

# **Biogeochemistry of dissolved organic matter in the Pacific Ocean (BioDOMPO)**

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## **Abstract**

Dissolved organic matter (DOM) is a major component of the carbon flux under the euphotic layer, supports the respiration of heterotrophic bacteria and determines the speciation, reactivity and transport of micro-nutritive metal elements (e.g. Fe, Cu, Co) essential for phytoplankton development in the ocean. However, its great physical (size) - chemical (reactivity) heterogeneity is a barrier to its characterization, so it is often studied globally (dissolved organic carbon, DOC) or through specific properties (absorption, UV, fluorescence). During this thesis we propose to study the biogeochemistry, speciation and reactivity of DOM on a large scale in the Pacific Ocean. This study will be based on the analysis of seawater samples collected along a section stretching from Alaska to Tahiti as part of an international collaboration (GEOTRACES US-GP15). During this study, DOM will be studied in a global, semi-specific and specific way in order to characterize the sources and sinks of the different fractions composing DOM. The analyses will be carried out using chromatographic, electrochemical, fluorimetric and mass spectrometric techniques. The results will make it possible to study for the first time in detail the reactivity size continuum, the involvement of DOM in the nitrogen cycle and to define if DOM is a large-scale CO<sub>2</sub> source or well. During this doctoral thesis, particular attention will be paid to the interactions between DOM and metallic trace elements. This thesis project is one of the first to propose to study trace elements and organic matter as a single whole in which the processes governing the DOM cycle cannot be separated from the reactivity of trace elements. In this sense, collaborations will be initiated with scientists involved in the study of the trace element cycle and their physico-chemical speciation in order to relate the dataset acquired in this thesis to the distributions of essential bio trace elements and thus identify the connections between trace element cycles and MOD. This thesis work is part of the international GEOTRACES program. Funding for the operation and scientific promotion (congress, publication) is secured. This project is the only French contribution to the US-GP15 expedition.

## **Main objectives and scientific goals**

The main objective of the PhD student will be to study the biogeochemistry of DOM on a large scale in order to constrain its dynamics and thus quantify the contribution of DOM to the biological pump of ocean carbon. To this end, we will study the sources and sinks of DOM in contrasting ocean domains, its contribution to the bioavailable nitrogen reservoir and its implementation in the biogeochemical cycle of bioessential trace metal elements (Fe, Cu, Co). All analytical methods and strategies are detailed in section (2). This study will be based on samples acquired during the fall of 2018 along the US-GEOTRACES Pacific 15 section. This study area (Figure 1; 23 stations 36 depths, ~820 samples) includes a wide variety of biogeochemical domains (HNLC, subtropical, equatorial resurgence), sedimentary input zones (Aleutian margin), hydrothermal (Aleutian arc, fuca juan) and atmospheric (ITCZ). In addition, during this expedition, contrasting oxygenation zones (OMZs), the equatorial upwelling system and the deep waters of the North Pacific were sampled. This diversity of biogeochemical zones will make it possible to draw an overview of MOD in the Pacific Ocean, to characterize the different types of ocean DOM (refractory, labile, complexing towards metals,...), to quantify their contributions to the DOC pool and to define the sources and wells specific to each

fraction. Moreover, according to the size-reactivity continuum model, the larger classes of organic matter would be more bioavailable and remineralized more quickly by microbes than the smaller classes, suggesting an accumulation of low molecular weight and highly oxidized molecules along the thermohaline circulation[1].

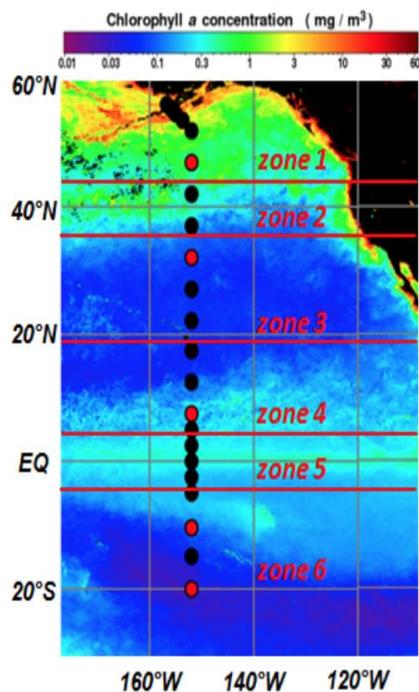


Figure 1 Tack and sampling station of the US- GEOTRACES GP15 section. Colors indicate surface Chlorophyll *a* concentrations during spring.

However, studies[2] suggest an accumulation of humic substances of microbial origin and resulting from the condensation of labile organic compounds along this same thermohaline circulation. To test these two antagonistic hypotheses, we will establish, using a chromatographic technique, the first distribution of the size spectrum of dissolved organic compounds at the scale of an ocean basin as well as the first quantitative study of the distribution of humic substances providing a large-scale view of the size-reactivity continuum. As primary production is limited by the availability of nitrogen in the Pacific oligotrophic zone[3], by defining the nitrogen composition of the DOM and by studying variations in the carbon-nitrogen ratio across different biogeochemical zones or during the mineralization process, this study will define whether the MOD constitutes a bioavailable nitrogen reservoir for planktonic communities in the Pacific subtropical oligotrophic zone. Finally, the interactions between DOM and bioessential trace elements will be explored. In particular, we will study the complexing capacity of humic substances, the distribution of specific copper and cobalt ligands such as glutathione and vitamin B12. These analyses will make possible to quantify the concentrations of specific ligands and identify direct connections between the DOM cycles and micronutrients such as iron and

copper[4] (identified as key elements by the international GEOTRACES program). This project proposes to study trace elements and organic matter as a single set in which the biological processes of production/mineralization of MOD cannot be separated from the geochemical reactivity (scavenging/oxidation-precipitation) of bio-essential trace elements. In this sense, collaborations will be initiated with scientists involved in the study of the cycle of trace elements and their physico-chemical speciation, in particular M. Saito and D. Repeta (WHOI, MA, USA), and J. Moffett (USC, CA, USA) and P Lam (UCSC, CA, USA) to relate the dataset acquired in this project to the distributions of essential bio trace elements and thus identify the connections between the TME and DOM cycles.

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## Methodology

This study proposes to study MOD according to 3 complementary analytical approaches. MOD will be quantified globally (COD analysis) as well as semispecifically using a size exclusion chromatographic technique with carbon, nitrogen and absorbance detector at 254nm (SEC-LC-OCD)[1]. In addition to COD quantification, this equipment allows the quantification of the carbon and nitrogen composition of the different MOD size classes and in particular humic substances and biopolymers (proteins, lipids,

saccharides). MOD will also be studied specifically using electrochemical and mass spectrometry techniques and potentially fluorimetric techniques. Indeed, specific analyses by mass spectrometry (LC-MS/MS)[2] on the biopolymer fraction collected from the column with size exclusion will make it possible to define more precisely the type of protein composing the MOD and thus to trace the production of labile organic matter or specific stresses (e.g. production of NtcA in the event of nitrogen stress[3]). The use of electrochemical techniques will make it possible to study the links between MOD and metallic trace elements. Indeed, these techniques make it possible to quantify the humic substances complexing metals[4] as well as specific copper or cobalt ligands such as glutathione[5] and vitamin B12[6]. The acquisition of data by SEC-LC-OCD does not require analytical development but simply a calibration phase of the equipment. Techniques for the analysis of electroactive humic substances and glutathione by electrochemistry are currently routinely used by the marine chemistry group and their calibration/installation does not have any particular blocking points. The main analytical lock of this project is the development of a method for the determination of marine proteins by liquid chromatography combined with a double mass spectrometer (LC-MS/MS). The aim here is to isolate the biopolymer fraction at the exit of the column with size exclusion in order to determine its protein composition.

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## Scientific environment and collaborations

In the lab, the PhD student will benefit from all the analytical facilities offered by LEMAR as well as from more than 20 years of internationally recognized experience in analytical chemistry of the marine chemistry group's. On a regional scale, this project will be carried out in collaboration with partners from the LSOL (Laser Spectrometry and Optics Laboratory) in Brest (Pr P. Giamarchi) and the LUBEM (University Laboratory of Biodiversity and Microbial Ecology). On an international scale, close collaborations with Prof. K Casciotti (Stanford University), Phoebe Lam (University of California Santa Cruz) and Mak Saito (Woods Hole Oceanographic Institute) will be initiated.

## Candidate

We are seeking for a graduate student with a university degree in marine / environmental chemistry or engineering in chemistry, applied sciences or general sciences, with synthesis and writing skills. The candidate's background must demonstrate experience (including an internship) in at least one of the following areas: analytical chemistry, organic speciation of metallic trace elements, (bio)geochemistry of organic matter, oceanographic chemistry. Skills in analysis by liquid chromatography or electrochemistry or mass spectrometry will be a plus. English language is essential and French spoken is recommended.