Copper complexing properties of fluorescent DOM in the New Caledonia lagoon (South Pacific)

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DOM has a key biogeochemical role in aquatic environment as it interacts with metals, pesticides and other anthropogenic contaminants (PAHs) affecting its bioavalability, transport and fate (Hirose, 2007). Considering its capacity to be transported on great distances, the dissolved organic matter (DOM), may contribute to the dispersal of the ETMs. Many studies concern coastal temperate environments but only a few data exist for tropical lagoons (Tedetti et al., 2011) and less in the Pacific. The soils from New Caledonia are made of laterites that have been mined for decades because of their high concentration in trace metals such as nickel, chromium, cobalt and manganese (Fandeur et al., 2009; Dublet et al., 2014; 2017). These mining operations generated a long-lasting dispersal of trace metals toward all coastal ecosystems (Metian et al., 2009; Hedouin et al., 2009; Biscere et al., 2015). A good knowledge of the concentration and nature of DOM is thus a key parameter for evaluating the actual impact of mining on coastal ecosystems through accurate estimation of the dispersal of trace metals at the land-sea interface in New Caledonia. The spectral characterization of DOM using excitation-emission matrices (EEMs) to identify groups of fluorescent compounds (fluorophores) was performed in tropical lagoons of New Caledonia (Martias et al., 2018) on the Western and Eastern coast of New Caledonia (Fig.1).



Fig.1. Transects at the Western and Eastern coasts of New Caledonia off Thio and Dumbea Bay (Noumea). The Eastern coast was also sampled (12 transects from the southern to northern tips during the CALIOPE cruises.

Sampling was done monthly on the two transects, off Dumbea and off Thio. The Dumbea transect (15 km)

originated from the River (DR1), Mangrove (DM1) and estuary system (CD1) to the Dumbea Bay (D39), and to the lagoon waters at the MOISE station. MOISE station (M99, Figure 1) is the 2012-present M.I.O. /IRD Observing station (SOMLIT data basis). The other transect was on three stations (12 km). During this sampling, samples were collected and filtered at the laboratory. Each sample was filtered at 0.2 μ m and conserved in SCHOTT^M glass bottles previously calcinated

at 450°C during 4 hours before analysis for TOC (TOCV Shimadzu at the Toulon MIO laboratory), CDOM absorption (LWCC) and FDOM, nutrients, pigments (HPLC, fluorimetry) and flow cytometry analyses. All samples were analyzed by spectrofluorimetry (HITACHI 4500 at MIO). Excitation emission matrix of fluorescence (EEMF) were collected on a 200-500 nm range for excitation and 280-550 nm range for emission with a 5 nm step at a temperature of 20°C. Before each analysis, the quartz cuve was rinsed 3 times with a 1M HCL solution and 3 times with the sample. The Rayleigh and Raman contribution were numerically removed from the detected fluorescence and the identification of the various fluorophores was done (Tedetti et al., 2011).

The CALIOPE 1, 2 and 3 cruises were done in October 2011, March 2014 and March 2016 (Dupouy et al., 2014; Favareto et al., 2018; Dupouy et al., in prep.). The complete analysis of FDOM and biogeochemical parameters were done for CALIOPE 03 (Martias et al., 2018). In addition, quenching experiments with Cu were performed at a fixed pH (i.e. pH=8.5) and calculation of the complexation constants was done considering a simple 1:1 model (Ryan & Weber, 1982) with one competition between the two components (Martias et al., 2017). Complexation constants calculated from curves for the three components, the humic-like, tyrosin-like and the tryptophan-like are presented.

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