RELATIONSHIPS BETWEEN PCB 153 AND STABLE NITROGEN ISOTOPES IN A GUIANA DOLPHIN (*Sotalia guianensis*) FOOD WEB, GUANABARA BAY, BRAZIL

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Introduction

Guanabara Bay, Southeastern Brazil, is the most anthropogenically impacted system of Brazilian coast[1]. Its drainage basin houses a population of 14 million people and 12 000 industries. As a consequence, discharge of domestic sewage and micropollutants are released daily into the Bay[2]. The concern about the pollution increases when the biomagnification process is considered, since high concentrations of some micropollutants reach high levels of the food web[3]. The biomagnification process is observed with greater intensity while investigating the environmental behavior of the most recalcitrant organochlorine compounds, such as PCB 153[4].

Guiana dolphin (*Sotalia guianensis*) is a coastal species that presents high site fidelity and occupies high levels of food webs[5]. Therefore, the species can be used as indicator of micropollutant trophic flow. Guiana dolphin is an opportunistic species, which preys on organisms from different habits and trophic levels. Teleost fish are the predominant food items, but crustaceans and cephalopods are also important in the diet of these mammals[6].

The nitrogen stable isotope measurements have been successfully used as a complementary tool for investigating contaminant transfer upward marine food webs[7,8]. This approach is possible because the nitrogen isotopic ratio in a consumer tissue is related in a predictive way to that in its diet[9] and several studies have used nitrogen stable isotopes as indicators of trophic level[7,8].

The present study aimed to evaluate the organochlorine compound flow through the Guanabara Bay food web by examining the relationship between the nitrogen isotopic ratio and PCB 153 concentration in Guiana dolphin and its prey.

Materials and methods

Blubber and muscle samples were collected from Guiana dolphins either incidentally captured in fishing operations or stranded on the beaches in Guanabara Bay, Southeastern Brazil, between 2000 and 2009 (n = 6). Muscle samples from nine prey species (one invertebrate and eight fishes) were acquired in fishing landings inside the Guanabara Bay: *Anchoa* spp., *Cynosnion leiarchus*, *Cetengraulis edentulus*, *Chloroscombrus chrysurus*, *Serranus auriga*, *Micropogonias furnieri*, *Mugil* spp., *Sardinella abrasiliensis*, *Litopenaeus schimitti*. Prey sampling was performed in winter 2008 (August to October) and summer 2009 (February and March).

The stable nitrogen isotope measurement was carried out in muscle tissue from Guiana dolphins and their prey species. After being dried at 60ºC, samples were ground into a homogeneous powder. Isotopic compositions were determined on a V. G. Optima isotope ratio mass spectrometer (Micromass) coupled to an elemental analyzer (Carlo Erba). The nitrogen isotopic ratios are expressed in delta notation (δ) as parts per thousand (‰), calculated according to: $\delta^{15}N = [(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1] \times 1000$. The standard used was the atmospheric nitrogen.

For PCB 153 determination, aliquots of 1g of blubber from Guiana dolphins and composite samples of muscle tissue from prey species were extracted in a soxhlet system with a mixture of hexane: dichloromethane (1:1). An aliquot (1ml) was mixed with 5mL of sulfuric acid for the clean-up. Two internal standards (PCB 103 and PCB 198), as well as the GC internal standard (TCMX), were added for quantification. The lipid content was determined gravimetrically. Analyses were performed on a gas chromatographer Agilent Technologies GC-7890 with electron capture detector (ECD). The method was validated through the analyses of standard reference materials (SRM 1945 and SRM 1588, National Institute of Standards and Technology), for which the obtained concentrations were within 10% compared to the certified values. The recovery of internal standards ranged from 80 to 120%. In addition to the above mentioned quality control measures, regular analyses of procedural blanks were performed (Relative Standard Deviation - RSD<20% for 8 replicates).

The PCB 153 concentrations were normalized to lipid weight in order to minimize interference from the variation of lipid contents among tissues and species[10]. Simple linear regression analysis was used for investigating relationships between $\delta^{15}N$ and logarithmic concentrations of PCB 153, as well as for determinating trophic magnification factors (TMF). TMF was calculated as the antilog of the regression slope with base 10 and can be used for quantifying food web biomagnification[11,12].

Results and discussion:

Summaries of PCB 153 concentrations and $\delta^{15}N$ values for Guiana dolphin and its prey species are given in Table 1.

Table 1: PCB 153 concentrations ($ng.g^{-1}$, lipid weight) and $\delta^{15}N$ values (‰) of Guiana dolphins (mean value, n = 6) and their preys species (composite samples) from Guanabara Bay, Southeastern Brazil. Data for PCB 153 concentrations in *S. guianensis* are for blubber, as well as they refer to muscle in fishes and crustaceans. Nitrogen isotopic ratios ($\delta^{15}N$) in *S. guianensis* and prey species refer to muscle.

Species	PCB 153	$\delta^{15}N$
Crustaceans		
Penaeidae		
Litopenaeus schmitti	208.5	9.4
Fishes		
Carangidae		
Chloroscombrus chrysurus	98.2	13.7
Clupeidae		
Sardinella brasiliensis	56.9	10.5
Engraulididae		
Anchoa spp.	1009.8	12.9
Cetengraulis edentulus	232.8	11.1
Mugilidae		
Mugil spp.	94.6	9.9
Sciaenidae		
Ctenosciaena gracilicirrhus		
Cynoscion leiarchus	561.4	11.5
Micropogonias furnieri	240.9	11.0
Serranidae		
Serranus auriga	301.1	12.5
Cetacea		
Sotalia guianensis	4597.5	13.7

A positive linear relationship was found between logarithmic concentrations of PCB 153 and $\delta^{15}N$ values ($p = 0.0016$; Fig.1). In general, prey species that showed the lowest $\delta^{15}N$ values (*Mugil* spp. and *S. brasiliensis*) presented also the lowest PCB 153 levels. Guiana dolphin displayed the highest trophic position and PCB 153 concentrations (Table 1). Trophic magnification factor (TMF) was 2.14, which indicates PCB 153 biomagnification in the Guanabara Bay food web. The PCB 153 has been considered one of the most recalcitrant PCB congeners and it is predominant in several studies regarding organochlorine concentrations in marine mammals[13].

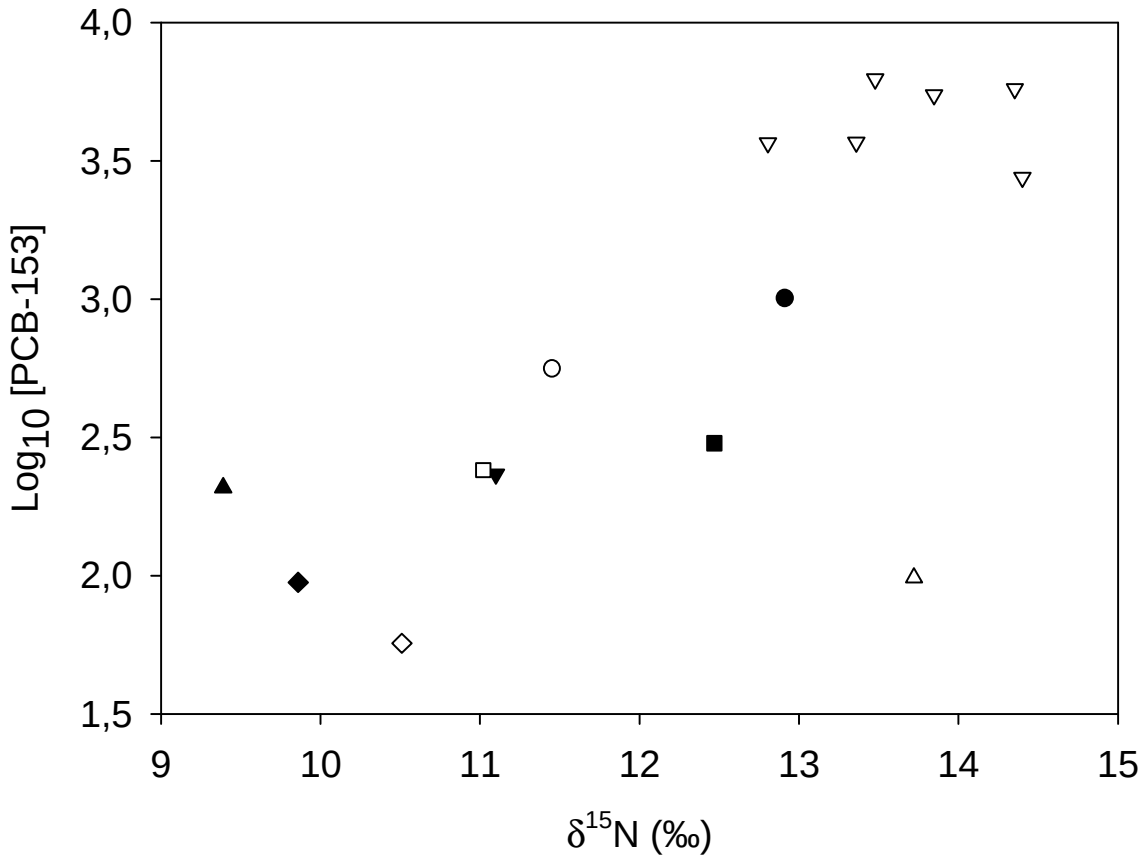

Fig. 1: Relationship between PCB 153 concentrations (lipid basis) and $\delta^{15}N$ (%) values in the Guanabara Bay food web: ● *Anchoa* spp., ○ *Cynoscion leiarchus*, ▼ *Cetengraulis edentulus*, △ *Chloroscombrus chrysurus*, ■ *Serranus auriga*, □ *Micropogonias furnieri*, ◆ *Mugil* spp., ▲ *Sardinella brasiliensis*, ◇ *Litopenaeus schmitti* and ▽ *Sotalia guianensis*. Data for PCB 153 concentrations in *S. guianensis* are for blubber, as well as they refer to muscle in fishes and crustaceans. Nitrogen isotopic ratios ($\delta^{15}N$) in *S. guianensis* and prey species refer to muscle.

Several studies have reported the high biomagnification potential of PCB 153[8,12,14]. Our results compare favorably with the TMF value reported in White Sea[15], but they are lower than most studies that dealt with food webs from Arctic and temperate regions[8,12,14] (Table 2). Muir *et al*.[15] believe that the difference between the biomagnification factor found for the White Sea and open ocean Arctic food webs would be due to the proximity to urban industrial areas and greater importance of benthic food sources. Concerning Arctic food web studies, Fisk *et al*.[12] reported a high value for the factor of biomagnification of PCB 153 in North Water, Polynya. To the same location, Hobson *et al*.[8] found an even apparently higher biomagnification factor. Evaluating the flow of several organochlorine contaminants in the food web from the Southern Beaufort-Chukchi Seas, Hoesktra *et al*.[14] found that PCB 153 was one of the compounds that showed the highest biomagnification factors, along with compounds that have undergone biotransformation (e.g. *p,p'*-DDE e oxychlordane).

It is expected for the biomagnification to be more clearly observed in homeothermic than in poikilothermic animals. In fact, Guanabara Bay food web was represented largely by fishes and only one dolphin species, while the other studies included some birds and marine mammal species. Besides, the low TMF value from our study can be also explained by low the PCB 153 concentrations in some species of relatively high trophic level,

especially for *C. chrysurus*. On the other hand, *L. schmitti* presented a higher PCB 153 concentration than expected, considering its trophic level in Guanabara food web (Fig. 1).

Table 2. Magnification factors for PCB 153 in Guanabara Bay and other marine food webs.

	Magnification factor	**Region**
Hobson *et al.* (2002)[8]	10.2	North Water, Polynya
Hoekstra *et al.* (2003)[14]	6.69	Beaufort–Chukchi Seas, Alaska
Fisk *et al.*(2001)[12]	9.7	Northwater, Polynya
Muir *et al.* (2003)[15]	2.93	White Sea, Russia
Present study	2.14	Guanabara Bay, Brazil

It is important to highlight that our study was carried out in a highly polluted estuarine tropical food web, which may presents differences on the availability of contamination in comparison to studies of open ocean Arctic and temperate food webs, as suggest by Muir *et al.*[15] for the White Sea food web. The present study was the first to link organochlorine compound concentrations and $\delta^{15}N$ values, demonstrating PCB 153 biomagnification in Guanabara Bay. However, additional studies including a higher number of species from distinct taxonomic groups are necessary for a better comprehension of organochlorine biomagnification processes in tropical food webs.

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