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Interrogating pollution sources in a mangrove food web using multiple stable isotopes

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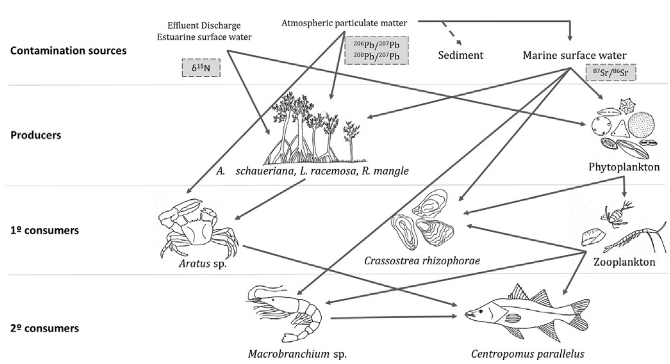
HIGHLIGHTS

- $\delta^{15}N$ was higher throughout a food web at the site with higher anthropogenic pressure.
- $\delta^{15}N$ suggests mangrove plants can be a biomarker for anthropogenic pollution.
- Sr ratio showed a greater influence of marine water in the studied estuaries.
- Pb isotope ratios suggest metal pollution is influenced by metallurgical activities.
- Mangrove plants are affected by anthropospheric particulate matter.

GRAPHICAL ABSTRACT



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ABSTRACT

Anthropogenic activities including metal contamination create well-known problems in coastal mangrove ecosystems but understanding and linking specific pollution sources to distinct trophic levels within these environments is challenging. This study evaluated anthropogenic impacts on two contrasting mangrove food webs, by using stable isotopes ($\delta^{13}C$, $\delta^{15}N$, $^{87}Sr/^{86}Sr$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) measured in sediments, mangrove trees (*Rhizophora mangle*, *Laguncularia racemosa*, *Avicennia schaueriana*), plankton, shrimps (*Macrobranchium sp.*), crabs (*Aratus sp.*), oysters (*Crassostrea rhizophorae*) and fish (*Centropomus parallelus*) from both areas. Strontium and Pb isotopes were also analysed in water and atmospheric particulate matter (PM). $\delta^{15}N$ indicated that crab, shrimp and oyster are at intermediate levels within the local food web and fish, in this case *C. parallelus*, was confirmed at the highest trophic level. $\delta^{15}N$ also indicates different anthropogenic pressures between both estuaries; Vitória Bay, close to intensive human activities, showed higher $\delta^{15}N$ across the food web, apparently influenced by sewage. The ratio $^{87}Sr/^{86}Sr$ showed the primary influence of marine water throughout the entire food web. Pb isotope ratios suggest that PM is primarily influenced by metallurgical activities, with some secondary influence on mangrove plants and crabs sampled in the area adjacent to the smelting works. To our knowledge, this is the first demonstration of the effect of anthropogenic pollution (probable sewage pollution) on the isotopic

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fingerprint of estuarine-mangrove systems located close to a city compared to less impacted estuarine mangroves. The influence of industrial metallurgical activity detected using Pb isotopic analysis of PM and mangrove plants close to such an impacted area is also notable and illustrates the value of isotopic analysis in tracing the impact and species affected by atmospheric pollution.

1. Introduction

An estuary is a semi closed water body connecting freshwater with the sea and having influence from both environments; the essence of understanding estuarine processes is connectivity which determines whether the areas are sinks for contaminants (Potter et al., 2010; Wolanski and Elliott, 2015). Connectivity exposes the estuaries to many pressures from both urbanisation and industrialisation, directly or indirectly (Elliott and Whitfield, 2011). Among those pressures, metal contamination in tropical areas is a serious problem for mangrove ecosystems given that sewage and industrial contaminants carried by rivers and other contamination sources, derived from coastal engineering work, affect the health status of estuarine environments (Hogarth, 1999).

Estuarine mangrove ecosystems have their biota influenced by several physical and chemical changes (i.e. salinity, sea level, organic matter) over which are superimposed the ecological structure and interactions. In turn, these characteristics influence the bioavailability of metal/metalloids in the aquatic ecosystem and favour their transfer from the lower to the higher trophic levels throughout the food web (Kulkarni et al., 2018; Lewis et al., 2011; Wolanski and Elliott, 2015). Such a trophic transfer may reach humans, particularly those who consume fish frequently (Jiang et al., 2010). However, trophic transfer is unlikely to be the only pathway for toxic metals/metalloids input in estuarine biota and is dependent on other human activities in the surrounding area which may also introduce such toxic elements into the estuarine ecosystem and its components, including mangrove, plankton, fish, etc.

While the contamination of estuarine environments by trace metals has long been of concern (McLusky and Elliott, 2004), there is poor information on flux rates through such systems, and on the processes governing the fate and effects of the trace metals (Luoma and Rainbow, 2008). In the southeast coast of Brazil, the environment of the State of Espírito Santo has long been negatively impacted by industrial metallurgy, including mining complexes, steel and smelting industries. Two estuaries from this area (Santa Cruz and Vitória Bay) have diverse environmental aerial contamination from metallic smoke particles (Arrivabene et al., 2015), and surface water contamination with Fe, Pb, As, Hg, Cr and Cu, which was correlated with metal/metalloid accumulation in *Centropomus parallelus* (fish) muscle (Souza et al., 2013). Metal accumulation has been detected in different species of mangrove plants, such as *Laguncularia racemosa* (Souza et al., 2014a), *Rhizophora mangle* (Souza et al., 2014b) and *Avicennia schaueriana* (Souza et al., 2015). However, these studies did not establish either the pollution source or the probable pollutant pathway and transport through the estuarine mangrove food web. Moreover, the estuarine mangrove ecosystems close to the industrial and domestic activities areas (Vitória Bay) were more affected than those located further north and away from the main pollution sources (Santa Cruz) (Arrivabene et al., 2015; Souza et al., 2013, 2014a, 2014b, 2015).

The presence of toxic elements in the food web depends on more than one factor and contamination of the surface water, sediment or particulate matter, can affect the ecosystem structure and its trophic relationships (Bayen, 2012; Laws, 1993). When contaminants are transported through the food web, the analysis of stable isotopes, such as carbon (δ^{13}C) and nitrogen (δ^{15}N) is a valuable tool to establish trophic levels and their contamination (Bond, 2010). δ^{13}C is a valuable marker for identifying different primary producers, while δ^{15}N is effective for assessing the trophic position, given that enrichment of the heavy nitrogen isotope occurs incrementally and with a constant rate (3–4‰) across trophic levels (Hobson et al., 2002).

As metal/metalloid contamination can originate from several sources, stable isotope ratios have been used to identify the origin (source) of metals and metalloids in the food web (Ikemoto et al., 2008; Peterson and Fry, 1987; Podio et al., 2013). For instance, the strontium isotopic ratio (^{87}Sr/^{86}Sr) is relatively constant in marine environments, while it changes with the geology and other land mass factors. Thus, ^{87}Sr/^{86}Sr can primarily reflects the bedrock geology of the neighbour continent, when the estuary is dominated by freshwater inputs. Conversely, the ^{87}Sr/^{86}Sr show values close to those for the marine environment which indicates that the estuary is dominated by seawater input, with little or no influence from land-based sources. Hence, the contamination in the estuary can be associated with either continental or marine inputs. Moreover, the lead isotopes ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) have been used as anthropogenic tracers (Chow et al., 1973, 1975; Chow and Earl, 1970, 1972; Chow and Johnstone, 1965) and are used as 'fingerprints' of environmental pollution (Cheng and Hu, 2010; Komárek et al., 2008).

The use of stable isotopes to assess the sources of environmental pollution has increased in recent years (Négrel et al., 2012) and there are frequent studies using single volatile stable isotopes (δ^{2}H, δ^{13}C, δ^{15}N, δ^{18}O, δ^{34}S) (e.g. Griboff et al., 2018; Monferrán et al., 2016), and occasionally combined ones (e.g. δ^{2}H and δ^{18}O for the evaluation of pollutant plumes in groundwater) (Negrel et al., 2017). The use of non-volatile stable isotopes (Pb, Sr, Hg, etc. signatures) is less frequent (Négrel et al., 2012; Négrel and Petelet-Giraud, 2012). Furthermore, the combined use of both volatile and non-volatile environmental stable isotopes is uncommon (Négrel et al., 2012), despite this combined use being valuable to distinguish the origin of food products (e.g. Baroni et al., 2015), which is a challenge similar to finding the source of an environmental contaminant.

Therefore, the main goal of this study was to assess differences in the behaviour of stable isotopes between two estuaries affected by different anthropogenic pressures, establishing new endpoints to verify the negative impact of both urban and industrial activities on aquatic ecosystems. We hypothesised that the evaluation of multiple stable isotopes in both mangrove ecosystems (Vitória Bay and /santa Cruz), and in the Tubarão (industrial) Complex (Vitória Bay), will allow linking the anthropogenic activity to different levels and sources of contamination in both estuaries. In turn this provides a valuable tool-kit for the evaluation of other estuarine mangrove systems affected by anthropogenic and industrial pollution worldwide.

2. Material and methods

2.1. Sampling areas

This study was conducted in two mangrove areas located in the state of Espírito Santo, Brazil: Vitória Bay and Santa Cruz, which are 10 and 70 km, respectively, from the industrial Tubarão Complex (Fig. 1). Sampling was carried out in March 2015, the end of the summer period in the southern hemisphere.

The mangrove ecosystem in Santa Cruz (19°56′26.2″S and 40°12′87.0″W) covers approximately 12 km^2, it is formed by two rivers, being part of the 'Piraquê-Açu' and 'Piraquê-Mirim' Mangrove Ecological Reserve. There is an extensive and well-preserved mangrove area,