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Characterization and sources of colored dissolved organic matter in a coral reef ecosystem subject to ultramafic erosion pressure (New Caledonia, Southwest Pacific)

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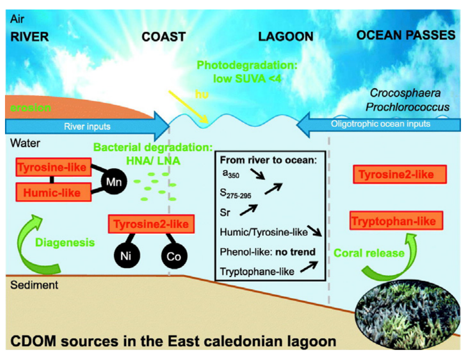
HIGHLIGHTS

- First report of CDOM and trace metals in the eastern lagoon of New Caledonia
- $S_{275-295}$ and $SUVA_{254}$ reveal the importance of CDOM photodegradation in the lagoon.
- CDOM in the lagoon coming from rivers, corals, bacterial activity and open ocean
- Relationships between fluorescent CDOM and Ni, Co and Mn concentrations

GRAPHICAL ABSTRACT



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ABSTRACT

The eastern lagoon of New Caledonia (NC, Southwest Pacific), listed as a UNESCO World Heritage site, hosts the world's second longest double-barrier coral reef. This lagoon receives river inputs, oceanic water arrivals, and erosion pressure from ultramafic rocks, enriched in nickel (Ni) and cobalt (Co). The aim of this study was to characterize colored dissolved organic matter (CDOM), as well as to determine its main sources and its possible relationships (through the use of Pearson correlation coefficients, r) with biogeochemical parameters, plankton communities and trace metals in the NC eastern lagoon. Water samples were collected in March 2016 along a series of river/lagoon/open-ocean transects. The absorption coefficient at 350 nm (a_{350}) revealed the influence of river inputs on the CDOM distribution. The high values of spectral slope ($S_{275-295}$, >0.03 m^{-1}) and the low values of specific ultraviolet absorbance ($SUVA_{254}$, <4 L mg-C^{-1} m^{-1}) highlighted the photodegradation of CDOM in surface waters. The application of parallel factor analysis (PARAFAC) on excitation-emission matrices (EEMs) allowed the identification of four CDOM components: (1) one humic- and one tyrosine-like fluorophores. They had terrestrial origin, exported through rivers and undergoing photo- and bio-degradation in the lagoon. These two fluorophores were linked to manganese (Mn) in southern rivers ($r = 0.46$–0.50, $n = 21$, $p < 0.05$). (2) A tryptophan-like fluorophore, which exhibited higher levels offshore. It would be potentially released from the coral reef. (3) A second tyrosine-like ("tyrosine 2-like") fluorophore. Linked to *Prochlorococcus* cyanobacteria ($r = 0.39$, $n = 47$, $p < 0.05$), this fluorophore would have an oceanic origin and enter in the lagoon through its

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southern and northern extremities. It also displayed relationships with Ni and Co content ($r = 0.53$–0.54, $n = 21$, $p < 0.05$). This work underlines the diversity of CDOM sources in the NC eastern lagoon.

1. Introduction

Dissolved organic matter (DOM, <0.2–0.7 μm), which is the basis of the microbial loop, plays a key biogeochemical role in marine environment (Chisholm, 2000; Carlson and Hansell, 2015; Santinelli, 2016). Chromophoric or colored dissolved organic matter (CDOM) is the component of DOM that absorbs light over a broad range of ultraviolet (UV) and visible wavelengths. The abundance and distribution of CDOM in the ocean is essentially controlled by in situ biological production, terrestrial inputs (sources), photodegradation, microbial consumption (sinks), and deep ocean circulation (Siegel et al., 2002; Nelson et al., 2007; Kowalczuk et al., 2013; Nelson and Siegel, 2013).

CDOM is the major factor controlling the attenuation of UV radiation in the ocean, protecting marine organisms against harmful solar effects (Mora et al., 2000; Sempéré et al., 2015), but may also compete with chlorophyll *a* (Chl *a*) for the attenuation of photosynthetically available radiation (PAR) (Nelson and Siegel, 2013). CDOM is highly photoreactive and efficiently degraded upon exposure to solar radiation. The photodegradation of CDOM in the surface waters leads to its bleaching (loss of absorption and fluorescence) (Helms et al., 2008; Andrew et al., 2013; Su et al., 2015) and to the production of free radicals, dissolved inorganic carbon, carbon monoxide, carbonyl sulfide, nutrients and low molecular weight organic compounds (Mopper et al., 2015). The photodegradation of CDOM therefore modifies DOM bioavailability to heterotrophic bacteria and significantly impacts the oceanic carbon cycle. Finally, CDOM, particularly humic substances, may interact with trace metals and organic pollutants, modifying their toxicity and fate in the aquatic medium (Gauthier et al., 1986; Mounier et al., 2011).

In coastal marine waters, CDOM may originate from various sources: (1) marine (autochthonous) sources with excretion/release/production at different scales from primary producers (Chen et al., 2017), bacteria (Jørgensen et al., 2011), zooplankton (Steinberg et al., 2004), fishes (Nimptsch et al., 2015), etc. … (2) terrestrial sources with OM from soil and higher plants carried to marine waters through rivers, runoff or groundwater (Del Vecchio and Blough, 2002; Benner et al., 2005; Lu et al., 2016), and (3) anthropogenic sources with OM released from domestic effluents (Tedetti et al., 2012; Carstea et al., 2016). In coastal (shallow) waters, sediments may also represent a source of CDOM for the water column during sediment resuspension events (Komada et al., 2002; Guigue et al., 2017). Hence, the great variety of CDOM sources and of transformation processes makes the coastal CDOM a complex and heterogeneous pool of organic molecules displaying a broad range of structure and reactivity (Benner et al., 2005; Cao et al., 2016). Whereas most research dealing with the dynamics of CDOM in coastal waters has focused on temperate or high latitude environments, the sources and dynamics of CDOM in tropical coral reef areas remain much less known (Tedetti et al., 2011; Rochelle-Newall et al., 2014; Nelson et al., 2015), although tropical environments have received special attention in recent years due to coral bleaching in the context of global change (Weishaar et al., 2003; Biscéré et al., 2017; Wolanski et al., 2017).

The eastern lagoon of New Caledonia (Southwest Pacific), listed as a UNESCO World Heritage site in 2008, hosts the world's second largest double-barrier coral reef after the Great Barrier Reef. The New Caledonian barrier reef, interspersed with passes, is 1500 km long and 100–1000 m width. The eastern lagoon of New Caledonia is impacted by river inputs and the flushing of oligotrophic oceanic water pushed into the lagoon by the external Vauban Current, large cyclonic gyres, tide, and trade winds (Cravatte et al., 2015) through narrow passages (Andre and Pelletier, 2009). Also, areas near the shore along New Caledonia's east coast have been extensively impacted by the extraction of ultramafic rock for nickel (Ni) and cobalt (Co) exploitation (Cluzel et al., 2001; Fandeur et al., 2009; Dublet et al., 2012, 2015), which accelerates the natural soil erosion. Due to their shoreline location, eroded ultramafic materials are directly transported to the lagoon, as evidenced by remote sensing or in situ measurements. Continuous releasing of trace metals from these ultramafic materials has durably impacted the lagoon ecosystem (Labrosse et al., 2000), including geochemical signatures on the shoreline (Fernandez et al., 2006), sediments and porewater in mangrove swamps (Marchand et al., 2011), benthic populations (Hédouin et al., 2011) and coral reef (Biscéré et al., 2017). No CDOM or trace metal measurements have however yet been conducted in the eastern lagoon of New Caledonia.

While the quenching effect of trace metals on CDOM has been identified with laboratory experiments (Ryan et al., 1983; Wu et al., 2010; Mounier et al., 2011), few works have highlighted the potential effect of CDOM-metal complexation in natural waters (Stijn et al., 2011). Indeed, the potential complexation between CDOM and trace metals could reduce their toxicity and thus have a positive ecological impact on marine ecosystems (Pandey et al., 2000). In the context of an oligotrophic lagoon undergoing the combined influence of the open ocean and water sheds under erosion pressures, a better understanding of CDOM origins is essential. Therefore, the objective of this study was to characterize and determine the main sources of CDOM in the eastern lagoon of New Caledonia, subjected to ultramafic erosion pressure, along a series of river/lagoon/open-ocean transects. The sampling period was the wet season in order to capture potential river plumes or biological bloom events in the lagoon. Along with CDOM, biogeochemical parameters, plankton communities and trace metals were determined to better differentiate terrestrial and marine sources of CDOM and its possible relationships with trace metals. To our knowledge, this work is the first investigation of the coupling between CDOM properties, trace metal concentrations and phyto- and bacterio-plankton communities in a coral reef ecosystem submitted to erosion pressure from mining activities.

2. Materials and methods

2.1. Study area

New Caledonia's main island (Grande Terre, 16,360 km^2) is surrounded by a 1500 km long and 100–1000 m width barrier reef (Fig. 1). Reef and lagoon together cover an area of approximately 22,200 km^2, 86% of which is lagoon. In the eastern lagoon, water depth varies from 40 to 80 m, with a submarine valley (Jollit et al., 2010), and water temperature is generally >25 °C. The barrier reef is almost totally submerged except at some locations. A specific feature of the eastern coast is the numerous rivers flowing into bays (Fig. 1). From South to North, these are the Yaté, Pourina, Koualoue-Ouinné, Thio, Canala, Houailou, Ponerihouen and Tchamba, Tiwaka and Ouaième. These rivers drain watersheds of different geological origins. The southern rivers drain ultramafic lands, while the northern rivers drain karstic lands (Bonvallot et al., 2013). The origin of surface water in the eastern lagoon is a mixture of water from rivers, depending on the rain intensity, and oceanic water arrivals through passes from the warm tropical area surrounding the Vanuatu island group (Marchesiello et al., 2010). New Caledonia's lagoon was affected by coral bleaching in February 2016 (Payri et al., 2017), and undergoes