Determination of heavy metals by inductively coupled plasma-optical emission spectrometry in fish from the Piracicaba River in Southern Brazil

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1. Introduction

The Piracicaba River Basin, located in the State of Sao Paulo, is considered to be one of the most polluted areas in Brazil [1]. The surrounding area is utilized heavily for the commercial production of sugar cane and eucalyptus trees, and agricultural runoff is a major source of pollution in the river system [2,3]. The heavy usage of fertilizers with high concentrations of metals also, undoubtedly, contributes to the heavy metal burden of this ecosystem [4]. In addition, some areas of the basin are heavily populated and, as recently as 1999, only 16% of the sewage was treated, thus causing additional acute problems for the water quality of the Piracicaba River [5].

The Piracicaba River has also been reported to contain large and heavy metal loads from industrial effluents in the populated and industrialized regions, and heavy metals have been detected throughout the food chain [6,7]. Recent studies by Piña et al. [8] showed that Geoffroy’s side-necked turtles (Phrynops geoffroanus) from this river basin contained extremely high levels of many different heavy metals. Some authors have suggested that the heavy metal content of the fish in the Piracicaba River basin serves as a biomonitor for the health of the river basin ecosystem, and an indicator for health concerns to the human populations that consume fish from the river [9,10]. This study was conducted to determine the heavy metal contamination in fish collected from the Tanquan region of the Piracicaba River, and to determine if humans that consume fish from this river system might be at risk for heavy metal-related health issues.

2. Materials and methods

2.1. Study area

The tissue samples were collected from fresh commercial fish at Vila do Tanquan (20°31′S, 48°32′W), a small village of fishermen at Piracicaba River, upstream from Barra Bonita Hydroelectric Reservoir in São Paulo, Southeastern Brazil. Eight monthly sample collections were conducted from March 2008 to October 2008. However, no collections were conducted from November to February because of reproductive seasonal legal ban of commercial fisheries [11].

2.2. Capture of fish

All fish sampled were collected from a single fisherman in order to assure regularity in fishing methods. Net fishing took place from 17:00 to 07:00. The fresh fish were acquired straight from the fisherman before any processing and then transferred to the laboratory on ice (40 min). Muscle samples (approximately 2 g, 1 × 1 cm) were collected
by scalpel incisions in the middle portion of the body, distal from opperculae, and stored at −20 °C Time from net-capture to the tissue sample storage at the freezer was between 3 and 17 h.

2.3. Preparation of samples

Fish samples were dried in an oven at 80–85 °C overnight. The samples were removed from the oven, allowed to cool, and ground in a clean mortar and pestle. Approximately 0.5 g of each sample was placed in a teflon microwave digestion bomb with 10 mL of concentrated HNO$_3$. The samples were allowed to ramp to 180 °C for 5 min, digest at 180 °C for 9.5 min, and cool down for 5 min in a MARS 5 microwave digestion system (CEM, Matthews, NC). The samples were then transferred to clean volumetric flasks, and diluted with H$_2$O to 10 mL. The samples were stored at 5 °C until ready for analysis of metals.

2.4. Analysis of metals

The samples were compared to a multi-element standard curve to determine the ppm of each analyte in the digested solution. The samples were analyzed three independent times on a Varian 715 ES fluent into the Piracicaba River. The Cr in the fish tissues was more than 35 times the Brazilian government’s recommended limit of human consumption.

All but three species of the fish tested exhibited levels of Ni above the detection limit. Eight of the species contained Ni levels more than 1.0 ppm. Furthermore, the caborja (H. littorale) exhibited mean levels of 13.5 ppm. As recently as 2006, De Vive et al. [10] reported high concentrations of Ni in fish from the Piracicaba River. Jordao et al. [20] showed that suspended particles, plants, and water samples collected from different locations in the Piracicaba River contained elevated levels of Ni. It is known that relatively low levels of nickel exposure can cause immunological and carcinogenic effects in humans [21].

There were also elevated levels of Zn in the fish tissue samples. These results are supported by a study [22] which reported that the Piracicaba River water had elevated levels of Zn, and that these high concentrations appeared to be due to industrial effluent. Zn is an important endogenous metal which has been shown to have important physiological functions in the areas of immune function [23], protein synthesis [24], wound healing [25], DNA synthesis [26], and a variety of other general biochemical functions. Although zinc is an important dietary supplement for humans, excessive zinc intake can cause a broad spectrum of physiological problems [27].

There was an obvious seasonal pattern to metal contamination in the fish samples. The levels of 12 of the 14 metals analyzed (Al, As, Cd, Co, Cr, Pb, Se, Sn, Sr, and Zn) were less than 35 times the Brazilian government’s recommended limit of human consumption.
Cu, Mn, Mo, Sr, and Zn) were higher in October than any other month. There are distinct wet and dry seasons in southern Brazil, with the rainy season beginning during the months of September or October, and continuing through April or May. It is interesting to note that the metal residues in the fish samples are elevated during October, at the start of the wet season. We postulate that the beginning of the rainy season washes metal contamination from the Piracicaba River Basin soils into the river, thus elevating the exposure of the fish during this time. Alternatively, a more plausible explanation for the seasonal fluctuations could be the reservoirs created by the damming of the Piracicaba River. The Piracicaba River has been completely dammed for hydroelectric energy production since the 1970s. The water level in dammed water courses is usually kept low at the rainy season to prevent inundations and high at the dry seasons to assure water supply for human purposes (i.e., urban, agricultural and industrial consumption). On the other hand, the water level in the river itself (out of the influence zone of the reservoirs) tends to be maintained at in opposite pattern, closer to natural: high in the rainy season and low at the dry season. In such circumstance, the river environment can be affected by changes in flow, sediment load, temperature and water quality [28]. The seasonal fluctuations in the metals are in direct contrast to a report by Rodgher et al. [17] in which the Piracicaba River water levels of Zn were 120 times higher in July than February. However, this same study reported much higher levels of Cd in February than in July. We found that the levels of Pb and Ni show high spikes in April and May, respectively. These anomalous results could be due to seasonal effluent waste streams containing these contaminants. It was interesting to note that several species of fish contained high levels of all metals tested. For instance, the piranha (S. spilopleura) had among the highest levels of nearly all of the 14 metals tested, relative to the other 15 species of fish. Similarly, the casudo (H. punctatus) was very high in all metals tested, and the curimbata (Procilodus lineatus) contained moderate–high levels of all metals determined. Curimbata (P. lineatus) and tilapia (Tilapia rendalli) contained detectable levels of all 14 metals, while the mandi (Pimelodus maculates) showed 13 of the 14 metals. In contrast, the bagre (Rhambda quelen) and pacu (Paractus mesopotamicus) contained measurable levels of only 6 of 14 metals. The casudo and curimbata are both bottom dwellers that feed on detritus, while the piranha is a predatory fish, and thus the high levels of metals in these species cannot be explained simply by feeding behaviors. Other fish species, such as the predatory dourado and pacu, were very low in nearly all metals examined. However, both of these species were very high in Sn, indicating that Sn might be a metal that has more potential for bioaccumulation in this ecosystem.

4. Conclusions

The results from this study showed that fish in the Tanguan region of the Piracicaba River are contaminated with a broad spectrum of heavy metals. The metal content is species-dependent, with some species showing high concentrations of all metals, and some showing low concentrations. The metal concentrations in the fish tissues were also time-dependent, with residues much higher during months during the rainy season (Table 2). We conclude that the regular consumption of some of these fish species, even during the dry season (May–August), when metal concentrations are lower, could pose serious human health risks. These health risks have been delineated in studies of heavy metal contamination in fish in Taiwan [29].

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