/bg-16-135-2019, 2019.

Quantitative study of the mineralogical composition of mineral dust aerosols by X-ray diffraction (Sophie Nowak)

A new procedure to quantify the mineralogical composition of dust aerosol samples is presented. X-Ray Diffraction measurements are performed on randomly oriented particles samples are combined with a Rietveld refinement. Applied to reference minerals, this procedure has proved to provide results both repeatable and similar to theoretical values. Crystalline phases of low mass mineral aerosol samples, including clays, are quantified with an unprecedented accuracy. This will improve in the future our knowledge of dust deposition on the ocean.



Reference: Nowak, S., Lafon, S., Caquineau, S., Journet, E., Laurent, B.: Quantitative study of the mineralogical composition of mineral dust aerosols by X-ray diffraction, *Talanta*, 186, 133-139, 2018.

2. Activities/main accomplishments in 2018 (projects, field campaigns, events, model and data intercomparisons, capacity building, international collaborations, contributions to int. assessments such as IPCC, interactions with policy makers or socio-economics circles, social sciences, and media).

AMOP PROGAM I: (Aurelien Paulmier, Veronique Garçon)

Oxygen availability drives changes in microbial diversity and biogeochemical cycling between the aerobic surface layer and the anaerobic core in nitrite-rich anoxic marine zones (AMZs), which constitute huge oxygen-depleted regions in the tropical oceans. The current paradigm is that primary production and nitrification within the oxic surface layer fuel anaerobic processes in the anoxic core of AMZs, where 30–50% of global marine nitrogen loss takes place. Here we demonstrate that oxygenic photosynthesis in the secondary chlorophyll maximum (SCM) releases significant amounts of O_2 to the otherwise anoxic environment. The SCM, commonly found within AMZs, was dominated by the picocyanobacteria *Prochlorococcus* spp. Free O_2 levels in this layer were, however, undetectable by conventional techniques, reflecting a tight coupling between O_2 production and consumption by aerobic processes under apparent anoxic conditions. Transcriptomic analysis of the microbial community in the seemingly anoxic SCM revealed the enhanced expression of genes for aerobic processes, such as nitrite oxidation. The rates of gross

O₂ production and carbon fixation in the SCM were found to be similar to those reported for nitrite oxidation, as well as for anaerobic dissimilatory nitrate reduction and sulfate reduction, suggesting a significant effect of local oxygenic photosynthesis on Pacific AMZ biogeochemical cycling.

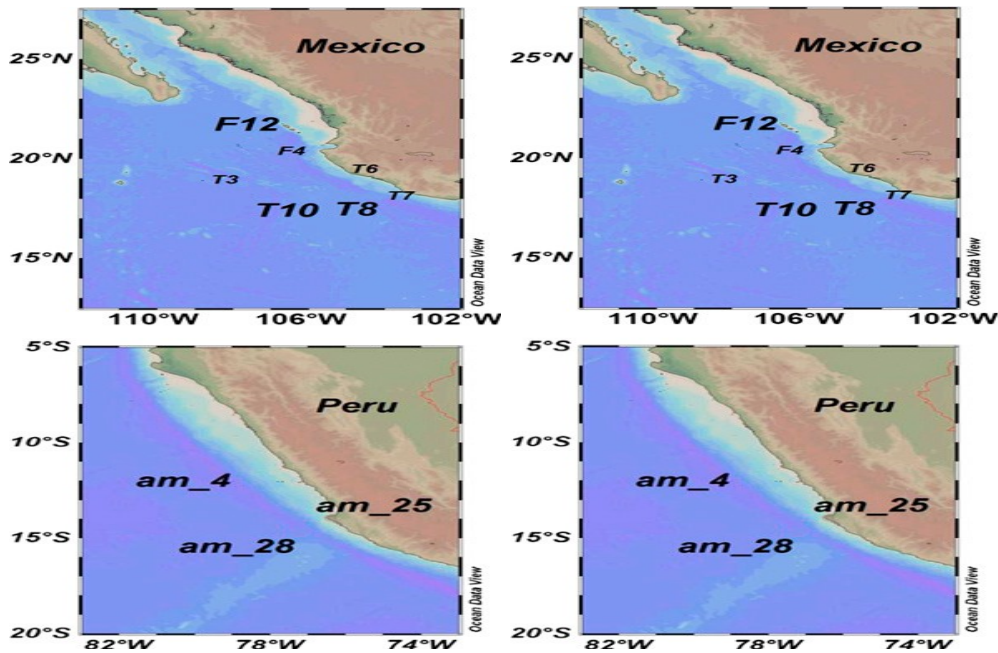


Figure 2: Representative station maps with Chlorophyllous Secondary Maximum (SCM) during the AMOP cruise off Peru (RV L'Atalante) and OMZoMBiE2 off Mexico (RV New Horizon) in 2014. from Garcia-Robledo et al. (2017).

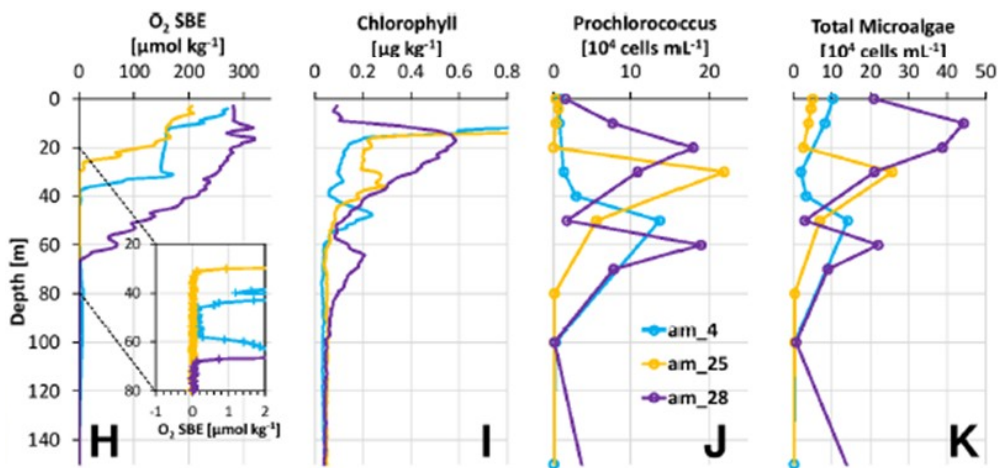


Figure 3: Profiles of the main characteristics in the upper part of OMZ (nanomolar O₂, H, chlorophyll concentration, I, Prochlorococcus, J. abundance, and total microalgae (Prochlorococcus, Synechococcus and pico-eukaryotes by cytometry of flux), K) for three representative stations off Peru (see Fig. 1). From Garcia-Robledo et al. (2017).

References: Garcia-Robledo, E., Padilla, C.C., Aldunate, M., Stewart, F.J., Ulloa, O., Paulmier, A., Gregori, G., and N.P. Revbesch, **Cryptic oxygen cycling in anoxic marine zones**. 2017, Proceedings of the National Academy of Sciences of the United of America (PNAS). www.pnas.org/cgi/doi/10.1073/pnas.1619844114.

AMOP PROJGRAM II: (Aurelien Paulmier, Marine Bretagnon, Veronique Garçon)

The fate of the organic matter (OM) produced by marine life controls the major biogeochemical cycles of the Earth's system. The OM produced through photosynthesis is either preserved, exported towards sediments or degraded through remineralisation in the water column. The productive eastern boundary upwelling systems (EBUSs) associated with oxygen minimum zones (OMZs) would be expected to foster OM preservation due to low O_2 conditions. But their intense and diverse microbial activity should enhance OM degradation. To investigate this contradiction, sediment traps were deployed near the oxycline and in the OMZ core on an instrumented moored line off Peru. Data provided high-temporal-resolution O_2 series characterising two seasonal steady states at the upper trap: suboxic ($[O_2] < 25 \mu\text{mol kg}^{-1}$) and hypoxic-oxic ($15 < [O_2] < 160 \mu\text{mol kg}^{-1}$) in austral summer and winter-spring, respectively. The OMZ vertical transfer efficiency of particulate organic carbon (POC) between traps (T_{eff}) can be classified into three main ranges (high, intermediate, low). These different T_{eff} ranges suggest that both predominant preservation (high $T_{\text{eff}} > 50\%$) and remineralisation (intermediate $T_{\text{eff}} 20 < 50\%$ or low $T_{\text{eff}} < 6\%$) configurations can occur. An efficient OMZ vertical transfer ($T_{\text{eff}} > 50\%$) has been reported in summer and winter associated with extreme limitation in O_2 concentrations or OM quantity for OM degradation. However, higher levels of O_2 or OM, or less refractory OM, at the oxycline, even in a co-limitation context, can decrease the OMZ transfer efficiency to below 50%. This is especially true in summer during intraseasonal wind-driven oxygenation events. In late winter and early spring, high oxygenation conditions together with high fluxes of sinking particles trigger a shutdown of the OMZ transfer ($T_{\text{eff}} < 6\%$). Transfer efficiency of chemical elements composing the majority of the flux (nitrogen, phosphorus, silica, calcium carbonate) follows the same trend as for carbon, with the lowest transfer level being in late winter and early spring. Regarding particulate isotopes, vertical transfer of $\delta^{15}\text{N}$ suggests a complex pattern of ^{15}N impoverishment or enrichment according to T_{eff} modulation. This sensitivity of OM to O_2 fluctuations and particle concentration calls for further investigation into OM and O_2 -driven remineralisation processes. This should include consideration of the intermittent behaviour of OMZ towards OM demonstrated in past studies and climate projections.

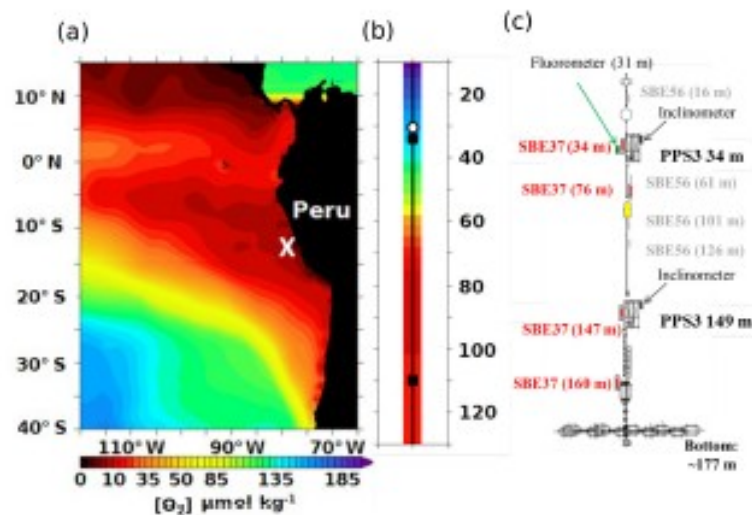


Figure 4: Study area, OMZ O_2 conditions and design of the mooring. (a) Map of the eastern South Pacific oxygen minimum zone (in red with $[O_2]$ minimal $< 20 \mu\text{mol/kg}$ from WOA2013 climatology). This map includes the location of the AMOP mooring (white cross, $77.40^\circ\text{W} - 12.02^\circ\text{S}$) off Peru. (b) Vertical distribution of the oxygen concentration at the mooring location (from WOA2013 climatology with the two sediment trap locations in the black square). (c) Design of the fixed mooring line including two sediment traps, PPS3 with two inclinometers at 34m near the oxycline and at 149m in the OMZ core, as well as five sensors of pressure, temperature, salinity and oxygen (SBE37-ODO63) at 34, 76, 147 and 160m, a fluorometer at 31 m, and complementary temperature sensors (SBE56).

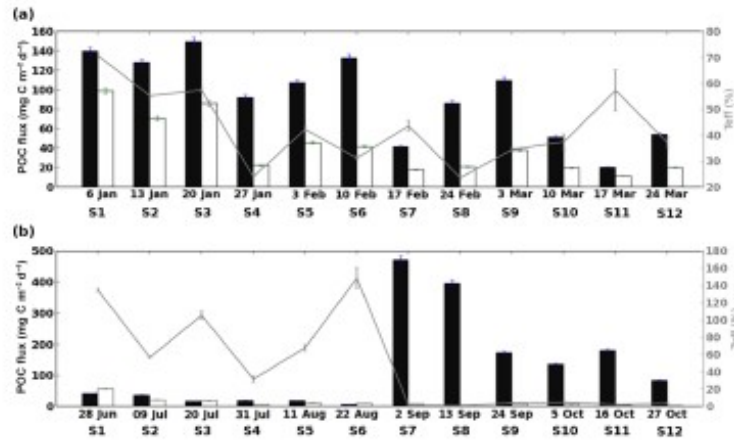


Figure 2: Time series in 2013 for POC flux (left-hand scale) at 34m (black bar) and 149m (white bar) and the corresponding transfer efficiency (T_{eff} ; from Eq. (1), grey line, right-hand scale), covering the AMOP summer (denoted AMOP1) (a) and AMOP winter–spring (denoted AMOP2) (b) periods. Error bars correspond to the accuracy of analytical determination for the POC flux, which is estimated through a logarithmic expansion of Eq. (1) for T_{eff} .

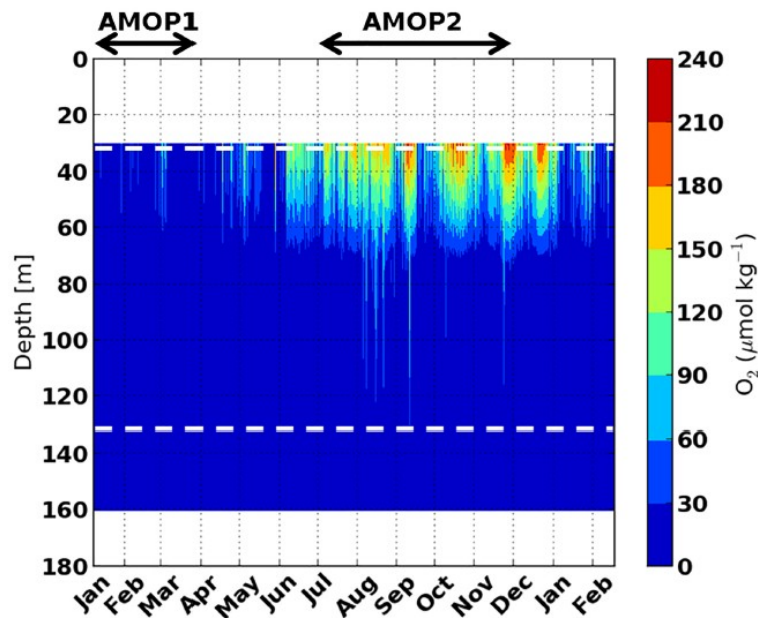


Figure 3: Time series in 2013 of the oxygen concentration ($\mu\text{mol}/\text{kg}$) covering the AMOP summer (denoted AMOP1) and AMOP winter–spring (denoted AMOP2) periods, acquired on the mooring location line through oxygen sensors at 34, 76, 147 and 160 m of depth with a 15 min acquisition frequency and vertically interpolated. The dashed horizontal white lines indicate the depth of the traps.

See: Bretagnon, M., Paulmier, A., Garçon, V., Dewitte, B., Illig, S., Leblond, N., Coppola, L., Campos, F., Velazco, F., Panagiotopoulos, C., Oschlies, A., Hernandez-Ayon, J.M., Vergara, O., Montes, I., Martinez, P., Carrasco, E., Grelet, J., Depretz de Gesincourt, O., Maes, C., and L. Scouarnec. Modulation of the vertical particle transfer efficiency in the Oxygen Minimum Zone off Peru. *Biogeoscience* 15, 5093-5111. <https://doi.org/10.5194/bg-15-5093-2018>

A MESOCOSM EXPERIMENT FOR THE STUDY OF BIOLOGICAL INFLUENCES ON ATMOSPHERIC PARTICLE EMISSIONS IN NEW ZEALAND COASTAL WATERS (karine sellegri),

In the frame of the Sea2Cloud and CARIM projects, an original set-up of mesocosms enclosing an air-sea interface was used from November 1st to November 22nd 2018 to relate marine emissions to the biogeochemical properties of coastal seawater. Emission processes were investigated in an

unperturbed control system, and under future conditions in which temperature and pH were manipulated to projected values for years 2100 and 2150. Two aerosol emissions processes were considered.

1-Secondary aerosol formation via nucleation of marine gas-phase precursors: At the global scale, a large fraction of the aerosol number concentration is formed by nucleation of low-volatility gas-phase compounds, a process that is expected to ultimately determine the concentrations of Cloud Condensation Nuclei (CCN). Nucleation occurrence over the open ocean is still debated, due to scarce observational data sets and instrumental limitations. In the CARIM mesocosm headspace, the number concentration of particles produced in the nanometer scale was monitored as a function of time, simultaneously with the biogeochemical composition of the seawater. Nanoparticle formation was observed to occur, showing the potential of marine gas-phase emissions to experience oxidation processes that lead to low-volatility compounds within the 30 minutes residence time in the mesocosm headspace. Relationships to seawater biology is under study.

2-Sea spray generation: Marine aerosol can also be emitted to the atmosphere as primary particles via the process of bubble bursting, which is dependant on the seawater physico-chemical properties. Even though the primary aerosol number emission fluxes are well defined for organic-free seawaters, the impact of the presence of organic compounds is still unclear. Sea Spray aerosol was artificially generated continuously from a bubble chamber containing the mesocosm seawater each day of the experiment. The sea spray was characterized for its size distribution, chemical composition, cloud droplet forming abilities (CCN), and ice crystal forming abilities (IN). The primary aerosol number fluxes were found to increase by a factor of 4 during the course of the experiments, with an apparent link to the eukaryotic nanoplankton population, possibly indicating an influence of the seawater microorganisms on the physical process of bubble bursting.

RESEARCH ACTIVITIES CONCERNING THE ATMOSPHERIC IODINE CHEMISTRY (Florent Louis, Sarah Khanniche, Dorra Khiri, Sonia Taamalli, Laurent Cantrel).

Gas-phase chemistry of iodine containing species is complex and studying its reactivity is challenging. Marine iodine is known to react with hydroxyl (OH) and hydroperoxyl (HO₂) radicals to form iodine oxides (I_xO_y) [1,2], thus affecting the HO₂/OH ratio in the atmosphere. Small iodine oxides include iodine monoxide and dioxides (IO and OIO) and their hydrated counterparts, hypoiodous and iodous acids (HOI, HOIO). Bigger iodine oxides have been detected in the atmosphere that include I₂O₂, I₂O₃, I₂O₄, and diiodine pentoxide (I₂O₅). Iodic acid HIO₃, whose most stable conformer is HOIO₂, was identified as one of the product of the IO + HO₂ reaction and has been shown to also be formed by the simple addition of OH to OIO. Moreover, HIO₃ corresponds to the hydrated form of I₂O₅. Very recently, Sipilä *et al.* [3] reported evidence of iodine oxide particle formation through addition of iodic acid followed by restructuring to I₂O₅; high HIO₃ concentrations were observed at Mace Head (Ireland) with a gas phase peak concentration greater than 10⁸ molecules cm⁻³. Very little is known about the gas-phase reactivity of iodic (HOIO₂) and iodous (HOIO) acids towards OH radicals. In 2017, we performed high-level ab initio calculations to determine their reaction mechanisms. The overall reactions are significantly dominated by the H-abstraction pathway at tropospheric temperatures (Figure 4).

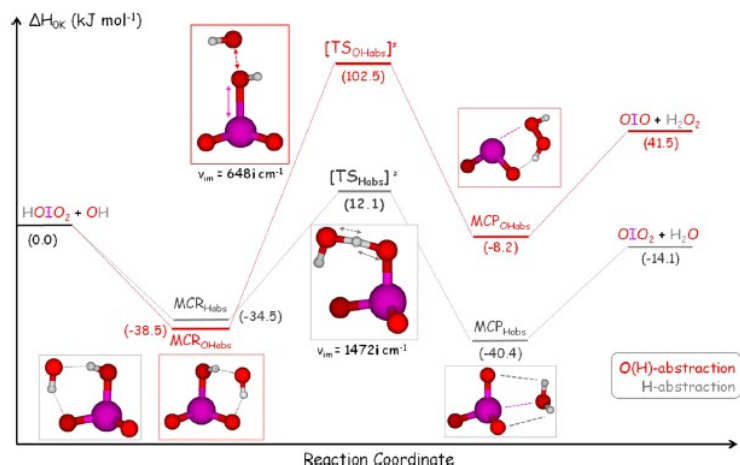


Figure 4. Reaction profiles at 0 K of the HOIO₂ + OH reaction [5].

The main outcomes of this work are as follows: (i) the lifetime of iodic acid toward its removal by OH radicals is extremely long by comparison to the one of iodous acid enabling its transportation to different locations around the Earth (marine, polar, and continental), as confirmed by recent field measurements; other possible loss pathways under clear sky (gas phase) and cloudy (aqueous phase) conditions could reduce its atmospheric lifetime. We are studying several topics:

1) reactivity of chlorine atoms with iodinated acids: Chlorine gas is recognized to be an efficient ozone destroyer in the stratosphere. Its efficiency strongly depends on the chlorine partitioning between its active forms (Cl, ClO) and inactive reservoir species (e.g. HCl). Because of their possible implications in the destruction of the stratospheric ozone layer, chlorine oxides have drawn the attention of atmospheric chemists. For instance the reaction of HOIO, HOOI with Cl led to the formation of HCl, HOCl, ClO, HOI, IO and OIO species. Despite the importance of iodous acid (HOIO) in atmospheric chemistry, computational studies on HOIO species are scarce and it is only very recently that experimental evidence of iodous acid in the gas phase has been reported in the literature [3]. The main objective of this work to provide reliable kinetic and thermodynamic data for the gas phase reaction of iodous acid isomers (HOIO and HOOI) with chlorine atoms.

2) reactivity of iodomethanol with hydroxyl radicals: Iodomethanol is one of the atmospheric degradation product of CH₃I, which is viewed as the dominant species with the highest mixing ratio [4]. The atmospheric fate of CH₂IOH has not yet been characterized in the literature either from experimental or theoretical studies. The main objective of this work to provide reliable kinetic and thermodynamic data for its gas phase reaction with the major photooxidant OH using high-level ab initio studies. This work will be extended to larger iodoalcohols such as 2-iodoethanol for which experiments will be performed at the LCE laboratory (Université Aix-Marseille, France).

3) Microhydration processes of halogenated compounds: We are studying the thermodynamics of the microhydrates of iodine nitrogen oxides (INOx). Monohydrates and dihydrates are investigated for five different INOx species (INO, INO₂, cis-IONO, trans-IONO, and IONO₂).

References

- [1] J.C. Gómez Martin, O. Galvez, M.T. Baeza-Romero, T. Ingham, J.M.C. Plane, M.A. Blitz, On the mechanism of iodine oxide particle formation, *Phys. Chem. Chem. Phys.*, 15 (2013) 15612-15622.
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- [3] M. Sipilä, N. Sarnela, T. Jokinen, H. Henschel, H. Junninen, J. Kontkanen, S. Richters, J. Kangasluoma, A. Franchin, O. Peräkylä, M.P. Rissanen, M. Ehn, H. Vehkamäki, T. Kurten, T. Berndt, T. Petäjä, D. Worsnop, D. Ceburnis, V.-M. Kerminen, M. Kulmala, C. O'Dowd, Molecular-scale evidence of aerosol particle formation via sequential addition of HIO₃, *Nature*, 537 (2016) 532-534.

[4] A. Saiz-Lopez A, J.M.C. Plane, A.R. Baker, L.J. Carpenter, R. von Glasow, J.C. Gómez Martín, G. McFiggans, R.W. Saunders, Atmospheric Chemistry of Iodine, Chem. Rev. 112 (2012) 1773-1804.

Acknowledgements

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DATABASES SETUP: (Catherine Schmechtig)

PEACETIME campaign:

http://www.obs-vlfr.fr/proof/php/PEACETIME/x_datalist_1.php?xxop=peacetime&xxcamp=peacetime

see also: <http://www.obs-vlfr.fr/proof/php/PEACETIME/peacetime.php> for PEACETIME

Oceanic concentrations and emissions toward atmosphere of carbon monoxide simulated by the PISCES biogeochemical model, <https://doi.org/10.17882/59311>)

http://www.obs-vlfr.fr/proof/php/PISCES_CO/pisces_co.php

For details: Conte Ludivine, Szopa Sophie, Séférian Roland, Bopp Laurent (2019). The oceanic cycle of carbon monoxide and its emissions to the atmosphere. Biogeosciences, 16(4), 881-902. <https://doi.org/10.5194/bg-16-881-2019>

3. Top 5 publications in 2018 (only PUBLISHED articles) and if any, weblinks to models, datasets, products, etc.

Bretagnon M., Paulmier A., GRichon, C., Dutay, J.-C., Bopp, L., Le Vu, B., Orr, J. C., Somot, S., and Dulac, F.: Biogeochemical response of the Mediterranean Sea to the transient SRES-A2 climate change scenario, Biogeosciences, 16, 135-165, doi:10.5194/bg-16-135-2019, 2019.

Garçon V., Dewitte B., Illig S., Leblond N., Coppola L., Campos F., Velazco F., Panagiotopoulos C., Oschlies A., Hernandez Ayon J., Maske H., Vergara O., Montes I., Martinez P., Carrasco E., Grelet J., Desprez Degesincourt O., Maes C., Scouarnec L., (2018). Modulation of the vertical particle transfer efficiency in the oxygen minimum zone off Peru. Biogeosciences, 15, 5093-5111, 10.5194/bg-15-5093-2018.

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Richon, C., Dutay, J.-C., Bopp, L., Le Vu, B., Orr, J. C., Somot, S., and Dulac, F.: Biogeochemical response of the Mediterranean Sea to the transient SRES-A2 climate change scenario, Biogeosciences, 16, 135-165, doi:10.5194/bg-16-135-2019, 2019.

C. Fortin, S. Khann[1] Nowak, S., Lafon, S., Caquineau, S., Journet, E., Laurent, B.: Quantitative study of the mineralogical composition of mineral dust aerosols by X-ray diffraction,

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S. Khanniche, D. Khiri, V. Fèvre-Nollet, P. Lebègue, F. Cousin, I. Cernusak, F. Louis, Reactivity of Hydrogen Peroxide with Br and I Atoms, *J. Phys. Chem. A*, 122 (2018) 1053-1063.

D. Khiri, I. Cernusak, F. Louis, A Theoretical Study of the Reactions of H Atoms with CH_3I and CH_2I_2 , *J. Phys. Chem. A*, 122 (2018) 6546-6557.

4. Did you engage any stakeholders/societal partners/external research users in order to co-produce knowledge in 2018? If yes, who? How did you engage?

PART 2 - Planned activities for 2019/2020 and 2021

1. Planned major field studies and collaborative laboratory and modelling studies, national and international (incl. all information possible, dates, locations, teams, work, etc.).

FUTURE AMOP: Following AMOP project, a second study is planned in the largest OMZ of the world, off Mexico, with an intercomparison project to revisit the paradigms of formation, maintaining, variability and functioning of the OMZs.

See also the French SOLAS National Report 2017

2. Events like conferences, workshops, meetings, schools, capacity building etc. (incl. all information possible).

3. Funded national and international projects / activities underway.

See also the French SOLAS National Report 2017

4. Plans / ideas for future projects, programmes, proposals national or international etc. (please indicate the funding agencies and potential submission dates).

See also the French SOLAS National Report 2017

5. Engagements with other international projects, organisations, programmes etc.

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Comments