Saltmarsh organic matter fluorescence and metal interaction (WOMS 2018)

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The peculiarity of New Caledonia soil is to be essentially formed by laterites excavated for decades because of their richness in Metal Trace Elements (MTEs) such as nickel, chromium, cobalt and manganese with a long-lasting impact on all coastal ecosystems (Dublet et al., 2014; Beaudrimont et al., 2017). Considering its capacity to be transported on great distances, the dissolved organic matter (DOM), may contribute to the dispersal of the ETMs. Mangroves can act as sources or sinks for DOM and MTEs (Marchand et al., 2006; Mounier et al., 2018). The capacity of DOM to form complexes with the MTEs could limit bio-absorption and bioaccumulation in living organisms. Objectives were to follow the FDOM along river-mangrove-lagoon continuums and to determine the MTEs complexation constants by quenching experiments on FDOM along a mining site (Northern Province, Koné, Figure 1 and Table 1).

Fig.1. Stations (Voh-Kone-Pouembout) north of New Caledonia (21.13°S, 164.89°E) sampled on the 14th of March 2018 during the CRESICA TREMOR project (Table 1).

River	Station	Type	Sal
Coco (Vavouto)	C1	River	0.17
	C2	Mangr. upstream	0.73
	C3	Mangr. downsntream	0.76
	C4	Lagoon upstream	34.38
	C5	Lagoon downstream	23.23
Temala / Fatenaoue (Chasse - Loup)	T1	River	0.07
	T2	Mangr. upstream 1	0.19
	T3	Mangr. upstream 2	0.21
	T4	Mang. downstream	0.97
	T5	Lagoon	25.07

Samples were filtered onto 0.2 µm into Teflon bottles were for ETM and kept at 4°C before ETMs analyses (ICP-Q-MS after pre-concentration SeaFAST S2, Saetvest, N., Elemental Scientific, US IMAGO LAMA) and into calcinated at 450°C during 4 hours glass SCHOTT bottles. Every sample was analyzed by spectrofluorimetry on a Perkin Elmer and quenching experiments quenching were made in duplicate with Copper addition (in a logarithmic scale, and keeping a PH=5). Excitation emission matrix of fluorescence (EEMF) were measured on a Perkin Elmer LS55 (200- 500 nm for exc. wavelengths, and 280-550 nm for em. wavelengths, with a step of 5 nm), at a thermostatic bath regulated temperature of 20°C, in quartz cuvettes rinced 3 times with HCL and 3 times with the sample. Rayleigh and Raman physical diffusion of light were numerically removed. Determination of fluorophores was done by CP/PARAFAC with a CORCONDIA test > 60% and calculations of the complexation constants was done considering a simple model (1:1: Ryan et Weber (1982) with one competition between the two components; Mounier et al., 2011, ProgMEEF and PROCESE).

Cu remained stable (< than 5 µg/L) in Temala and Coco rivers, while Ni was higher in Coco, nearer to the nickel exploitation site (Fig. 2). ETMs concentrations were maximum at the river sources but still high in the lagoon (35 in salinity). Four components were identified, with 3 common to the 2 rivers , i.e. defined as 2 terrestrial humic-like (1) C1, (λex/λem = 280-380/480 nm) and (2) C2, (λex/λem = 220-340/450 nm) ; a 3) C3 tryptophane-like T1 (λex/λem = 240-300/380 nm). Another humic-like fluorophore was also identified in the mangrove (λex/λem = 245(330) /466 nm) but did not appear when both rivers were processed together.
The complexation capacity (KS) at every station of the 2 transects vs the logarithm of the total concentration ligands (CL), for component C1 is shown Fig 3. Values of log (KS) remained between 4 and 6 and values of Log (CL) between 6,6 and 5,6. The Coco river shows values around 6,5 for salty environments and values near 5,9 for fresh waters. There is no effect of salinity for the Temala. Similar results were obtained for component C2.
After heavy rains encountered in March 2016, there was no gradient of Ks nor of ETMs on the continuum river-mangrove-lagoon for two rivers sampled (Temala and Coco), through the lateritic watershed of Koniambo.

These preliminary results must be completed by experiments during dry season. Moreover, studying tide cycles, up and downstream of the mangrove will be done with automatic samplers allowing to both sample CDOM and ETMs. Also, similar quenching experiments should be done with Ni, the major ETM in New Caledonia.

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