

### Report for the year 2016 and future activities

**SOLAS** France

compiled by: R. Losno

This report has two parts:

- Part 1: reporting of activities in the period of January 2016 – Jan-Feb 2017

- Part 2: reporting on planned activities for 2017/2018 and 2019.

#### PART 1 - Activities from January 2016 to Jan/Feb 2017

#### 1. Scientific highlight

#### VAHINE project special issue

A special issue on the project VAHINE (VAriability of vertical and tropHIc transfer of diazotroph derived N in the south wEst Pacific) conducted by Sophie Bonnet is released (http://www.biogeosciences.net/special\_issue193.html). In the ocean, the availability of N is one of the most influential factors controlling primary productivity. Biological N2 fixation, i.e., the reduction of atmospheric N<sub>2</sub> gas to biologically available ammonium (NH<sub>4</sub><sup>+</sup>), constitutes the major source of new N for the surface ocean (140 ± 50Tg N yr<sup>-1</sup>), significantly larger than riverine and atmospheric inputs. By maintaining a pool of bioavailable N, this process sustains oceanic productivity over broad timescales and space scales. However, a critical question that has been poorly studied is the transfer and fate of diazotroph-derived N (DDN) in the pelagic food webs. The actual flux of DDN that supports the growth of different groups of autotrophic and/or heterotrophic plankton and can be transferred up the trophic chain, remineralized and/or exported from the euphotic zone is unknown. To answer these questions, a triplicate mesocosm (55 000L) experiment was conducted in the southwest Pacific (New Caledonia; 22°29.073 S, 166°26.905 E) in January-February 2013 within the framework of the ANR-INSU-IRD-GOPS-funded VAHINE project. This study, which involved 25 scientists from 7 institutes, yielded a comprehensive data set on community-level responses to a diazotroph bloom and its impact on community changes, biogeochemical cycles and export.





*Figure 1:* Drawing representing the main features of the mesocosms (left) and Right View of the experiment from the side and the seafloor: during (a–c) and after the deployment (d). Panels (e, f): collection of sediment traps by the scuba divers (photos: J. M. Boré and E. Folcher, IRD).

From: Bonnet, S., Moutin, T., Rodier, M., Grisoni, J.-M., Louis, F., Folcher, E., Bourgeois, B., Boré, J.-M., and Renaud, A.: Introduction to the project VAHINE: VAriability of vertical and tropHIc transfer of diazotroph derived N in the south wEst Pacific, Biogeosciences, 13, 2803-2814, doi:10.5194/bg-13-2803-2016, 2016.

2. Activities/main accomplishments in 2016 (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, etc.)

### Nitrogen and Phosphorous Atmospheric deposition and its biogeochemical impact in the Mediterranean basin (MERMEX-CHARMEX, Camille Richon, François Dulac):

Atmospheric deposition represents a significant source of nutrients at the Mediterranean basin scale. We apply natural anthropogenic nitrogen deposition fields simulated with the global model LMDz-INCA and the natural desert dust deposition simulated with the regional model ALADIN-Climat as additional nutrient sources to the high resolution oceanic biogeochemical model NEMOMED12/PISCE. Time series of modeled deposition fluxes are compared to available measurements. This comparison with measurements shows that both variability and intensity ranges are realistic enough for our main purpose of estimating the atmospheric deposition impact on Mediterranean biogeochemical tracers such as surface nutrient concentrations, chlorophyll a and plankton concentrations. Our results show that atmospheric deposition is one of the major sources of nitrogen and phosphorus for some regions of the oligotrophic Mediterranean Sea. More than 18 10<sup>9</sup>gN month<sup>-1</sup> are deposited to the whole Mediterranean Sea. This deposition is responsible for an average increase of 30 to 50 % in primary production over vast regions.

Natural dust-derived deposition of phosphorus is sparser in space and time (0.5 10<sup>9</sup>g month<sup>-1</sup> on average over the entire basin). However, dust deposition events can significantly affect biological production. We calculate fertilizing effects of phosphate from dust to be low on average (6 to 10 %) but up to 30% increase in primary productivity can be observed during the months when surface water stratification occurs. Finally, these fertilizing effects are shown to be transmitted along the biological chain (primary production, Chl a, phytoplankton, zooplankton, grazing, see Figure 2).



**Figure 2:** Relative influence (%) of atmospheric deposition on biological tracers for the summer season (JJA)

## Variability of mineral dust deposition in the western Mediterranean basin and south-east of France (DEMO project, G. Bergametti and B. Laurent, funded by ADEME and INSU, MISTRALS - ChArMEx).

To investigate dust deposition dynamics at the regional scale, five automatic deposition collectors named CARAGA (Collecteur Automatique de Retombées Atmosphériques insolubles à Grande Autonomie in French, see Laurent et al., 2015 for more details) have been deployed in the western Mediterranean region during 1 to 3 years depending on the station. The sites include, from south to north, Lampedusa, Majorca, Corsica, Frioul and Le Casset (southern French Alps) (Figure 3). Deposition measurements are performed on a common weekly period at the five sites (Vincent et al., 2016). The mean dust deposition fluxes are higher close to the northern African coasts and decrease following a south–north gradient, with values from 7.4 gm<sup>-2</sup>.year<sup>-1</sup> in Lampedusa (35°31' N, 12°37' E) to 1 gm<sup>-2</sup>.year<sup>-1</sup> in Le Casset (44°59' N, 6°28' E). The maximum deposition flux recorded is of 3.2 gm<sup>-2</sup>.wk<sup>-1</sup> in Majorca with only two other events showing more than 1 gm<sup>-2</sup>.wk<sup>-1</sup> in Lampedusa, and a maximum of 0.5 gm<sup>-2</sup>.wk<sup>-1</sup> in Corsica. The maximum value of 2.1 gm<sup>-2</sup>.year<sup>-1</sup> observed in Corsica in 2013 is much lower than existing records in the area over the 3 previous decades (11–14 gm<sup>-2</sup>.year<sup>-1</sup>). From the 537 available samples, 98 major Saharan dust deposition

events have been identified in the records between 2011 and 2013. Vincent et al. (2016) used complementary observations provided by both satellite and air mass trajectories to identify the dust provenance areas and the transport pathways from the Sahara to the stations for the studied period. Despite the large size of African dust plumes detected by satellites, more than 80% of the major dust deposition events are recorded at only one station, suggesting that the dust provenance, transport and deposition processes (i.e. wet vs. dry) of dust are different and specific for the different deposition sites in the Mediterranean studied area (Vincent et al., 2016). The results tend to indicate that wet deposition is the main form of deposition (in the sense that no precipitation was detected at the surface) is far from being negligible, and contributes 10 to 46% to the major dust deposition events, depending on the sampling site.



*Figure 3:* Location of the CARAGA samplers constituting the deposition network deployed in the western Mediterranean basin and southern of France.

### The GEOVIDE project / link with the SOLAS project: Quantification of trace element atmospheric deposition fluxes (Shelley et al., 2017)

Atmospheric deposition is an important input route of trace elements (TEs) to the global ocean. As atmospheric inputs impact phytoplankton community health and dynamics, atmospheric TE fluxes, and in particular atmospheric iron fluxes, are a key component of marine biogeochemical models. Trace element concentrations were determined in dry (aerosols) and wet (precipitation) deposition samples from the North Atlantic, north of 40°N, during the GEOVIDE cruise (GEOTRACES cruise GA01) in May/June 2014. Atmospheric aerosol loading in the study region was low (~ 2-500 ng m <sup>3</sup>) throughout the cruise, as inferred from the very low aerosol Ti concentrations determined (0.0084–1.9 ng.m<sup>-3</sup>). Wet deposition appeared to be of roughly equal or greater importance than dry deposition to the total depositional flux of TEs, which is consistent with other regions of the Atlantic Ocean outside of the influence of the Saharan plume. It can be challenging to convert aerosol chemical composition data into reliable flux estimates, due to the uncertainties associated with the parameterisation of dry deposition velocity, and precipitation rate. Therefore, the goal of this study was to compare TE flux estimates derived from two different techniques: (1) the traditional approach of summed wet and dry deposition TE fluxes, using concentration data, precipitation rates, and dry deposition velocities and, (2) using the inventory of the cosmogenic radioisotope beryllium-7 (<sup>7</sup>Be) in the upper ocean as a proxy for atmospheric deposition. These two approaches yielded TE flux estimates that were in excellent agreement (within one standard deviation) for about half of the TEs under investigation. However, for the remaining TEs differences between the flux estimates ranged from two to forty times, with the traditional approach generally



#### Dust from Patagonia (DFP) project (R. Losno):

Zihan Qu defended his PhD on the dust emission from Patagonia and South Africa. After three years of continuous weekly based aerosol sampling for chemical analyses, we have replaced in may at Rio Gallegos (Argentina) aerosol sampling with an optical particle counter operating at one hour frequency. During 2016, we have observed a very low background of about 1µg.m<sup>-3</sup> of atmospheric aerosol with frequent and short pulses up to 50µg.m<sup>-3</sup> (Figure 5). These pulses occur during dry periods when fine particles present in the soil are no longer sicked by humidity. A seasonality is observed with higher emission in summer time.



*Figure 5:* example of particle emission pulses in measured in Southern PatagoniaMajor peaks are related to the air dryness and temperature, telling that dust emission in Southern Patagonia is strongly dependent on the soil wetness conditions.

#### PARCS and MACA mesocosm projects (Karine Sellegri):

The joint PARCS (WP3) and IPEV MACA project mesocosm experiment is underway in Svalbard during the first 2 weeks of March 2017. Coordinated by Karine Sellegri (LaMP) and Barbara d'Anna (IRCELYON), 3 mesocosms have been set up in a habour. Doses of pollutants (sulphate, ammonium and nitrate) are being added to examine effects on marine biology and primary/secondary aerosol emissions.



Figure 6: Picture of mesocosms installation

#### SAM Project (K. Sellegri):

Abstract Earth, as a whole, can be considered as a living organism emitting gases and particles into its atmosphere, in order to regulate its own temperature. In particular, oceans may respond to climate change by emitting particles that ultimately will influence cloud coverage. At the global scale, a large fraction of the aerosol number concentration is formed by nucleation of gas-phase species, but this process has never been directly observed above oceans. Using semicontrolled seawater-air enclosures, we show evidence that nucleation may occur from marine biological

emissions in the atmosphere of the open ocean. We identify iodine-containing species as major precursors for new particle clusters' formation, while questioning the role of the commonly accepted dimethyl sulfide oxidation products, in forming new particle clusters in the region investigated and within a time scale on the order of an hour. We further show that amines would sustain the new particle formation process by growing the new clusters to larger sizes. Our results suggest that iodine-containing species and amines are correlated to different biological tracers. These observations, if generalized, would call for a substantial change of modeling approaches of the seato-air interactions.

#### AMOP (PI: A. Paulmier, co-PIs: B. Dewitte, C. Maes and V. Garçon):

AMOP is a trans-disciplinary project based on a cruise, a fixed mooring, and modeling activities, associated with an effort of experimental development (instrumentation, sensors). It is aimed at better understanding the Oxygen Minimum Zones (OMZs) and the ocean deoxygenation, with a focus on the OMZ off Peru (Figure 7). It gathers a consortium of scientists from Peruvian and French institutions (IMARPE, IGP, UNAC; LEGOS, MIO, OOV, MARBEC, LATMOS, LEMAR, LPO, OOB, EPOC, LOCEAN, ISTO, US IMAGO, DT INSU) and benefit from a collaboration Germany (SFB754 «Climate-biogeochemistry Interactions in the Tropical Ocean») and other countries: Mexico (CICESE; UABC); Denmark (University of Aahrus); Spain (IEO, CO-Malaga); Chile (CEAZA); USA (UCLA). It is in the line with international programs (Integrated topics of SOLAS Science Plan 2015-2025) and regional networks (LMIs DISCOH and PALEOTRACES 2).

#### Work in progress

- Final O<sub>2</sub> CTD calibration with Winkler data and on the STOX-zero adjustment for cruise and mooring data: under progress (contribution: Jacques Grelet, Carole Saout / GLAZEO, Emilio Garcia-Robledo, Aurélien Paulmier);

- Ocean Science Meeting: New Orleans (USA) on February 21-26th, 2016, including an AMOP side meeting.

- Two full days AMOP workshop: at the MIO (Marseille, FRANCE) on October 12-13th, 2016, for discussions and organization of the preliminary scientific results and for the definition of the different tasks in 2017.





BIOAMAZON (IRD-FAPEMA, Brésil), EU F7 CARBOCHANGE (N. Lefevre):

The Amazon is a CO<sub>2</sub> source for the atmosphere with fugacities (fCO<sub>2</sub>) in the river about 10 times stronger than the surface fCO<sub>2</sub> values in the tropical Atlantic. When Amazonian water mixes with the ocean, its turbidity decreases and it brings nutrient salts to the poor waters of the ocean. A significant biological activity develops itself and photosynthesis leads to high concentrations of chlorophyll in the surface ocean, detectable by satellite, with CO<sub>2</sub> consumption. The oceanic values of fCO<sub>2</sub> then become significantly lower than the atmospheric fCO<sub>2</sub> value, which creates a CO<sub>2</sub> sink. The ship MN Colibri, a ship traveling between France and Guyana (Kourou) for space programs, is equipped with an autonomous system for measuring fCO<sub>2</sub> in the ocean and the atmosphere since 2006. From 30 trips Of the MN Colibri (2006-2013), the air-sea flow of CO<sub>2</sub> in the Amazon flood (Figure 8 **a-j**, negative values in blue). The current climate of CO<sub>2</sub> does not reproduce the Amazon plume (Figure 8, **k-1**, **m-n**, positive values in green-yellow). The CO<sub>2</sub> flux of the tropical Atlantic recalculated by taking into account the Amazon plume shows that current estimates overestimate the balance of about 10% (Ibánhez et al., 2015, 2016).



**Figure 8:** *a-j* Distribution of  $fCO_2$  (in µatm) in the Amazon plume (salinity <35) from 2010 to 2014 for May (Amazon rainfall) and August (retroflection of the North Brazil current). *k-I.* Distribution of climatological  $fCO_2$  Takahashi et al. (2009) with reference year 2000. *m-n*. Distribution of  $fCO_2$  from the climatology of Landschützer et al. (2014).

### Atmospheric Iodine Chemistry, part of MiRE project, ANR (F. Louis, <u>florent.louis@univ-lille1.fr</u>, et al.):

Marine iodine is known to react with hydroxyl (OH) and hydroperoxyl (HO<sub>2</sub>) radicals to form iodine oxides ( $I_xO_y$ ), thus affecting the HO<sub>2</sub>/OH ratio in the atmosphere (Figure 9). 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  $I_2O_2$ ,  $I_2O_3$ ,  $I_2O_4$ , and diiodine pentoxide ( $I_2O_5$ ). Iodic acid HIO<sub>3</sub>, whose most stable conformer is HOIO<sub>2</sub>, was identified as one of the product of the IO + HO<sub>2</sub> reaction and has been shown to also

be formed by the simple addition of OH to OIO. Moreover,  $HIO_3$  corresponds to the hydrated form of I2O5. Very recently (Sipilä et al.) reported evidence of iodine oxide particle formation through addition of iodic acid followed by restructuration to  $I_2O_5$ ; high  $HIO_3$  concentrations were observed at Mace Head (Ireland) with a gas phase peak concentration greater than 108 molecules cm<sup>-3</sup>.



Figure 9: Gas-phase iodine chemistry leading to the formation of I<sub>x</sub>O<sub>y</sub> species

Very little is known about the gas phase properties of iodic acid. In 2016, we performed high-level ab initio calculations to characterize the microhydration processes of iodic acid containing one and two water molecules (Khannische et al., 2016a). The relevance of such investigations is underlined by the high solubility of HIO<sub>3</sub> species, which will dissolve in water and form aqueous solutions of iodate ( $IO_3^-$ ). Mono- and di-hydration of iodic acid are favored processes at tropospheric and ambient conditions with the formation of molecular clusters HOIO<sub>2</sub>\_1wa and HOIO<sub>2</sub>\_2wa (Figure 10) at T below 310 K.



Figure 10: Optimized structures of HOIO2 with one and two water molecules

lodine pentoxide and HIO<sub>3</sub> correspond to the anhydride and hydrated forms, respectively and are key species of iodine (V) oxides. However, to date the kinetics of the reaction involving  $I_2O_5$  and iodic acid are not explicitly considered in the atmospheric model. To overcome this, high level quantum chemistry tools were used to determine the thermokinetic parameters governing the conversion of  $I_2O_5$  to iodic acid in gas phase upon exposition to water (Khannische et al., 2016b). It can be concluded that at atmospheric conditions, the homogeneous gas phase reaction of hydration of  $I_2O_5$  into HIO<sub>3</sub> is too slow with respect to the nucleation process that leads to the formation of  $I_2O_5$  particles.

This work was part of the MiRE Project (Mitigation of Outside Releases in Case of Nuclear Accident), which is funded by the French National Research Agency (ANR) through the Programme d'Investissement d'Avenir (PIA) under Contract "ANR-11-RSNR-0013-01". The authors also appreciate the support from PIA managed by the ANR under Grant Agreement "ANR-11-LABX-0005-01" called Chemical and Physical Properties of the Atmosphere (CaPPA) and also the support by the Regional Council "Nord-Pas-de-Calais" and the "European Funds for Regional Economic Development".

BISOU : Bioavailability and solubility of iron present in mineral dusts and volcanic ashes (2016-2018).PI: E. Journet (<u>emilie.journet@lisa.u-pec.fr</u>).

The oceanic biological C pump is driven by the efficiency of phytoplanktonic photosynthesis, which depends on nutrient availability. The research focuses on Fe, a limiting nutrient in vast areas of the surface ocean. Deposition of mineral dust and volcanic ash can supply Fe to these regions. The potential of dust and ash to alleviate Fe limitation in the ocean is usually assessed in terms of Fe solubility and its various mineralogical and atmospheric controls. However, Fe solubility measurements do not necessarily reflect Fe bioavailability. Here, we propose to link, for the first time, Fe solubility determinations with Fe bioavailability assessments. The mineralogy and water-soluble Fe fraction of ash and dust will be measured, and their effect via dry and wet deposition processes on starved phytoplankton cultures will be considered (Figure 11). The project will shed light on factors that dictate the short- and long-term impact of dust and ash deposition on the oceanic biological pump.



Figure 11: Evolution of cell physiology (quantum photosynthetic efficiency Fv / Fm) of iron starved Dunaliella tertiolecta after addition of "pur" minerals (square plot) of volcanic ash (triangle plot) and desert dust (rhombus plot). (Ammar et al., First results presented at EGU 2017 conferences)

Water isotopes: a tracer of ocean-atmosphere-ice water fluxes (LOCEAN; G. Reverdin, G. Aloisi; Univ. of Iceland Reykjavik, M. Benetti)

In the past year, we have put together an archive of atmospheric boundary layer and surface data in the Atlantic Ocean relevant for water fluxes, including water isotopes in the atmospheric boundary layer (Benetti et al., 2016). We have also compiled our surface observations in sea water over the Atlantic Ocean and western Mediterranean to better understand how air-sea water fluxes (evaporation, precipitation, but also inflow from continents and ice) imprint the surface ocean isotopic properties (Reverdin et al., 2017). In particular, this emphasizes the humidity of the air as a key factor in evaporative flux properties, as well as the special properties of near-equatorial rainfall under the ITCZ.

During the **WAPITI cruise** (P.I. J.-B. Sallée) continuous measurements of water vapour and surface sea water isotopic properties in the Southern Ocean from the Magellan Channel to the southern Weddell Sea (January-March 2017), over a wide range of weather conditions, including some very dry air flowing from the Antarctic continents. The sea water isotopes in the southern Weddell Sea are strongly imprinted by the formation and/or melt of sea ice, evaporation in contact with the very cold continental air, as well as with exchan

Benetti, M., G. Reverdin, A. Loisi, and A. Sveinbjörnsdottir, (2017). Stable isotopes in surface waters of the Atlantic Ocean: indicators of ocean-atmosphere water fluxes and oceanic mixing processes. J. Geophys. Res. Oceans, doi 10.1002/2017JC012712.

Benetti, M., H.C. Steen-Larsen, G. Reverdin, A.E. Sveibjörnsdottir, G. Aloisi, M.B. Berkelhammer, B. Bourlès, D. Bourras, G. de Coëtlogon, A. Cosgrove, A.-K. Faber, J. Grelet, S.B. Hansen, R. Johnson, H. Legoff, N. Martin, A.J. Peters, T.J. Popp., T. Reynaud, et M. Winthe (2017)r. Stable isotopes in the atmospheric marine boundary layer water vapour over the Atlantic Ocean, 2012-2015. Scientific Data/Nature.. doi:10.1038/sdata.2016.128

Ibánhez, J.S.P., Araujo, M., and Lefèvre, N. (2016). The overlooked tropical oceanic CO2 sink. Geophysical Research Letters 43, doi: 10.1002/2016GL068020.

Khanniche, S., F. Louis, L. Cantrel, I. Cernusak (2016a), A Theoretical Study of the Microhydration of Iodic Acid (HOIO<sub>2</sub>), Comp. Theor. Chem., 1094 98-107.

Khanniche, S., F. Louis, L. Cantrel, I. Cernusak (2016b), Computational study of the  $I_2O_5 + H_2O = 2$  HOIO<sub>2</sub> gas-phase reaction, Chem. Phys. Lett., 662 114-119.

Sellegri, K., et al. (2016), Evidence of atmospheric nanoparticle formation from emissions of marine microorganisms, Geophys. Res. Lett., 43, doi:10.1002/2016GL069389.

Shelley R. U., Roca-Martí M., Castrillejo M., Sanial V., Masqué P., Landing W. M., van Beek P., Planquette H., Sarthou G. Quantification of trace element atmospheric deposition fluxes to the Atlantic Ocean (>40°N; GEOVIDE, GEOTRACES GA01) during spring 2014. Deep Sea Research Part I: Oceanographic Research Papers, 119, 34–49. http://doi.org/10.1016/j.dsr.2016.11.010

Vincent J., Laurent B., Losno R., Bon Nguyen E., Roullet P., Sauvage S., Chevaillier S., Coddeville P., Ouboulmane N., Giorgio di Sarra A., Tovar-Sánchez A., Sferlazzo D., Massanet A., Triquet S., Morales Baquero R., Fornier M., Coursier C., Desboeufs K., Dulac F. and Bergametti G. (2016), Variability of mineral dust deposition in the western Mediterranean basin and south-east of France, *Atmospheric Chemistry and Physics*, 16 (14), 8749-8766. doi:10.5194/acp-16-8749-2016

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ges of water (and melt) of the continental ice shelves (Fichner ice shelf).



**Figure 12:** from Benetti et al. (2017) showing the surface sea water d<sup>18</sup>O distribution as a function of salinity in the tropical and northern Atlantic Ocean. The dashed lines are linear regressions on subsets of the data. They outline different fresh water sources (light blues: from higher latitudes; yellow and red from equatorial South America and equatorial Atlantic). Notice also the smaller slope in the western Mediterranean indicative of the low humidity of the evaporative flux in this region.

3. Top 5 publications in 2016 (only PUBLISHED articles) and if any, weblinks to models, datasets, products, etc.

Benetti, M., G. Reverdin, A. Loisi, and A. Sveinbjörnsdottir, (2017). Stable isotopes in surface waters of the Atlantic Ocean: indicators of ocean-atmosphere water fluxes and oceanic mixing processes. J. Geophys. Res. Oceans, doi 10.1002/2017JC012712.

Benetti, M., H.C. Steen-Larsen, G. Reverdin, A.E. Sveibjörnsdottir, G. Aloisi, M.B. Berkelhammer, B. Bourlès, D. Bourras, G. de Coëtlogon, A. Cosgrove, A.-K. Faber, J. Grelet, S.B. Hansen, R. Johnson, H. Legoff, N. Martin, A.J. Peters, T.J. Popp., T. Reynaud, et M. Winthe (2017)r. Stable isotopes in the atmospheric marine boundary layer water vapour over the Atlantic Ocean, 2012-2015. Scientific Data/Nature.. doi:10.1038/sdata.2016.128

Ibánhez, J.S.P., Araujo, M., and Lefèvre, N. (2016). The overlooked tropical oceanic CO2 sink. Geophysical Research Letters 43, doi: 10.1002/2016GL068020.

Khanniche, S., F. Louis, L. Cantrel, I. Cernusak (2016a), A Theoretical Study of the Microhydration of Iodic Acid (HOIO<sub>2</sub>), Comp. Theor. Chem., 1094 98-107.

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Shelley R. U., Roca-Martí M., Castrillejo M., Sanial V., Masqué P., Landing W. M., van Beek P., Planquette H., Sarthou G. Quantification of trace element atmospheric deposition fluxes to the Atlantic Ocean (>40°N; GEOVIDE, GEOTRACES GA01) during spring 2014. Deep Sea Research Part I: Oceanographic Research Papers, 119, 34–49. http://doi.org/10.1016/j.dsr.2016.11.010

Vincent J., Laurent B., Losno R., Bon Nguyen E., Roullet P., Sauvage S., Chevaillier S., Coddeville P., Ouboulmane N., Giorgio di Sarra A., Tovar-Sánchez A., Sferlazzo D., Massanet A., Triquet S., Morales Baquero R., Fornier M., Coursier C., Desboeufs K., Dulac F. and Bergametti G. (2016), Variability of mineral dust deposition in the western Mediterranean basin and south-east of France, *Atmospheric Chemistry and Physics*, 16 (14), 8749-8766. doi:10.5194/acp-16-8749-2016

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4. Did you engage any stakeholders/societal partners/external research users in order to coproduce knowledge in 2016? If yes, who? How did you engage?

#### PART 2 - Planned activities from 2017/2018 and 2019

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

Exploitation of the OUTPACE campaign (Oligotrophy to UlTra-oligotrophy PACific Experiment): Special issue in Biogeosciences.

The OUTPACE oceanic cruise was undertake between February 18 and April 3, 2015 in the Pacific Ocean on board the R/V L'Atalante.

The overall goal of OUTPACE (Oligotrophy to UITra-oligotrophy PACific Experiment) was to obtain a successful representation of the interactions between planktonic organisms and the cycle of biogenic elements in the western tropical South Pacific Ocean across trophic and  $N_2$  fixation gradients. Within the context of climate change, it is necessary to better quantify the ability of the oligotrophic ocean to sequester carbon through biological processes. OUTPACE was organized around three main objectives which were: (1) To perform a zonal characterization of the biogeochemistry and biological diversity of the western tropical South Pacific during austral summer conditions, (2) To study the production and fate of organic matter (including carbon export) on three contrasting trophic regimes (increasing oligotrophy) with a particular emphasis on the role of dinitrogen fixation, and (3) to obtain a representation of the main biogeochemical fluxes and dynamics of the planktonic trophic network. (Extract from the abstract of Moutin, T., Doglioli, A., De Verneil, A., and Bonnet, S.: The Oligotrophy to the UITra-oligotrophy PACific Experiment (OUTPACE cruise, Feb. 18 to Apr. 3, 2015), Biogeosciences Discuss., doi:10.5194/bg-2017-50, in review, 2017)



Figure 13: The OUTPACE web site picture

International Conference on Atmospheric Chemical and Biological Processes: Interactions and Impacts (ATMOCHEMBIO), 19-21 June 2017, in Clermont-Ferrand (https://atmochembio.sciencesconf.org/)

Scientific committee: Dr. Pierre AMATO, ICCF, France, Dr. Marcello BRIGANTE, ICCF, France, Dr Laurent DEGUILLAUME, LaMP, France, Dr. Anne-Marie DELORT, ICCF, France, Dr. Janine FROHLICH, Max Planck Institute for Chemistry, Germany, Dr. Christian GEORGE, IRCELYON, France, Pr. Frank KEPPLER, Germany, Dr. Gilles MAILHOT, ICCF, France, Dr. Cindy E. MORRIS, Plant Pathology Research Unit, France, Dr. Géraldine SARTHOU, LEMAR, France, Dr. Virginie VINATIER, ICCF, France, Pr. Davide VIONE, Turin, Italy

## The Cryosphere and Atmospheric Chemistry (CATCH, Jennie Thomas, jennie.thomas@latmos.ipsl.fr):

This is an emerging IGAC activity on Chemistry, Biology and Physics in Cold Regions cosponsored by SOLAS. French SOLAS researchers are involved.

The CATCH mission is to facilitate atmospheric chemistry research within the international community, with a focus on natural processes specific to cold regions of the Earth. Cold regions include areas which are seasonally or permanently covered by snow and ice, from the high mountains to the polar ice sheets and sea ice zones as well as regions where ice clouds that undergo chemistry are found.

CATCH scientists will aim to understand and predict:

- How aerosols are formed and processed in cold regions;
- How cold region aerosols act as and impact cloud properties;
- Feedbacks between climate change and atmospheric chemistry that are determined by changes in the cryosphere;
- How the ice core record can be used to understand global environmental change;
- How physical, chemical, biological, and ecological changes in sea ice and snow impact atmospheric chemistry;
- How microbiology adapts and impacts biogeochemical cycling of elements in ecosystems of cold environments; and
- Establish background composition (trace gases and aerosols) in cold regions that are undergoing industrialization as well as impacted by climate change.

### PEACETIME (ProcEss studies at the Air-sEa Interface after dust deposition in the MEditerranean sea) G. Guieu and K. Desboeufs.

PEAcEtIME proposes to study the fundamental physical, chemical and biological processes and their interactions at this key interface in the MS. Our objective is to assess how these mechanisms impact, and will impact, the functioning of the marine biogeochemical cycles, the pelagic ecosystem and the feedback to the atmosphere. This 4-year project proposes in particular to focus on a crucial mechanism forcing the biogeochemical coupling between the ocean and the atmosphere: atmospheric Saharan dust deposits. The strategy is designed to ensure that the knowledge acquired is used to understand that forcing across the MS today and in the future.

PEAcEtIME strategy is two-fold: (1) a cruise in the central MS in May when strong dust deposition events usually occur and (2) substantial atmospheric and oceanic modeling developments (from 0D to 3-D). PEAcEtIME is structured around 5 scientific tasks (plus a coordination Task 0 and an outreach Task 6) and associated strategies: 3 tasks address the main fundamental processes put into action by atmospheric deposition that will be studied mainly during the PEAcEtIME cruise, i.e. impact of atmospheric deposition on (Task 1) marine nutrient budget, (Task 2) biogeochemical processes in today and future climate conditions, and (Task 3) radiative budget. Task 4 will be dedicated to track a Saharan dust deposition event during the cruise. Task 5 will enhance our understanding of dust deposition forcing on marine biogeochemical cycles, the functioning of the pelagic ecosystem and the feedback to the atmosphere, taking benefit from atmospheric modeling and from the data acquired during the cruise to improve coupled dynamical/biogeochemical model. Finally, all proposed activities, during the cruise and in the laboratories in France and abroad, will nourish an important effort in outreach and communication (Task 6). During the cruise, in addition to the work performed at stations, continuous sampling will be operated along the whole transect (~2000 miles) to follow intensively a group of relevant parameters in very contrasted areas, from the European coasts to North off Africa. The strategy is completed by original on-board perturbation experiments (by the mean of minicosms).

The project is supported by a large consortium consisting of leading French institutions as well as several international collaborators with expertise on the topic. Sea going scientists as well as land based observations and modelers are involved. The synergy and expertise in the complementary disciplines along with the main responsibilities of the groups involved is made explicit in the table below. In total, PEAcEtIME associates ~80 people (of which 39 will embark the cruise + 1 film maker) from 14 research laboratories in France and 12 research laboratories abroad (6 embarking people, funding support by MISTRALS: MERMEX and CHARMEX joint project).



Figure 14: Cruise track of the campaign to be held in May 2017 on R/V Pourquoi Pas ?

The PEACETIME cruise is departing from La Seyne (France). Onboard the French oceanographic research vessel "Pourquoi Pas ?", a team of 40 scientists will study the impact of atmospheric deposition on the ocean during 33 days. (Twitter: @peacetimecruise, Website : http://peacetime-project.org/). An international and multidisciplinary scientific team will travel the central and western Mediterranean in search of atmospheric deposition of Saharan dust. Their aim is to study processes at the interface between the atmosphere and the ocean in this region of the world where atmospheric input plays a key role as a nutrient source for the marine biosphere. This campaign will allow to better understand how atmospheric deposition affects the functioning of the pelagic ecosystem in order to more accurately predict the future of biodiversity in the Mediterranean.

On board, the scientific team will combine in situ observations in the atmosphere and ocean with process studies in the water column. This will allow to characterize the chemical, biological and

physical properties of the atmosphere, the marine surface micro-layer, and the deeper layers of the Mediterranean. In order to optimize the chances of observing a deposition of Saharan dust in situ during the cruise, the cruise track is in a zone where the probability of this type of event is greatest. In the event of such an occurrence, the vessel will be diverted from its original transect to the identified deposit area. Another specific features of this campaign is to embark "climatic reactors" that are devices reproducing on a small scale the air-sea exchanges under current and future environmental conditions (acidification and increase of the temperature of the sea water).

This coordinated multidisciplinary effort will better characterize the impact of atmospheric deposition in the ocean and their feedback to the atmosphere in a nutrient-poor system such as the Mediterranean Sea. PEACETIME is a GEOTRACES Process-study (GApr09) and received support from SOLAS and IMBER.

**Surface water isotopes and air-sea exchanges around Anrtarctica (G. Reverdin)**: At the beginning of 2017, surface water isotopic composition was measured on different cruises around Antarctica (in particular, ACE) and in the Weddell Sea (WAPITI), as well as atmospheric measurements to document air-sea exchanges of water isotopes (through evaporation/precipitation) and to separate this contribution from inputs from the continent and ice shelves in the ocean heat and freshwater budget. One objective is to clarify the mechanisms of formation of shelf water and deep Weddell Sea water.

#### The BIOCAP project / link with the SOLAS project:

1- A potential source of Fe binding organic ligands to the surface ocean from wet deposition. This abstract will be presented at the ATMOCHEMBIO meeting (19-June 2017, Clermont-Ferrand)

M. Cheize, A.C. Baudoux, E. Bucciarelli, A. Tagliabue, K. Desboeufs, A.R. Baker, G. Sarthou

Iron (Fe) is an essential micronutrient for all marine organisms. More than 99% of Fe (III) is bound to natural organic ligands in seawater. One of the main inputs of iron to the surface open ocean is dry and wet aerosol deposition. We measured for the first time Fe organic speciation by voltammetry (CLE-ACSV) in seven rainwater samples collected over the Eastern Tropical North Atlantic Ocean during the AMT 19 Cruise (2009). The potential involvement of bioaerosols on Fe organic speciation in wet deposition was also investigated. In these rainwaters, concentrations of total dissolvable Fe (unfiltered) ranged from 25 nM to 635 nM, while concentrations of Fe organic ligands varied between 40 and 1100 nM. Conditional stability constants were characteristic of strong Fe-binding ligands (~10<sup>22</sup> M<sup>-1</sup>). The highest Fe and organic ligand concentrations were associated with the highest aluminium and silicon concentrations from a Saharan dust wet deposition event. Genomic approach revealed the presence of bacteria and yeast in the rainwater events. Their capacity to produce siderophores was tested, highlighting their ability to produce strong Fe specific organic ligands in different environmental conditions including in salty, nutrient rich and depleted media. This suggests that bioaerosols may be a source of Fe organic ligands to the open ocean that has not been considered yet. Preliminary global modeling experiments will also be discussed in terms of potential atmospheric input of Fe organic ligands to the surface of the ocean.

# 2- Iron Organic Complexation In Cloud Water Samples From The Puy De Dôme Station (France). This abstract will be presented at the ATMOCHEMBIO meeting (19-June 2017, Clermont-Ferrand)

J. Boutorh, G. Sarthou, A.G. Gonzalez, M. Cheize, H. Planquette, E. Bucciarelli, Mickaël Vaïtilingom, Laurent Deguillaume, Virginie Vinatier, Anne-Marie Delort, G. Mailhot

Iron (Fe) is a key nutrient for all microorganisms, being involved in many metabolic processes [1]. Recent studies evidenced the impact of organic ligands on Fe speciation and solubility in aerosol rainwater, and cloudwater samples (e.g. [2-5]). It was also demonstrated that Fe complexation with organic ligands increases the photochemical efficiency (OH radical formation) and the Fe stabilization ([6,7]). However, so far, the exact nature, role and sources of Fe binding ligands in the atmosphere are still largely unknown. One hypothesis is that the production of Fe-specific organic ligands by atmospheric bacteria could play a key role on the Fe organic speciation. To test this hypothesis, we first adapted to cloudwater samples a competitive ligand exchange-adsorptive cathodic stripping voltammetry method (CLE-ACSV) recently developed for rainwater samples ([3]). The method was validated with artificial matrices containing model Fe ligands (pyoverdin, oxalate, and ethylenediamine-N,N'-disuccinic acid - EDDS), at three different pH (6.00, 5.65, and 5.37). Although the sensitivity was sufficiently high for the three pH values, the detection limits were much

higher for the two lowest pH values (~ 0.3 nM) compared to the one at pH 6 (0.05 nM). We then analysed six natural cloudwater samples collected at the Puy de Dôme station (France) at pH 6. Total Fe concentrations measured by SF-ICP-MS varied between 40 and 226 nM. Results clearly evidenced the presence of Fe-binding ligands in excess to the total Fe concentration in two of the cloudwater samples. The excess Fe-binding ligand concentrations ranged from 80 to 100 nM. Our results showed, for the first time, that Fe present in cloudwater could be bound to organic ligands, with conditional stability constants close to the pyoverdin, a siderophore excreted by bacteria. These results are consistent with the potential production of siderophores by cloud microorganisms ([5]). Iron complexation by siderophores could have a significant impact on the cloud chemistry and its oxidant capacity ([8]), as well as on the global Fe biogeochemical cycle.

#### References

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[6] Huang W. et al., J. Photochem. Photobiol. A, 2012, 239, 17-23

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

Ocean Acidification Workshop, organized in Dakar, Senegal, Februry 2017, co-sponsored by SOLAS, Future Earth Coast, OA-ICC, IRD, etc..

SOLAS-France meeting, July 5<sup>th</sup> 2017, IPGP, Paris.

SOLAS-Summer School at Cargèse (France, Corsica) in preparation planned July 23th to August 3th, 2018, including french SOLAS scientists (Cécile Guieu, Aurelien Paulmier, Véronique Garçon) in the organization and scientific committees.

3. Funded national and international projects / activities underway (if possible please list in order of importance and indicate to which part(s) of the SOLAS 2015-2025 Science Plan and Organisation (downloadable from the SOLAS website) the activity topics relate – including the core themes and the cross cutting ones)

Sorry, this is not an extensive list

ANR-BIOCAP (2013-2017, ANR13BS060004)

ANR-GEOVIDE (2014-2018, ANR13BS060014)

PRIMEQUAL-ADEME (contract no. 0962C0067)

MISTRALS (Mediterranean Integrated Studies at Local and Regional Scales) programme as part of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx) and Marine Ecosystem Response Mediterranean Experiment (MERMEX)

4. Plans / ideas for future projects, programmes, proposals national or international etc. (please precise to which funding agencies and a timing for submission is any)

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

#### Comments