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Quantitative model of carbon and nitrogen isotope composition to highlight phosphorus cycling and sources in coastal sediments (Toulon Bay, France)

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HIGHLIGHTS

- Quantitative multiple-end-member mixing model using C and N isotopes.
- Differentiation of anthropogenic and non-anthropogenic (diagenetic) P.
- Revelation of point and non-point sources of P.
- Assessment of diagenetic P background in Toulon Bay.

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ABSTRACT

Nutrient loadings from either point or non-point sources to the environment are related to the growing global population. Subsequent negative impacts of nutrient loading to aquatic environments requires a better understanding of the biogeochemical cycling and better tools to track their sources. This study examines the carbon (C), nitrogen (N) and phosphorus (P) discharge and cycling in a Mediterranean coastal area from rivers to marine sediments and assesses the anthropogenic contributions. Carbon and N concentrations and isotope compositions in rivers particles, surface sediments, and sediment cores were investigated to build up a quantitative multiple-end-member mixing model for C and N isotopes. This model predicts the contribution of four natural and one anthropogenic sources to the sediments and highlighted the anthropogenic fraction of P based on the relationship with anthropogenic $\delta^{15}N$. Although P is a monoisotopic element and total P concentration has been the sole index to study P loading, this study suggests an alternative approach to differentiate anthropogenic and non-anthropogenic (diagenetic) P, revealed point and non-point sources of P, and the corresponding P loading. Also, the diagenetic P background has been calculated for the 50-cm sediment layer of the whole Bay.

1. Introduction

Coastal and estuarine areas are among the most productive, diverse, and economically important ecosystems for human society, and play a primordial role in biogeochemical cycling and storage of carbon (C) and other nutrients. However, these ecosystems are widely and globally threatened, mostly by anthropogenic pressure (Hobbie, 2000; Paerl, 2006; UNEP, 2006; Wetz et al., 2008). One of the greatest threats to these ecosystems is eutrophication due to nutrient loading by either point sources (e.g., waste water discharge) or non-point sources (e.g., surface runoff, atmospheric

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deposition) (Bohlin et al., 2006; Church et al., 2006; Savage et al., 2010; Vaalgamaa et al., 2013) leading to an increasing frequency of harmful algal blooms (Kimbrough et al., 2008; Paerl, 2008, 2006; Vitousek et al., 1997).

Sedimentary accumulation of organic matter (OM) and C–N isotope composition have been used widely to track origins of the OM and changes in nutrient availability in surface waters (Bohlin et al., 2006; Church et al., 2006; Di Leonardo et al., 2012; Harmelin-Vivien et al., 2008; Ogrinc et al., 2005; Teranes and Bernasconi, 2000; Vaalgamaa et al., 2013; Yokoyama et al., 2006). The carbon source for terrestrial plants is atmospheric CO_2 with a $\delta^{13}C$ which decreased from −7.5‰ in the 1980s to −8.5‰ today, relative to the Vienna PeeDee Belemnite (Cuntz, 2011). Dissolved inorganic carbon (DIC) typically has $\delta^{13}C$ values very similar to that of atmospheric CO_2 (e.g., $\delta^{13}C$-DIC = −7.53 ± 0.83‰ in the Mississippi River, (Cai et al., 2015)). For land vegetation, C3 and C4 plants using different assimilation pathways are differentiated by typical $\delta^{13}C$ ranges of −24‰ to −34‰ and −10‰ to −20‰, respectively (Dean, 2006; Meyers, 1997). However, most aquatic vegetation obtains its carbon from DIC resulting in $\delta^{13}C$ ranging from −18 to −28‰ (Bohlin et al., 2006; Dean, 2006; Kendall et al., 2001). The ranges of $\delta^{13}C$ values in land and aquatic vegetation overlap and that makes them indistinguishable by $\delta^{13}C$. However, between freshwater and marine organic matter, there is a significant difference in $\delta^{13}C$ (freshwater and marine phytoplankton: −30‰ and −20 to −22‰, respectively (Bohlin et al., 2006; Bouillon et al., 2012; Meyers, 1997)). Also, among aquatic marine macrophytes, physiological differences result in variation in $\delta^{13}C$ values in seagrasses and macroalgae (Parker, 1964; Stephenson et al., 1986); a value of −10.5 ± 3.3‰ has been reported in 195 observations of seagrasses (Hemminga and Mateo, 1996) while a range from −12 to −18‰ is observed for macroalgae (Belicka et al., 2012).

Concerning N, biogeochemical processes tend to enrich ^{15}N leading to a positive drift in $\delta^{15}N$, except for some methanogenic and nitrogen-fixing organisms (e.g., cyanobacteria) (Cloern et al., 2002; Dean, 2006). Relative to atmospheric N_2, $\delta^{15}N$ ranges from +2‰ to +3‰ in soils (Vaalgamaa et al., 2013), and −2‰ to +5‰ in chemical fertilizers (Vaalgamaa et al., 2013) while it ranges between +7‰ and +9‰ in estuarine and marine phytoplankton (Cloern et al., 2002; Vaalgamaa et al., 2013). Also, a peculiarly high value of $\delta^{15}N$ between 10‰ and 25‰ is typical of ammonia volatilization in animal manure (Choi et al., 2003) and could be used to track agricultural and urban point sources (e.g., treated/untreated sewage discharge) (Bohlin et al., 2006; Savage et al., 2010; Vaalgamaa et al., 2013). In summary, terrigenous material has lower values for $\delta^{15}N$ and $\delta^{13}C$ than estuarine and marine OM (Ogrinc et al., 2005; Vaalgamaa et al., 2013).

In addition, eutrophication history could be recorded by C–N isotopes; previous studies (Church et al., 2006; Teranes and Bernasconi, 2000) have reported (i) a significant positive correlation between $\delta^{13}C$ and total sediment P indicating variations in primary production and (ii) a change in sedimentary $\delta^{15}N$ related to an increase in dissolved nitrate, either by algal uptake or a variation in N sources (e.g., wastewater vs. agricultural inputs). However, diagenetic P cycling is complex; P deposits in sediments in either inorganic or organic forms can be released into porewater due to carrier phase dissolution (e.g., iron oxyhydroxides) and organic matter decomposition, potentially followed by P scavenging via adsorption and/or precipitation processes (Anschutz et al., 2007; Dang et al., 2014a; Krom and Berner, 1981; Ruttenberg, 2003). Also, P accumulated in surface sediments may be of anthropogenic origin and it is not obvious how to differentiate diagenetic P enrichment from anthropogenic P in sediments (Anschutz et al., 2007; Dang et al., 2014b; Ruttenberg, 2003). Unlike C and N, P is a monoisotopic element; it is not possible to track the P sources and biogeochemical processes controlling P cycling by isotope composition.

In summary, very large ranges for C and N isotope composition are observed reflecting the high diversity of their sources in the environment. In addition, some minor modifications of C–N isotope composition are possible during the environmental cycling of OM. For example, early diagenesis could alter the C–N isotope composition in sediments, mostly by selective degradation of organic compounds and isotope fractionation during degradation (Ogrinc et al., 2005 and references therein). However, this alteration is considered less significant for C (i.e., <2‰) than N (Bohlin et al., 2006; Ogrinc et al., 2005). Nevertheless, contradictory conclusions have been reported for the direction of N isotopic shift during decomposition. It appears that the observed change in N isotopic composition (if any) is not related to the residual N pool but to the microbially added nitrogen which depends on the N substrate (see discussion in Bouillon et al. (2012) and Lehmann et al. (2002)).

Understanding the nutrient cycling in coastal areas is challenging due to (i) a multiplicity of sources (several natural and anthropogenic components), (ii) complex biogeochemical processes capable of altering original isotope compositions and (iii) reciprocal interactions with primary production. Resolving this complex system would permit a better evaluation of the contribution from each source and pinpoint human signatures on nutrient inputs to vulnerable coastal areas. However, although multiple OM sources have been identified in natural coastal sediments, widely used mixing models have only two end-members, terrestrial and marine materials (Bohlin et al., 2006; Harmelin-Vivien et al., 2008; Li et al., 2016; Loneragan et al., 1997; Ogrinc et al., 2005; Ramaswamy et al., 2008). There are far fewer studies on natural sediments with the application of a quantitative multiple-end-member mixing model (Das et al., 2008). However, stable isotope mixing models using multiple sources have been extensively used in food-web studies (see discussion in Erhardt et al. (2014) and Phillips et al. (2014)).

Toulon Bay (NW Mediterranean, SE French coast) offers a coastal study area subjected to anthropogenic pressure. Whereas the vulnerable Toulon Bay ecosystem is nationally classified as a ZNIEFF (Natural zone of interest for ecology, flora and fauna), type II (of great interest), it hosts several anthropogenic activities: the French Navy Base, yacht clubs, marinas, and aquaculture. Two small urbanized rivers (Las and Eygoutier) and two treated sewage submarine outlets are the main terrestrial/anthropogenic inputs to the sea (point sources), in addition to land runoff (non-point source). Also, the Bay is divided into two non-equal parts, an enclosed western little Bay and a large Bay open to the sea. Previous studies have revealed serious contamination of the entire ecosystem of Toulon Bay, and the situation is more dramatic in the little Bay than the large Bay (Cossa et al., 2014; Dang et al., 2015a, 2015b, 2014b; Pougnet et al., 2014; Tessier et al., 2011); in the little Bay, the seagrass meadow of *Posidonia oceanica* has totally disappeared over the last 30 years, harmful phytoplankton has proliferated, and zooplankton diversity has decreased (Bernard et al., 2001; Jamet et al., 2005; Jean et al., 2012). Also, the invasive macroalgae (*Caulerpa taxifolia* and *Caulerpa racemosa*) have been colonizing the protected *P. oceanica* beds (Belsher et al., 2003) and are largely expanding (up to 480 ha, i.e., 54% of the area is covered by *Caulerpa taxifolia* (Bellan-Santini and Ruitton, 2013)).

Therefore, this study aims to develop a quantitative multiple-end-member mixing model using C and N isotope composition in the coastal sediments of Toulon Bay to better highlight anthropogenic contributions to the nutrient balance (from either point or non-point sources) and sedimentary cycling of these nutrients. The proposed model is based on concentrations of C, N, P, Mg, Iodine