FINAL REPORT PROGRAM LEFE

Program LEFE/ Cyber	Project Title BioDOMPO : Biogeochemistry of Dissolved Organic Matter in the Pacific Ocean	Years 2018 – 2022

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Contribution to GEOTRACES

Other funding sources : ISBLue, Région Bretagne, UBO

Context : *Dissolved organic matter (DOM) is a major component of the carbon flux below the euphotic layer, supports the respiration of heterotrophic bacteria and determines the speciation, reactivity and transport of micro-nutrients (e.g. Fe, Cu, Co) essential for phytoplankton development in the ocean.*

Objectives / scientific questions: The main objective of the project BioDOMPO was to study the biogeochemistry of DOM at the scale of the Pacific Ocean in order to constrain its dynamics and thus quantify its contribution to the oceanic biological carbon pump. We studied the sources and sinks of DOM in contrasting biogeochemical domains from subpolar gyre to the subtropical south Pacific. The contribution of DOM to the bioavailable nitrogen reservoir was quantified and we investigated the role of Pacific DOM in the biogeochemical cycling of bio-essential trace metals (Fe, Cu) notably in hydrothermal environments.

Main results Dissolved organic carbon (DOC) supports about 29% of microbial remineralization in the Pacific Ocean. The degradation of DOC with aging of water masses in the Pacific Ocean was described by a simple first-order kinetic model with the degradation rate of 1.24 10^{-4} an^{-1}. The production of refractory DOC or the contribution of DOC to the microbial carbon pump was estimated to be 0.12 ± 0.03 GtC per year. This flux is in the same order of magnitude as the global COP burial flux (0.1 GtC yr-1).

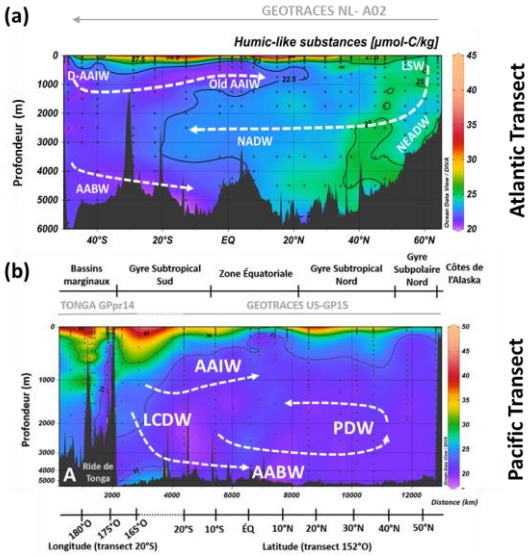

Figure 1 : Vertical (depth, vertical axis) and spatial (latitude, horizontal axis) distribution of dissolved organic carbon concentrations (colors, z-axis) of the humic substance fraction in (a) the western Atlantic (GEOTRACES section A02) and (b) the Pacific Ocean (GEOTRACES sections US-GP15 and TONGA)

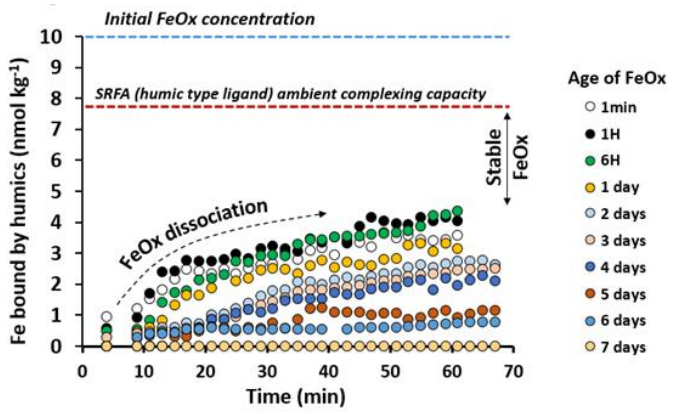

Figure 2 : Kinetic monitoring of the amount of iron complexed by a humic-type ligand as a function of the age of iron oxyhydroxides.

We established the first measurements of organic carbon and nitrogen content in the humic substances (HS) fraction along the entire Atlantic and Pacific Ocean (Figure 1). We also measured for the first time the binding capacity of humic substances all along the overturning circulation. Combining these results with ancillary data (e.g. T, S , O2,, …), we found that the preferential remineralization of nitrogen compare to carbon leads to a non-mineralizing oxidation of humic substances (no loss of carbon). This oxidation has the effect of increasing the

oxygen:carbon (O:C) ratio of the material with the appearance of carboxyl, phenolic, and carbonyl functions, suspected to be the main sites of metal complexation by HS (Buck et al., 2018; Bundy et al., 2015; Fourrier et al., 2022a). This project also demonstrated that iron oxyhydroxides become refractory to humic solubilization 1 week after their formation (Figure 2). This important result suggests that iron release by hydrothermal vents may not be stabilized/solubilized by organic ligands as thought before.

Future of the project *: Beyond the pursuit of valorization. the PI is waiting for an opportunity to get new samples from the South Pacific Ocean. He will be involved in the MARGO project (PI S Blain) that takes place in the Southern Ocean and will continue to explore DOM biogeochemistry in the vicinity of the Kerguelen Archipelago.*

8 articles published, submitted and close to submission

Fourrier†, P., **Dulaquais, G**., Guigue, C., Giamarchi, P., Sarthou, G., Whitby, H., & Riso, R. (**2022**). Characterization of the vertical size distribution, composition and chemical properties of dissolved organic matter in the (ultra) oligotrophic Pacific Ocean through a multi-detection approach. *Marine Chemistry*, *240*, 104068. .

Fourrier†, P., **Dulaquais, G.,** & Riso, R. (**2022**). Influence of the conservation mode of seawater for dissolved organic carbon analysis. *Marine Environmental Research*, *181*, 105754**.**

Dulaquais, G., Fourrier†, C. Guieu, C., Mahieu†, L., Riso R., Salaun P., Tilliette C., Whitby H. **(accepted for publication in 2023)** The role of humic type ligands in the bioavailability and stabilization of dissolved iron in the Western sub-Tropical South Pacific Ocean. *Frontiers in marine sciences*

Portlock, G., Fourrier†, P., Riso, R., Omanovic, D., **Dulaquais**, **G**, Whitby, H., Salaun*, P. (subm) Humic substances in the oligotrophic western tropical South Pacific: an intercomparison of electrochemical techniques. Subm.to *Marine chemistry*

Dulaquais, G., Fourrier† P. Casciotti, K., Lam, P., Cutter, G. (subm) Vertical and spatial distribution of dissolved organic matter in the Pacific Ocean, insights from the USGP15 cruise. Subm. to *Global Biogeochemical Cycles*

Fourrier†, P. & G. Dulaquais (subm.) Low molecular weight thiols: A major component of non-volatile dissolved organic sulfur in the Pacific Ocean. Subm to *L&O letters*

Fourrier†*, L., Whitby, H., Dulaquais, G., Salaun, P., Tilliette, C, Guigue, C., Tedetti, M., Lefevre, D. Fourrier, P., Bressac, M., Sarthou, G., Bonnet, S., Guieu, C., Pascal, P.[1] (in prep). Iron-binding by dissolved organic matter in the Western Tropical South Pacific (GEOTRACES cruise GPpr14) in prep for submission to *Frontiers in marine sciences*

Lory, C., **Dulaquais G.,** Camps, M., Whitby, H., Fourrier†, P., Mahieu†, L., Fourquez, M., Tedetti, M., Guieu, C., and Bonnet*, S. Exopolymeric substances (EPS) released by *Crocosphaera watsonii*: an overlooked ligand of highly bioavailable iron **in prep.**

4 international conferences

Dulaquais G, Fourrier† P, Laës A, Sarradin P-M, Sarthou G, Waeles M & Riso R (2020 August) Fate of Dissolved Organic Matter in Deep Sea Hydrothermal Fluids *Goldschmidt 2020, Virtual*

Fourrier†, P., **Dulaquais, G**., Tilliette, C., Guieu, C., & Riso, R. (2021). Vertical and spatial distribution of the iron-humic complex during the TONGA GPpr14 expedition. *Goldschmidt 2021• Virtual• 4-9 July*.

Portlock., G., P. Fourrier† ,**G**. **Dulaquais,** R. Riso, S. Bonnet, C. Guieu, F. Gazeau, P. Salaun, H. Whitby (**2022**) Distribution of thiol and electroactive humic substances during the 2019 TONGA cruise, *Ocean sciences meeting, February 2022*

Mahieu† L; Whitby H; **Dulaquais G**; Tilliette C; Bressac M; Arnone V; González-Santana D; Sarthou G;Planquette H; Guieu C; Bonnet S; Salaün P (**2022**) Iron-binding ligands distribution and binding strength in the shallow hydrothermal system of the Tonga Arc compared to surrounding deep waters Challenger 150: The Challenger Society Conference 2022, London, UK

1 PhD thesis + 1 participation to a PhD thesis

2019-2022 Co-director (70%) of the marine chemistry thesis of Pierre Fourrier (UBO), currently ATER at Intechmer (Cherbourg). Thesis title: Biogeochemistry of organic matter in the Pacific Ocean.

2019-2023 Participation in the supervision of the PhD (University of Liverpool) in marine chemistry of Léo Mahieu during his visit at LEMAR for the analysis of organic speciation of dissolved iron, currently post-doctoral fellow at the University of South Florida (Miami, USA). Thesis title: Organic speciation of dissolved iron during the Geotraces TONGA expedition in the southwest Pacific Ocean.

Data availablility

Data are from TONGA available at SEANOE (https://www.seanoe.org/html/about.htm) and on request to gabriel.dulaquais@univ-brest.fr for GEOTRACES USGP15 cruise