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Trophic relationships and mercury biomagnification in Brazilian tropical coastal food webs

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ABSTRACT

The present study investigated trophic relationships and mercury flow through food webs of three tropical coastal ecosystems: Guanabara, Sepetiba and Ilha Grande bays. The investigation was carried out through carbon and nitrogen stable isotopes ($\delta^{13}C$, $\delta^{15}N$) and total mercury (THg) determination in muscle from 35 species, including crustacean, cephalopod, fish and dolphin species. Detritivorous species showed the lowest average $\delta^{15}N$ values in all bays. These species were ^{13}C enriched in Sepetiba and Ilha Grande bays, suggesting the presence of ^{13}C enriched macroalgae in their diet. The highest mean $\delta^{15}N$ values were found in fish and benthic invertebrate feeders, as well as in species presenting demerso-pelagic feeding habit. The carbon and nitrogen isotopic findings showed different trophic relationship in food webs from Sepetiba, Guanabara and Ilha Grande bays. Guanabara Bay showed to be depleted in $\delta^{15}N$ compared to both Sepetiba and Ilha Grande bays. The latter finding suggests substantial contribution of atmospheric nitrogen fixation by cyanobacteria. A positive linear relationship was found between log THg concentrations and $\delta^{15}N$ values for Guanabara and Ilha Grande bays, but not for Sepetiba Bay. Our findings showed trophic magnification factors (TMF) above 1, demonstrating that THg is being biomagnified up the food chains in Rio de Janeiro bays.

1. Introduction

In ecosystems, organisms interact through complex trophic relationships, which involve energy and nutrient flow between trophic levels. Understanding trophic relationships, as well as quantitatively assessing trophic levels is of fundamental importance for the comprehension of ecosystem structure (Lindeman, 1942). In this context, carbon and nitrogen stable isotope measurements have been successfully used for determinating the potential sources of primary productivity, as well as for assessing trophic levels in food webs, respectively (Das et al., 2003a; Fry and Sherr, 1984; Michener and Kaufman, 2007). Therefore, these measurements provide important information about trophic structure and energy flow through ecological communities (Cabana and Rasmussen, 1996; Peterson and Fry, 1987; Vander Zanden et al., 1999). This approach is possible because the stable isotope composition of a consumer is the weighting average of those of its food source in a predictive way (DeNiro and Epstein, 1978; Michener and Schell, 1994; Minagawa and Wada, 1984; Peterson and Fry, 1987).

Some micropollutants, like mercury (Hg), undergo increase in concentrations upward trophic levels, reaching high concentrations in top-chain organisms (Renzoni et al., 1998). The high potential for Hg biomagnification in aquatic systems is due to the organic form of the metal (mainly methylmercury – MeHg), which in marine vertebrates accumulates preferentially muscle (Baeyens et al., 2003; Francesconi and Lenanton, 1992; Wagemann et al., 1998). With regard to the absorption of mercurial species through the gastrointestinal tract, MeHg is the most efficiently taken up form of Hg (Wagemann et al., 1998). Therefore, studying trophic relationships among organisms is also important for a better understating of contaminant bioaccumulation and biomagnification processes. In this context, several studies have used nitrogen stable isotopes as indicators of trophic level for investigating contaminant transfer upward marine food webs (Atwell et al., 1998; Das et al., 2003b; Dehn et al., 2006; Loseto et al., 2008a; McKinney et al., 2011).

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Although there are a number of food web studies dealing with stable isotope ratios and micropollutant flow, these investigations usually focus on northern hemisphere areas, mainly in temperate and polar regions (e.g., Das et al., 2003a; Dehn et al., 2006; Hobson et al., 2002). In tropical areas, only a few studies have dealt with trophic relationships in estuarine and marine food webs using stable isotope measurements (Abreu et al., 2006; Corbisier et al., 2006; Lin et al., 2007). Tropical regions are characterized by high species richness (Begon et al., 2006), which probably promotes more complex trophic relationships due to greater diversity of food items for each species (Paine, 1966).

The present study focuses on three different tropical coastal food webs located in a region under high anthropogenic pressure, the Rio de Janeiro State. Nevertheless, these environments present different degradation levels. Guanabara Bay is the most degraded area among the studied bays. The estuary is considered to be the most degraded system of Brazilian coast (FEEMA, 1990; Kjerfve et al., 1997). Sepetiba Bay presents an intermediate degree of contamination, but it has undergone a significant increase in pollution over the last decades (Lacerda et al., 1987; Molisani et al., 2004). Besides, the Sepetiba Bay drainage basin harbors an expanding industrial park (IFIAS, 1998), which can result in worsening of the degradation scenario. Among the systems considered in the present study, Ilha Grande Bay is the most preserved one. The estuary is considered to be a biodiversity hotspot and includes a high number of protected areas (Creed et al., 2007a).

The objectives of the present study were: (1) to investigate the trophic relationships among organisms from food webs of three tropical coastal ecosystems: Guanabara, Sepetiba and Ilha Grande bays, (2) to compare the trophic structure from the three food webs investigated, (3) to calculate the trophic magnification factors (TMF) of total mercury (THg) between the Guiana dolphin and its prey, and (4) to assess the influence of several factors, such as the trophic position of the Guiana dolphin, on Hg accumulation.

2. Material and methods

2.1. Sampling

Muscle samples were obtained from Guiana dolphins, *Sotalia guianensis*, that were either incidentally captured in gillnet fishery or stranded on the beaches of the three bays of Rio de Janeiro State between 1995 and 2009: the Guanabara Bay ($n = 20$), the Sepetiba Bay ($n = 44$) and the Ilha Grande Bay ($n = 10$). All samples were stored at −20 °C until analysis.

The species preyed by *S. guianensis* were previously identified from stomach content analysis. They include fish, cephalopod and crustacean species (Azevedo et al., 2008; Azevedo, unpublished data). Sampling was performed in winter 2008 (August to October – dry season) and summer 2009 (February and March – wet season). Samples from 34 prey species (five invertebrate and 29 fish species from distinct feeding habitats) were acquired in fishing landings inside Guanabara, Sepetiba and Ilha Grande bays (813 individuals). All specimens were sampled at the body length on which Guiana dolphins prey (Azevedo et al., 2008; Azevedo, unpublished data). Concerning the scianid fish *Micropogonias furnieri*, the specimens were sorted out in two groups regarding their length. *M. furnieri* fitting the size on which Guiana dolphins exert predation were categorized in group "d", as well as individuals larger than 40 cm were placed in group "40". The specimens were weighed, measured and dissected. All samples were frozen and stored at −20 °C until analysis.

Seston samples were collected using 75-nm-mesh plankton net in the inner part, at low tide, as well as in the entrance, at high tide, of each bay. This sampling was carried out in July 2008 (winter) and January 2009 (summer).

2.2. Stable isotope measurements

Stable isotopes measurements of carbon and nitrogen were carried out in muscle samples from Guiana dolphins, fishes and invertebrates. After being dried at 60 °C (72 h), samples were ground into a homogeneous powder. Since all muscle samples from the present study presented low lipid content (C:N < 4.0), no lipid extractions were carried out (Post et al., 2007). Stable isotope measurements were performed on a V.G. Optima (Isoprime, UK) isotope ratio mass spectrometer coupled to an N-C-S elemental analyzer (Carlo Erba). Reference materials (IAEA CH-6 and IAEA-N1) were also analyzed and the precision of replicate analyses was 0.3‰. Stable isotope ratios are expressed in delta notation as part per thousand. Carbon and nitrogen ratios are expressed relative to the V-PDB (Vienna Peedee Belemnite) standard and to atmospheric nitrogen, respectively.

2.3. Total mercury (THg) determination

Aliquots of approximately 0.4 g of muscle (wet weight) were digested with 1 mL of hydrogen peroxide and 5 mL of sulfuric:nitric acid mixture (1:1). The solution was then heated to 60 °C for 2 h in a water bath, which was followed by the addition of 5 mL of potassium permanganate 5% solution and heating to 60 °C for more 15 min. After overnight digestion, THg concentration was determined by Cold Vapor/AAS (FIMS-400, Perkin-Elmer) with sodium borohydride as reducing agent. Blanks were carried through the procedure in the same way as the sample. The standard reference material DORM-3 (National Research Council, Canada) was analyzed in every run and our results were in good agreement with certified values (mean recovery ± SD = 101.44 ± 3.57%).

2.4. Statistical analysis

Mean carbon and nitrogen isotopic values were calculated for Guiana dolphins and for each prey species. The fish species were classified into five feeding types (see Tables 1 and 2). The Kolmogorov–Smirnov test was used in order to test for normality of the data. ANOVA and post hoc Tukey tests were used for comparing nitrogen and carbon isotopic values among feeding types (including cephalopod and crustacean species) and among the three bays. The nonparametric Kruskal–Wallis and post hoc multiple comparison tests were applied when the data distribution did not follow the rules of normal distribution. The nonparametric Mann–Whitney *U* test was performed for comparison between seasons (winter × summer sampling). Simple linear regression analysis was used for investigating relationships between $\delta^{15}N$ and logarithmic concentrations of THg, as well as for determinating trophic magnification factors (TMF). TMF is calculated as the antilog of the regression slope with base 10 and can be used for quantifying food web biomagnification (Borgå et al., 2011; Fisk et al., 2001). Therefore, this tool was used for calculating Hg biomagnification in different ecosystems.

3. Results and discussion

3.1. Trophic relationships

Summaries of $\delta^{13}C$ and $\delta^{15}N$ values for cephalopods, crustaceans, fishes and Guiana dolphins are given in Tables 1 and 2, respectively, as well in Fig. 1.

Carbon isotope ratios have proved to be useful in identifying the relative input of dietary resources from different food webs, as $\delta^{13}C$