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MERCURY AND PLANKTON IN TROPICAL MARINE ECOSYSTEMS: A REVIEW

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ABSTRACT

Mercury (Hg) is an exogenous and harmful metal that accumulates in the tissues of organisms along food chain. Bioaccumulation by plankton is therefore of great significance for understanding marine processes concerning Hg accumulation and biomagnification throughout the food chain. Plankton has a short life cycle and plankton species composition respond quickly to environmental changes in the water column, making it a water quality indicator. There is a consensus that Hg enters the food chain via phytoplankton, and then is accumulated by the other links in the chain, via trophic transfer. While Hg is bioconcentrated from water by phytoplankton, comparatively little is known about the concentrations, dynamics, and controls on Hg bioavailability in marine ecosystems. Plankton is one of the last matrixes studied by Hg researchers in a systematic manner. As the base of food chain, these organisms have been the subject of several studies on the biological effects of Hg contamination in coastal ecosystems worldwide, such as in Australia, coast of California (USA) and Baltic Sea. However, few studies in the literature have focused on tropical marine ecosystems. In this review, mercury data on tropical marine plankton is presented based on previous studies on the Tropical Pacific, in Arabian Sea, Gulf of Thailand and the South Atlantic. These studies have contributed to our understanding of mercury behavior, fate, and transport of this element in tropical marine ecosystems. The lack of results in the scientific literature about Hg in marine plankton could be attributed to difficulty in collection, preparation and analysis of this type of samples. Collection is dependent of parameters like luminosity, moon phase, tidal cycle, depth of the water column and physical and chemical parameters of water that influence in the quantitative and qualitative taxonomic groups of plankton present.
Keywords: Bioaccumulation; biomagnification; trophic transfer; methylmercury; inorganic mercury.

RESUMO

MERCÚRIO E PLÂNCTON EM ECOSSISTEMAS MARINHOS TROPICAIS: UMA REVISÃO.
O mercúrio (Hg) é um metal exógeno e prejudicial à saúde que se acumula nos tecidos dos organismos ao longo das cadeias alimentares. O estudo da bioacumulação do Hg pelo plâncton é de grande importância para a compreensão dos processos marinhos relacionados à sua acumulação e biomagnificação. O plâncton é um indicador da qualidade da água, pois, tem um ciclo de vida curto, e a sua composição de espécies responde rapidamente às mudanças ambientais da coluna d' água. Há um consenso de que o Hg entra na cadeia alimentar via fitoplâncton, que posteriormente, é bioacumulado pelos demais elos da cadeia através da transferência trófica. Enquanto o fitoplâncton bioconcentra o Hg da água, comparativamente, pouco se sabe a respeito das concentrações, dinâmicas e controles sobre a biodisponibilidade e assimilação do Hg nos ecossistemas marinhos. O plâncton é uma das últimas matrizes a ser estudada de forma sistemática em pesquisas sobre Hg. Estes organismos da base da cadeia alimentar têm sido objeto de vários estudos sobre os efeitos biológicos da contaminação dos ecossistemas aquáticos, como os ocorridos na Austrália, costa da Califórnia (EUA) e Mar Báltico. Entretanto, poucos deles reportaram este assunto em ecossistemas marinhos tropicais. Nesta revisão são apresentados alguns dados sobre o mercúrio em plâncton marinho tropical, baseando-se em estudos desenvolvidos no Oceano Pacífico Tropical, no Mar Arábico, no Golfo da Tailândia e no Atlântico

Sul. Estes estudos contribuíram para um melhor entendimento sobre o comportamento, destino e transporte do mercúrio nos ecossistemas marinhos tropicais. A escassez de dados sobre o Hg em plâncton marinho pode ser atribuída à dificuldade de coleta, preparo e análise destas amostras. As coletas comumente são influenciadas por alguns parâmetros, os quais definem quantitativamente e qualitativamente os grupos taxonômicos de plâncton presentes. Dentre esses parâmetros podem ser citados a luminosidade, fase da lua, ciclo das marés, a profundidade da coluna de água e parâmetros físicos e químicos da água.
Palavras-chave: Bioacumulação; biomagnificação; transferência trófica; metilmercúrio; mercúrio inorgânico.

RESUMEN

MERCURIO Y PLANCTON EN ECOSISTEMAS MARINOS TROPICALES: UNA REVISIÓN. El Mercurio (Hg) es un metal exógeno y nocivo que se acumula en los tejidos de los organismos a través de la cadena alimenticia. La bioacumulación por parte del plancton es por lo tanto de gran importancia para el entendimiento de los procesos en los ecosistemas marinos relacionados con la acumulación y biomagnificación del mercurio en las cadenas alimenticias. El plancton puede ser utilizado como un indicador de calidad del agua ya que por sus cortos ciclos de vida y su composición de especies responde rápidamente a los cambios que ocurren en la columna de agua. Existe consenso en cuanto a que el Hg ingresa a la cadena alimenticia a través del fitoplancton y que posteriormente se acumula en otros eslabones de la cadena mediante transferencia trófica. Aunque el Hg presente en el agua es bioacumulado por el fitoplancton, poco se sabe acerca de las concentraciones, dinámicas y controles que afectan la biodisponibilidad del Hg en los ecosistemas marinos. El plancton es una de las últimas matrices estudiadas de manera sistemática en las investigaciones sobre el Hg. Como base de la cadena alimenticia, estos organismos han sido objeto de varios estudios sobre los efectos biológicos de la contaminación por mercurio en ecosistemas costeros a nivel mundial, tales como Australia, la costa de California (EUA) y el Mar Báltico. Sin embargo, pocos estudios en la literatura se han enfocado en los ecosistemas marinos tropicales. En esta revisión son presentados algunos datos sobre el mercurio en plancton marino tropical, con base en estudios desarrollados en el Océano Pacífico Tropical, el Mar Arábigo, el Golfo de Tailandia y el Océano Atlántico Sur. Estos estudios han contribuido al entendimiento del comportamiento del mercurio, su destino y transporte en los ecosistemas marinos tropicales. La escasez de datos de mercurio en el plancton marino puede ser atribuida a las dificultades en la recolección, preparación y análisis de este tipo de muestras. Los muestreos son con frecuencia influenciados por algunos parámetros (luminosidad, fase lunar, régimen de mareas, profundidad de la columna de agua, etc.) que definen cualitativa y cuantitativamente los grupos taxonómicos de plancton presentes.
Palabras clave: Bioacumulación; biomagnificación; transferencia trófica; metil-mercurio; mercurio inorgânico.

INTRODUCTION

Great concern exists regarding the increase of environmental pollution, that results in the increase of intensive and extensive use of chemical products, the release of potentially toxic substances and industrial and urban effluents, as well as their effects on ecosystems and, consequently, on humans (Boening 2000). With the increase of industrial, agricultural and mining activities, as well as the population growth observed in recent centuries, several contaminants (organic matter, organic pollutants and a large number of metal compounds) have been released into the environment, especially into the atmosphere and aquatic and terrestrial ecosystems (Srogi 2008). The contaminants of metal compounds present in the effluents of anthropogenic activities have low solubility in water, thus resulting in low concentrations, even in areas close to their emission point.

Mercury Hg is a metal of environmental interest that shows naturally high concentrations in several regions. Environmental exposure to mercury via food chain, particularly for higher trophic level consumers, including humans, is significantly higher, since this metal presents high toxicity and the ability to undergo biomagnification along the trophic chains (Agusa *et al*. 2007).

Mercury has no known normal metabolic function (i.e. xenobiotic) and its presence in living organisms is potentially hazardous. It occurs in different chemical and physical forms. The most abundant are elemental Hg (Hg^o), divalent mercury (Hg^{+2}), methylmercury (MeHg, CH_3Hg^+), dimethylmercury (DMHg, CH_3HgCH_3), and ethylmercury (EtHg, $CH_3CH_2Hg^+$), each of which is unique with regard to exposure pattern, metabolism, and toxic effects. The toxicity of mercury compounds depends not only on the form of mercury and the route of entry, but also on dosage (Gibiĕar *et al*. 2007). Mercury compounds can affect productivity, reproduction and survival of coastal and marine animals, and can eventually be hazardous to human health (WHO 1989).

This metal in its more toxic organic form, methylmercury, is bioaccumulated up to a million times over the aquatic trophic chain from its base (plankton) by adsorption to the body surface to organisms at the top of the food chain (predatory fish and mammals) by food ingestion.

While MeHg is bioconcentrated from water by marine phytoplankton (Mason *et al*. 1996, Lawson & Mason 1998, Kehrig *et al*. 2010, 2011), comparatively little is known about the concentrations, dynamics, and controls on MeHg bioavailability and uptake in marine environments. MeHg is further biomagnified (10^3−10^4) between trophic levels from phytoplankton to top-predators (2−4 trophic levels), and the initial bioconcentration of MeHg by phytoplankton represents the greatest single contribution to the food chain. Uptake of dissolved MeHg by primary producers establishes a pool of bioavailable contaminant that can be accumulated by heterotrophic organism. Nearly all of the MeHg accumulated by zooplankton (Wang & Fisher 1998) and fish (Hall *et al*. 1997) is from their diet, and inorganic mercury complexes accumulated by phytoplankton are not as readily assimilated by grazers (Mason *et al*. 1996) and thereby not transferred to fish. The factors influencing MeHg bioconcentration by primary producers in marine ecosystems and, by extension higher trophic levels, are not well known. However, bioavailability and chemical species (especially free ions) influences mercury toxicity and its bioaccumulation by organisms in the marine environment (Wang & Rainbow 2005).

Plankton is one of the last ecological groups studied by Hg researchers in a systematic manner. Probably, this was due to sampling and analytical constraints. There is a consensus that Hg enters the food chain via phytoplankton, and then is accumulated by the other links in the chain, via trophic transfer. Trophic processes that transfer mercury to higher levels must include the mercury concentrations/speciation and characterization of plankton communities, at least to the level of large groups. In general, Hg accumulation by plankton is size-dependent, and is not related to the taxonomic groups' composition of planktonic organisms (Kainz & Mazumber 2005). Also, the inclusion of plankton and abiotic environmental variables relationships might better explain temporal and spatial patterns of mercury burdens in larger animals of interest for human health and nature conservation.

In this context, tropical ecosystems, which combined contain as much as 75% of the global biodiversity, have been neglected. Coastal waters of the tropics and subtropics possess unique and highly productive ecosystems, including mangrove forests, seagrass meadows, and coral reefs. The negative effects of chemical contaminants on tropical marine ecosystems are of increasing concern as human populations expand adjacent to these communities. Watershed streams and ground water carry a variety of chemicals from agricultural, industrial, and domestic activities, while winds and currents transport pollutants from atmospheric and oceanic sources to these coastal ecosystems (Peters *et al*. 1997).

PLANKTON

Plankton is a group of autotrophic and heterotrophic drifting organisms in aquatic environments that are the base of food chain in these environments. Included in this group are bacterioplankton, phytoplankton and zooplankton. Plankton abundance and distribution depend on nutrient concentrations, chemical and physical conditions of water, and the abundance of other plankton. Their abundance varies horizontally, vertically and seasonally. In one trophic level above the prokaryotes, there are the free-living protist, mainly formed by diatoms, dinoflagellates and protozoa, which are responsible for primary production. Protozoa, especially ciliates and flagellates, are also able to participate in the bacterial consortia, stimulating the bacterial activity and also being the

link among the base and the other trophic levels. This biotic interaction occurs through the characteristics of predation, foraging and dispersal ability presented by ciliates and flagellates (Sigee 2005).

PLANKTON AND MERCURY

Primary producers play a significant role in nutrient cycling, water quality and energy flow as a food source for heterotrophic organisms. They also represent an important exposure route of mercury (Watras *et al.* 1998) to primary consumers, such as zooplankton and filter-feeder molluscs (Okay *et al.* 2000, Anandraj *et al*. 2008). The reduction of primary production affects the amount of food available to organisms of other trophic levels, especially aquatic herbivores and/or planktivorous in the marine ecosystem (Yap *et al.* 2004). On the other hand, zooplankton occupies an intermediate position between primary producers and large consumers such as fish, and determines the characteristics of matter cycling and energy flow through the ecosystem (Swar & Fernando 1980). Zooplankton has the ability to accumulate both inorganic and organic forms of mercury from the aquatic environment, from either ingested food and/ or directly from the dissolved phase (Wang & Fisher 1998).

Autotrophic and heterotrophic organism in the 'microbial loop' are key components in the transfer of carbon and elements, including mercury, through marine food chains (Fenchel 2008), influencing the biogeochemical cycling of the aquatic ecosystem, as well as being major contributors to vertical fluxes (Fisher *et al*. 2000). The 'microbial loop' is supposed to be an especially important feature in the ecology of tropical waters, where temperature, dissolved organic carbon contents (DOC) and solar radiation are permanently abundant.

The study of the microbial food chain can be considered essential in the understanding of the energy flow and nutrient cycling loading in the coastal ecosystem (Burford *et al.* 2008). The term 'microbial loop' was originally coined by Azam *et al.* (1983), and includes several trophic levels of the microbial food chain and a large fraction of the organic carbon particulate. These processes can influence the bioaccumulation of trace elements by estuarine microorganisms. The total amount of trace elements accumulated by prokaryotes (microplankton) will affect the quantity of trace metals transferred trophically along the food chain, due to the fact that mesoplankton (copepods and cladocerans) grazing on microplankton (diatoms and dinoflagellates) and both of these plankton fractions served as food source for small fish (Fenchel 2008). The nature of metal binding in microplankton also possesses the potential to significantly affect trophic transfer (Ng *et al*. 2005).

The main effect of the 'microbial loop' on mercury cycling in the water column is the acceleration of organic matter mineralization and thus regenerates the nutrients for primary production (Fenchel 2008). A large fraction of the organic matter that is synthesized by primary producers becomes dissolved organic matter (DOM) and is taken up almost exclusively by bacteria. Most of the DOM is respired to carbon dioxide and a fraction is assimilated and re-introduced into the classical food chain (phytoplankton to zooplankton to fish) (Fenchel 2008). Therefore, the dynamics of mercury through the base food chain is influenced by the 'microbial loop'. A simplified scheme of the 'microbial loop' and trophic transfer of mercury, as methylmercury, through a marine aquatic food chain is presented in Figure 1.

The assimilation of dissolved mercury in the water column is an important route for the bioaccumulation of mercury by aquatic organisms that have small body size and greater relative surface area, such as microplankton (Reinfelder *et al.* 1998). However, with the increase in body size of aquatic organisms, as in the case of mesoplankton, a decrease in the contribution of dissolved mercury in the water is observed, and consequently, the trophic transfer becomes the more efficient means for assimilation and accumulation of mercury in the form of methylmercury (Mason *et al.* 2000).

Dissolved methylmercury, which is the most biologically available organic form of mercury, is bioaccumulated up to a million times in microscopic particles, including phytoplankton and bacteria, at the base of aquatic trophic chain by adsorption to their body surface in the water column (Mason *et al.* 1996; Miles *et al.* 2001). These methylmercury-enriched particles are then consumed by zooplankton, which in turn are a primary food source of larval, juvenile, and some adult fish (Hall *et al.* 1997). Zooplanktonic organisms such as copepods assimilate

methylmercury (MeHg) much more efficiently than inorganic mercury (Hg_{inorg}), presenting the relative assimilation efficiency of MeHg to Hg_{inorg} of 2.0 (Lawson & Mason 1998). Kainz & Mazumder (2005) demonstrated that a bacterial diet could be better at predicting variations of MeHg concentrations in zooplankton (copepods) than essential algal (phytoplankton) diet.

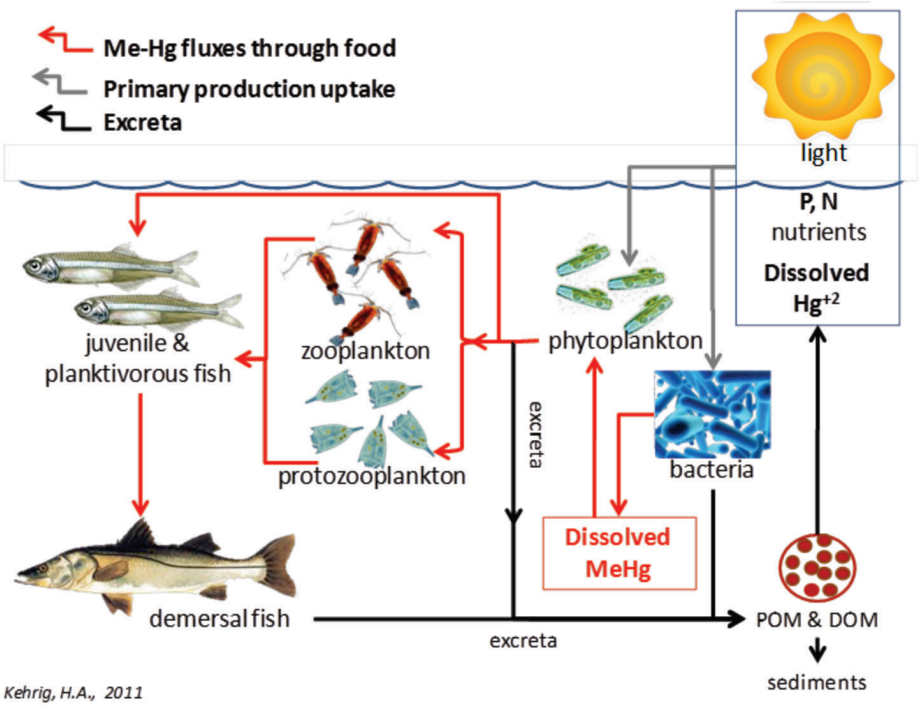

Figure 1. 'Microbial loop' and trophic transfer of methylmercury (MeHg) through a marine food chain.

Plankton has a short life cycle and their species composition respond quickly to environmental changes in the water column making it a water quality indicator (Berzins & Pejler 1987). Planktonic algae have been so far used as bioindicators of deteriorating water quality due to the fact that they are used to estimate trophic status in aquatic systems and are good indicators of nutrient loading by nitrogen and phosphorous. Some variations in plankton community structure, mainly zooplankton, have been associated with variations in the concentrations of mercury in fish tissues (Stemberger & Chen 1998, Chen & Folt 2005). Thus, physical and biogeochemical characteristics of the aquatic environment that affect growth dynamics of phytoplankton and the zooplankton communities that depend on them may also affect uptake of mercury into the pelagic-based food chain (Stewart *et al*. 2008).

Planktonic community provides the most reliable index of increased eutrophication and changes in water quality in aquatic systems (Linton & Warner 2003). Considerable evidence indicates that coastal eutrophication has affected the cycling of carbon, nitrogen and phosphorous in coastal systems, increasing the primary production and planktonic biomass, changing the biogeochemical cycles of mercury. Thus, coastal eutrophication may potentially affect metal uptake, toxicity and trophic transfer in aquatic food chains (Wang *et al*. 2001). However, there is only limited knowledge about the influence of coastal eutrophication on the uptake of metals by aquatic organisms (Wang *et al*. 2001).

Under bloom dilution, as the algal biomass increases, the concentration of mercury as methylmercury per cell decreases, resulting in a lower dietary input to the grazer (zooplankton) and reducing bioaccumulation in algal-rich eutrophic systems (Pickhardt *et al*. 2002). In this case, there is a reduction of trophic transfer of Hg through the food chain and the consequent reduction of Hg biomagnification (Chen & Folt 2005).

The study of mercury, mainly as methylmercury bioaccumulation by marine autotrophic and heterotrophic organisms is of great significance. Therefore, it is of great importance to obtain a better understanding of the tropical coastal processes

concerning the accumulation of mercury and its possible biomagnification throughout the base of the marine food chain. Organisms at the base of food chain have been subject of several studies of the biological effects of contamination on plankton in coastal ecosystems worldwide (Barwick & Maher 2003, Stewart *et al*. 2004, Telesh 2004, Thompson *et al*. 2007). However, in the literature few studies have been documented for tropical marine ecosystem worldwide (Knauer & Martin 1972, Hirota *et al*. 1979, Zindge & Desai 1981, Hirota *et al*. 1983, Thongra-ar & Parkpian 2002, Al-Majed & Preston 2000, Al-Reasi *et al*. 2007, Kehrig *et al*. 2009a, 2009b, 2010, 2011).

Some tropical lakes worldwide have been investigated extensively (Bowles *et al*. 2001, Kidd *et al*. 2003, Campbell *et al*. 2008, Huguet *et al*. 2010) and have contributed to our understanding of mercury behavior, fate, and transport of this element in freshwater systems. Furthermore, tropical coastal waters are less monitored than marine environments in the Temperate and Polar Regions, in particular the South Atlantic Ocean, which is often considered less contaminated then the northern ocean.

The lack of results in the scientific literature about Hg in marine plankton could be attributed to difficulty in collection, preparation and analysis of this type of samples. Collection is dependent of parameters like luminosity of the day, moon phase, tidal cycle and depth of water column and physical and chemical parameters of water, which influence in the quantitative and qualitative taxonomic groups of phytoplankton and zooplankton present. In general the marine plankton taken by horizontal hauls produce little amount of dry mass in the sample, which difficult chemical analysis of total and/or methylmercury.

SOME STUDIES ABOUT MERCURY AND PLANKTON IN TROPICAL MARINE ECOSYSTEMS

One of the first studies developed in the Tropical Pacific Ocean, from September to December of 1975, measured total mercury in zooplankton collected in eight stations in order to obtain data as a standard for unpolluted waters (Hirota *et al*. 1979). Mercury was determined in each zooplankton group that was sorted to the important groups. The maximum value of total mercury (0.13µg $Hg.g^{-1}$on dry wt.) was found in ctenophores samples at Fiji waters (17°52.0'S and 175°25.0'E) and the minimum value was recorded (0.019µg $Hg.g^{-1}$ on dry wt.) in thaliaceans at northeastern Australia coast (16°12.0'S and 146°39.0'E). The total mercury values in Hirota *et al.* (1979) study (average: 0.058µg $Hg.g^{-1}$) were lower than those found previously in zooplankton samples (0.081 to 0.448µg $Hg.g^{-1}$, average: 0.130µg $Hg.g^{-1}$) collected in a transect between Hawaii and Monterey, California, USA, by Knauer & Martin (1972).

Zooplankton, copepod, were collected in three inland sea regions, Yatsushiro-kai (Minamata Bay), Ariake-kai and Seto-naikai, along the coast of Western Japan from April of 1979 to February of 1981 (Hirota *et al*. 1983). The values of total mercury obtained for copepods from Minamata Bay were higher (over 0.4µg.g^{-1}, on dry wt.) than those in the other two regions investigated in this study. Such results suggested that Minamata Bay, where Minamata Disease was caused by discharge of methylmercury about twenty-five years ago, was still polluted by mercury. The mercury contends of copepod collected at Seto-naikai were the lowest found in this study (0.08µg $Hg.g^{-1}$), indicating that this environment was not polluted by mercury (Hirota *et al*. 1983).

Mercury is a national pollutant in Thailand that is situated in the tropical monsoon belt of Southeast Asia. Considering the data obtained from several reports beginning in 1974, the higher mercury concentrations in Thai coastal water were found in the early period, especially from 1979 to 1986, than in recent years. In order to document this period status of mercury contamination in Thai coastal environments, composite plankton, without any reference about plankton size classes and their taxonomic groups, were collected at Inner Gulf of Thailand from 1976 to 1977. These samples presented low values of total mercury (0.00295 ± 0.0007µg $Hg.g^{-1}$ on wet wt) that ranged from 0.002 to 0.0045µg $Hg.g^{-1}$ (Thongra-ar & Parkpian 2002).

Concentrations of total mercury and methylmercury were measured in 27 zooplankton samples that were collected with a 250 µm mesh net at a coastal food chain of the Gulf of Oman (18 for A'Seeb and 9 for Matrah). The tropical aquatic ecosystem of the Gulf of Oman, the northern part of the Arabian Sea situated between Oman and Iran

is extremely arid with very low precipitation levels. Zooplankton samples principally were constituted of copepods, the most dominant and diverse group of zooplankton for the Arabian Sea and Gulf of Oman. Total mercury concentrations of zooplankton samples ranged from 0.010 to 0.037µg $Hg.g^{-1}$ on wet wt. The mean concentrations for samples collected were 0.020 ± 0.008 and 0.022 ± 0.008µg $Hg.g^{-1}$ for Matrah and A'Seeb, respectively. The MeHg proportion of Hg spanned from 1 to 19% (Al-Reasi *et al*. 2007). The range reported in Al-Reasi *et al.* (2007) study was higher than that (0.003 – 0.010µg $Hg.g^{-1}$ wet wt.) determined by Al-Majed & Preston (2000) for samples from Kuwait Bay, a northern embayment of the Arabian Gulf. Methylmercury found in zooplankton samples from Kuwait Bay accounted for 25% of Hg. However, Hg range was well below that documented for polluted water bodies such as Bombay harbor (0.103–0.139µg $Hg.g^{-1}$) (Zindge & Desai 1981).

One of the first studies with different size classes of plankton and trace elements in the South Atlantic Ocean was carried out in a tropical area of the Brazilian Southeast coast from August of 2005 to October of 2007 (Kehrig *et al*. 2009a, 2009b, 2010, 2011). Methylmercury and mercury were determined in a 'microbial loop' composed by three size classes of autotrophic and heterotrophic microorganism samples, 1.2-70µm (seston, SPM), 70-290µm (microplankton) and ≥290µm (mesoplankton) from five sampling stations within a polluted eutrophic bay, Guanabara Bay (22°S, 43°W), and one external point under the influence of the bay (Point 6; Figure 2). In this bay, an important source of mercury is a chor-alkali plant, which is located in the most polluted area of its drainage basin, in the northwest portion of the bay. Guanabara Bay plays an important role as a nursery for several groups of primary producers (diatoms), bacteriovorous and herbivorous protists (Tintinnida and other ciliates) and the copepods, which occupied the highest trophic level in the 'microbial loop' at its aquatic ecosystem.

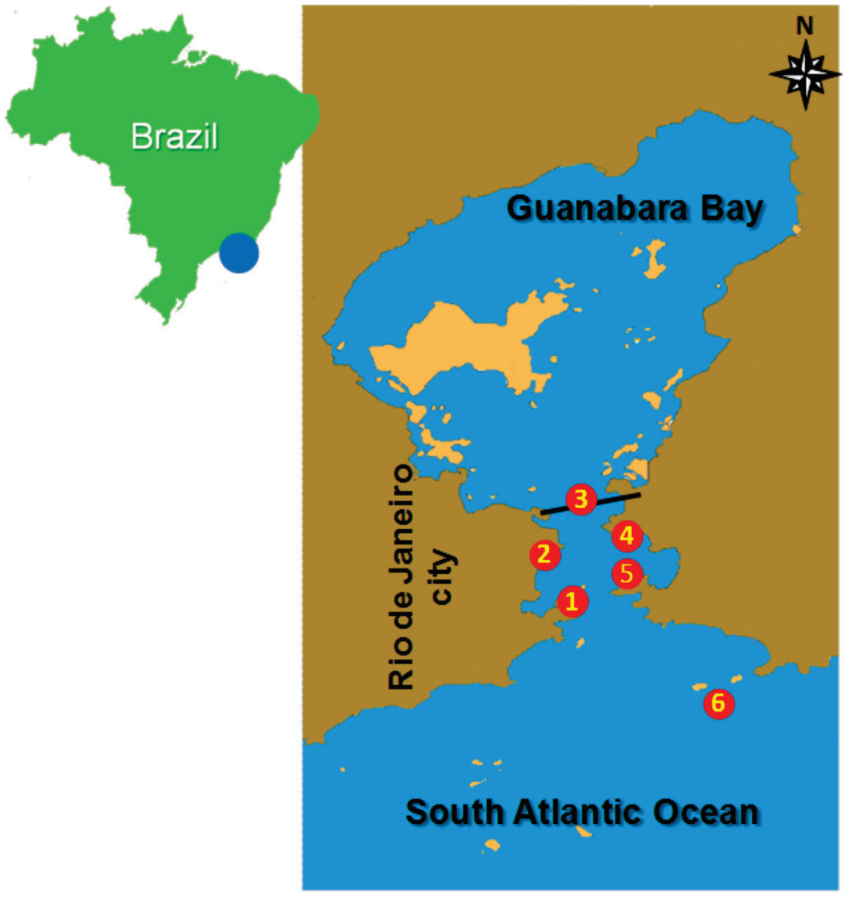

Figure 2. Sampling points in Guanabara Bay (Rio de Janeiro, Brazil).

Planktonic organisms were sampled from the superficial water layer of Guanabara Bay on August 2005, at neap tide cycle during the day. The ecological composition of the planktonic community found could be considered typical of Guanabara Bay (Kehrig *et al*. 2009a). It is mostly composed of cyanobacteria, diatoms, dinoflagellates, copepods, cladocerans and fish eggs and larvae as previously observed by Valentin *et al*. (1999). The highest density of fish eggs and larvae was detected closer to the entrance of the bay (Points 1 and 5; Figure 2) and its main circulation channel (Point 3; Figure 2) as previously observed by Valentin *et al*. (1999). The increasing phytoplankton biomass in Guanabara Bay for the past three decades indicates a progressive eutrophication of this ecosystem. However, the high density of copepods and cladocerans in mesozooplankton population of this bay indicated a good water quality, due to the fact that these microcrustaceans are sensitive to environmental degradation (Valentin *et al*. 1999).

In this same study conducted on August 2005, no difference was observed in spatial comparisons of methylmercury and mercury concentrations among the five sampling stations within Guanabara Bay, and also between them and the external point under the influence of the bay (Point 6; Figure 2). The different composition of plankton taxonomic groups among the sampling stations did no present influence on the concentrations of these pollutants in all organism size classes. However, methylmercury and mercury concentrations increased with the organism size class, presenting significant difference (Kruskal-Wallis ANOVA). The mean mercury concentration ranged from 168.5 ± 136.8μg.kg^{-1} dry wt. for seston, 28.3 ± 11.1μg.kg^{-1} dry wt. for microplankton and 104.7 ± 73.4μg.kg^{-1} dry wt. for mesozooplankton. The increasing ratios of methylmercury to mercury (44% for seston, 60% for microplankton and 77% for mesozooplankton) at successively higher trophic levels of the microbial food chain corresponded to a transfer from the lower trophic level, primary producers (cyanobacteria and diatoms), protist bacteriophagous (tintinnids) to primary consumers (copepods, nauplii, cladocerans and fish larvae – mesozooplankton), suggesting that biomagnification is occurring throughout this food chain. The lowest methylmercury and mercury concentrations found in the planktonic microorganisms in the five sampling stations within Guanabara Bay were probably related to the eutrophic conditions of this ecosystem, elevated suspended particles content and high biological productivity (Kehrig *et al*. 2009a).

On August 2005, water partition coefficients (PCs) in microplankton were fourfold higher for MeHg than for Hg_{inorg}; and water PCs in mesoplankton were twenty-six times higher for MeHg than Hg_{inorg}. Difference between microplankton and mesoplankton MeHg bioaccumulation factor (BAF) was higher (0.60 log units) than Hg_{inorg} BAF (0.24 log units), indicating that trophic transfer of MeHg between planktonic organisms is more efficient than Hg_{inorg} transference. MeHg concentrations, proportion of mercury as MeHg and its biotransference factors (BTFs) in the microplankton and mesoplankton increased with increasing trophic level while biotic concentrations of Hg_{inorg} and proportion of mercury as Hg_{inorg} decreased indicating that MeHg was indeed the biomagnified species of mercury (Kehrig *et al*. 2010).

Chlorophyll *a* and the total of organic carbon (TOC) in suspended particulate matter (SPM) or seston, which was collected at the five sampling stations within Guanabara Bay, ranged from 6.6 to 27.7μg.L^{-1} and 0.9 to 2.3mg.L^{-1}, respectively. MeHg concentrations in SPM ranged from 8.3 to 47.2μg.g^{-1} and were approximately 13% of the total mercury (Hg). Dissolved MeHg in water was low and ranged from 0.16 to 0.42ng.L^{-1}. The predominant chemical species of mercury in estuarine water is inorganic, since only 11.2% of Hg in water was presented as MeHg. The highest concentrations of MeHg in water were found in sampling stations close to the bay mouth (Points 1 and 5; Figure 2), near the confluence of Atlantic Ocean and estuarine waters. However, SPM samples from these stations presented the lowest MeHg concentrations (Kehrig *et al*. 2011).

MeHg in microplankton collected at the five sampling stations within Guanabara Bay ranged from 9.3 to 23.0μg.kg^{-1} dry wt. The highest MeHg concentrations in microplankton were found in samples from Points 1 and 5; Figure 2. The microplankton samples collected at these stations were composed of cyanobacteria, diatons, dinoflagellates and tintinnids (approximately 2%, 65%, 1% and 32%, respectively). MeHg found in microplankton and the number of cyanobacteria present in it showed a positive and significant correlation (R^2=0.72; $p<0.01$) (Kehrig *et*

al. 2011). The activity of sulfate-reducing bacteria, or cyanobacteria, is associated to the methylation process of Hg_{inorg}; i.e. with the formation of methylmercury (Coelho-Souza *et al*. 2006). In brazilian aquatic ecosystems, cyanobacteria is a significant component of the marine nitrogen cycle and an important primary producer in many areas of the ocean, where they are associated with the organification of mercury through methylmercury production; however showing low methylation potentials (Coelho-Souza *et al*. 2006).

MeHg in microplankton and TOC in SPM showed an inverse and significant correlation (R^2=0.85; p<0.001) (Kehrig *et al*. 2011). This inverse relationship was observed due to the fact that organic carbon interacts very strongly with Hg, affecting its speciation, solubility, mobility and toxicity in the aquatic ecosystems. TOC reduces the bioavailability of MeHg such that bioaccumulation factor decreases with increasing organic content of the exposure medium (Wright & Mason 2000). The samples from the point close to Marina (Point 2; Figure 2) presented the lowest MeHg in microplankton (9.3µg.kg^{-1}) and also, the highest concentrations of TOC (2.3mg.L^{-1}) in SPM.

The samples of microplankton from Point 2; Figure 2 were composed of diatoms (approximately 60%) and did not present any cyanobacteria in its composition. A significant and positive correlation was observed between the concentration of chlorophyll *a* and the number of cyanobacteria present in plankton (R^2=0.75; p<0.05). According to the results found for chlorophyll *a*, this environment presents a high primary productivity that is accomplished by the autotrophic organisms present in microplankton, as cyanobacteria and diatoms (Kehrig *et al*. 2011).

CONCLUDING REMARKS

Accumulation of Hg in marine plankton is understudied. Plankton is probably the marine ecological group that will be most severely affected by climate changes, but in coastal areas this might be hidden by other most pressing man-driven phenomena as eutrophication and reduced oxygen levels. One of the questions that plankton studies will help to answer is the relationship between mercury cycling in red tide events. How will they affect each other? As these phenomena will be more frequent with climate changes due to water temperature rise, dissolved oxygen depletion and increased sewage contamination of coastal areas, will mercury uptake and transfer become more efficient? Or will there be a more significant flux from the water column to the sediments as the algal bloom dies and decays?

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