ATTENUATION OF METALLIC CONCENTRATIONS MODEL APPLIED TO A POLLUTED BAY IN BRAZIL

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ABSTRACT: New procedures for the evaluation of metallic mobility, based on geographical modeling has not yet been fully tested and may represent a promising path for the understanding of the behavior of these pollutants. In the present work a simple model that assess mobility of metals (Cd, Hg and Pb) in the sediment is applied to the sediments of the Guanabara Bay, Rio de Janeiro, Brazil. This model is based on the spatial distribution of metals in surface sediments and generates values that describe the attenuation of the metal concentrations from a hot spot in different directions. The faster the concentrations fall from the hot spot (strong attenuation) the less mobile is the metal. Concentrations of Cd, Hg and Pb were obtained from a 13 station heavy metals monitoring program carried out by the Rio de Janeiro State Environmental Agency (FEEMA) from 1980 through 1986. The attenuation of concentrations model show that the metals lead and mercury are not very mobile. Their concentrations are extremely high in the western São João de Merití station (Hg reaches 5.5 mg kg^{-1} and Pb reaches130 mg g^{-1}) but are not spread throughout the bay. On the other hand Cd seem more mobile and constitute a significant contaminant throughout the bay. These conclusions are not very clear from the analysis of distribution maps alone, and the attenuation model is a significant contribution.

INTRODUCTION

A number of studies had indicated that there is a lack of correlation between total metal concentrations and toxicity (e.g.: Kraepiel et al., 1997; Duursma, 1998). In these studies, the chemical association of the metals were considered more important, in defining its toxicity, than total concentrations alone. Chemical associations are also important in determining mobility, that in turn, will outline the boundaries affected by the toxic metal.

The search for determining chemical associations of metals gave rise to the development of a myriad of chemical procedures that selectively extract metals, among them, the partial extractions and sequential extractions are the most widespread (e.g. (Tessier et al., 1979; Barrocas, P.R.G. and Wasserman, 1998). Even though the selective procedures have been used since the early seventies, until today, these methods are subject to criticism, for they do not reproduce environmental condition, but are merely operational extractions (Biester and Scholz, 1997).

The search for procedures that yield reliable informations on the mobility of metals is far from being resolved. Nonetheless, the procedures developed until now are focused on chemical or physical fractionations, that frequently are operational and do not reproduce environmental processes. New procedures, based on geographical modeling has not yet been fully tested and may represent a promising path for evaluating metal mobility (Wasserman and Queiroz, 2003).

In the present work a simple model that assess mobility of metals in the sediment is tested in the Guanabara Bay, Rio de Janeiro, Brazil. This model is based on the spatial distribution of metals in surface sediments and generates values that describe the attenuation of the metal concentrations from a hot spot in different directions. The faster the concentrations fall from the hot spot (strong attenuation) the less mobile is the metal. Metallic concentrations were obtained from a FEEMA (State of Rio de Janeiro Environmental Agency)monitoring program that sampled sediments yearly in 13 stations and lasted from 1980 through 1986.

METHODS

Study area. Guanabara Bay (Figure 1) is a tropical ecosystem adjacent to Rio de Janeiro city, where 7 million people live. It is the second largest bays in Brazil, covering an area of 381 km^2. Its mean depth is 7.7 m with an estimated water residence time of 20 days (Coelho and Fonseca, 1981). Its watershed area is more than 4,000 km^2, where about 7,000 industries are installed. This impressive concentration of industries is responsible for 25% of the organic pollution and almost all of the toxic substances and heavy metals released. It is estimated that 22 kg of cyanides, 4,200 kg of phenols, 1,800 kg of sulfides and 4,800 kg of heavy metals are dumped every day by industrial effluents.

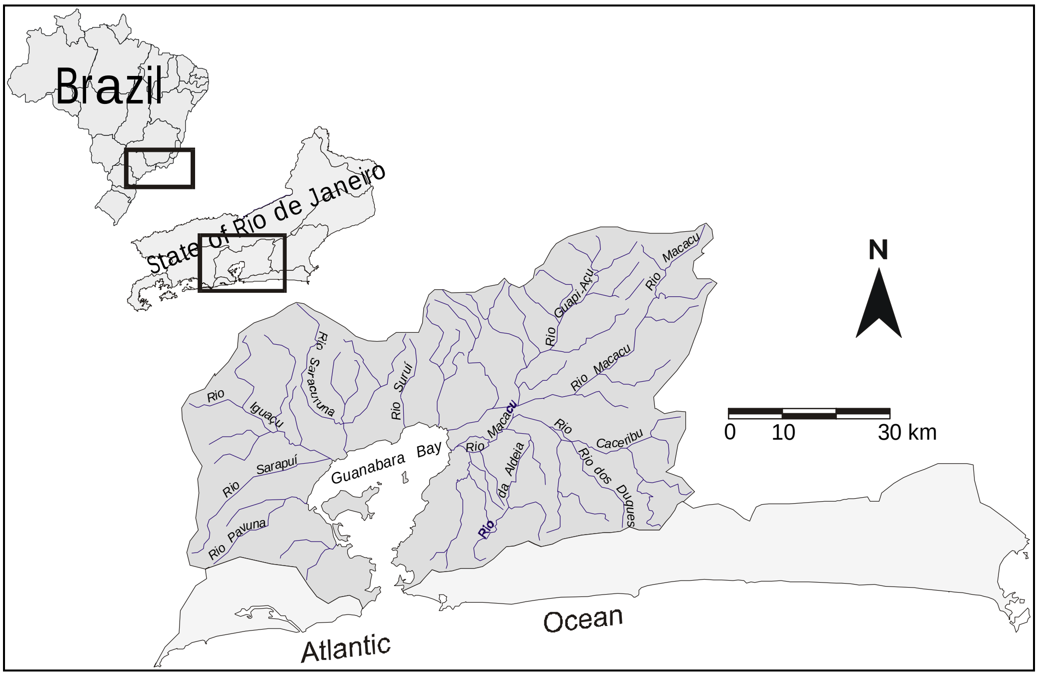

Figure 1: Guanabara bay location and its drainage basin

The most polluted river is the São João de Merití, that dumped most of the mercury, cadmium and lead that is present in the bay sediments (Rego et al., 1993). Nevertheless, non-point sources of metals are widespread throughout the bay, coming from domestic sewage, dockyard, petroleum refining, leather tanning, plating, etc (FEEMA, 1990).

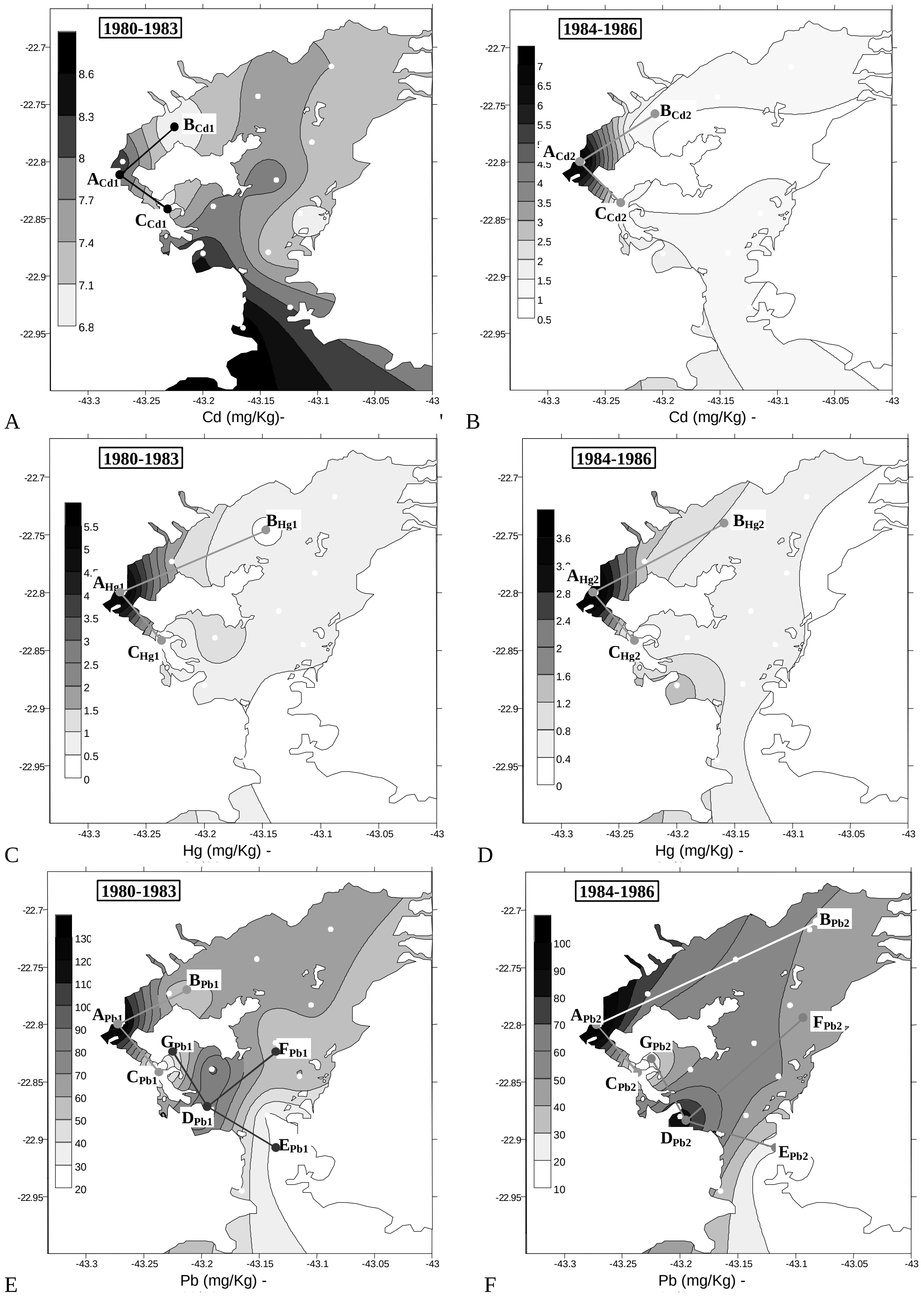

FIGURE 2: Cadmium, mercury and lead distributions in the sediments of the Guanabara Bay in the periods of 1980-1983 (A,C and E) and 1984-1986 (B, D and F).

Metallic concentrations. Data for mercury lead and cadmium concentrations in sediments from Guanabara Bay were obtained from a heavy metals monitoring program with yearly sample collection (from 1980 through 1986), performed by the State of Rio de Janeiro Environmental Agency (FEEMA). The samples were extracted with a mild procedure (0.1 N HCl) and metals were analyzed by flame atomic absorption spectrometry (F-AAS). The results were plotted in contour maps (figure 2) with the program Surfer using the Krigging method of interpolation. Krigging method has proven useful for it produces iso-concentrations maps from irregularly spaced data, avoiding isolated bull's-eye type contours.

Attenuation of concentrations model. The concept of attenuation of concentrations proposed here is distinct from the 'natural attenuation' largely applied in soil and groundwater sciences (Waters et al., 1998). The principle of the attenuation of concentrations is based on the distance between contours of concentrations of a metal, determining its degree of geographic homogeneity. The smaller are the distances between the contours, the faster concentrations decrease (less homogeneous distribution) and in such conditions the mobility of the metal is low. On the other hand, for bigger distances between contours, the distribution of the metal is homogeneous due to its higher mobility. In order to distinguish our model from the "natural attenuation" (as applied in ground water sciences), the term "attenuation of concentrations" is proposed.

The attenuation of the concentration (hereafter called "*A*") is given by the slope coefficient from a first degree equation (y = ***A***x + b) describing the decrease in concentration from a hot-spot (HS in figure 3a) until lower concentrations (B or C in Figure 3a). The straights from segments HS - B and HS - C are plotted in the graph of Figure 3b and the slopes in the given equations correspond to *A*. It is worth note that the value of the second term of the equation (b) is meaningless for the model. Further, the negative sign is due to the fact that the higher concentrations are plotted on the left hand of the graph, therefore has no meaning for the model.

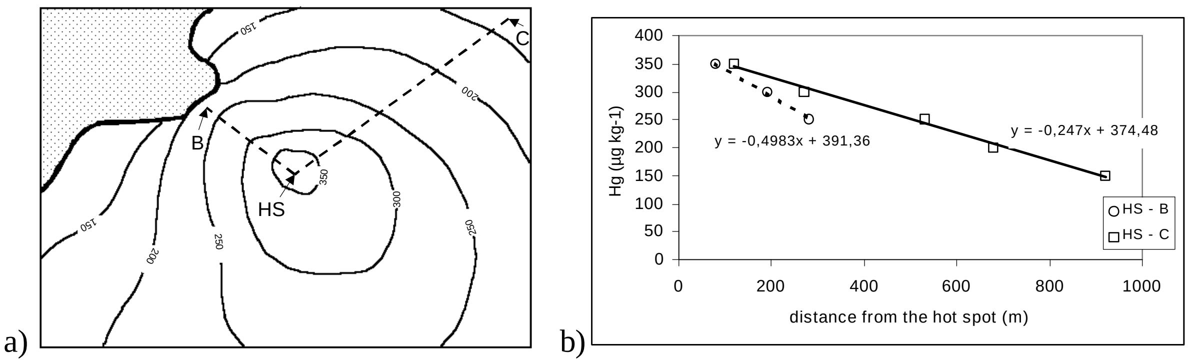

FIGURE 3: Schematic representation of the attenuation of concentrations model (after (Wasserman and Queiroz, 2003)

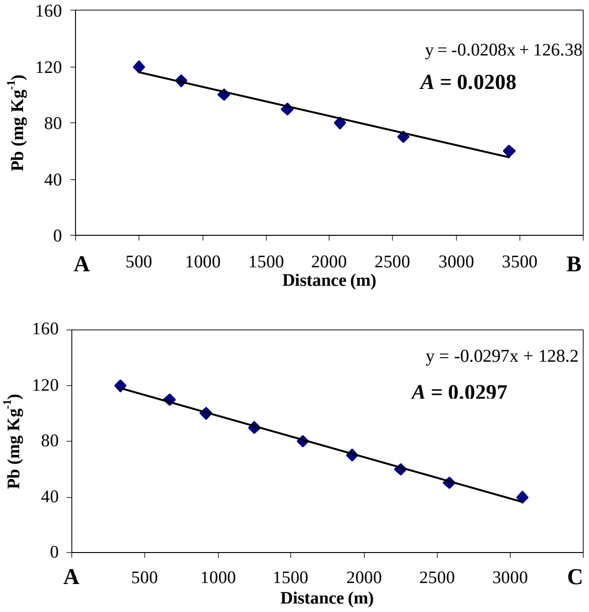

FIGURE 4: Two examples of the application of the attenuation model. The graphs are obtained form Pb concentrations in 1980-1983

TABLE 1: Attenuation of concentrations calculated from the segments plotted in Figure 2

Metal	Period	Figure	Segment	*A*
Cd	80 - 83	2A	AB	0,0004
			AC	0,0002
	84 - 87	2B	AB	0.0022
			AC	0.0021
Hg	80 - 83	2C	AB	0,0008
			AC	0.0011
	84 - 87	2D	AB	0,0008
			AC	0.0011
Pb	80 - 83	2E	AB	0.0208
			AC	0.0297
			DE	0.0153
			DF	0.0066
			DG	0.0121
	84 - 86	2F	AB	0.0029
			AC	0.0260
			DE	0.0115
			DF	0.0099
			DG	0.0185

RESULTS AND DISCUSSION

From the segments plotted in Figure 2, 18 graphs like those presented in figure 4 were constructed and the values of *A* were reported in Table 1.

The variation of the attenuation of concentrations observed in the last column of Table 1 indicate that the metals have significantly different behaviors and different mobilities. The lower values observed in the period 1980-1983 for cadmium are related with a homogeneous distribution as a consequence of strong mobility of this element as established in the literature (Yeats and Bewers, 1983). In the following years (1984-1986), cadmium concentrations decrease is generally observed, that is accompanied of a significant increase in attenuation values, indicating reduction of mobility.

Since FEEMA started to monitor metals in the sediments from Guanabara Bay, a number of industries were pulled to reduce their metallic spills in the Guanabara Bay. This is very well documented for mercury, because in the end of the 1970’s a Chlor-alcali plant alone dumped 90% of the total mercury in the Bay (1.4 tones year^{-1}, (FEEMA, 1985). In the beginning of the eighties, that industry reduced the effluents to insignificant concentrations. The control of the sedimentary concentrations pulled many industry voluntarily reduce their effluents, therefore explaining the reduction in cadmium concentrations. On the other hand, as the mobile cadmium is washed away from the bay, the remaining cadmium is tightly bound to gechemical carriers (mainly organic matter) resulting in the increase in the values of the attenuation of concentrations observed in Table 1 form the period 1984-1986.

Another, still unpublished work in the Todos os Santos Bay – Bahia, Brazil (Tainheiros Cove) using the model of attenuation of concentrations, presented values ranging from 0.00008 to 0.00080 (averaging 0.00040, Wasserman and Queiroz, 2003), showing that the values in this work can be considered high, although they fall in the same order of magnitude. In Guanabara bay, it has been shown that particularly organic matter is an important mercury carrier (Barrocas, P.R.G. and Wasserman, 1998), therefore, the formation of immobile mercury-organic matter complexes is expected.

It is interesting to note that although mercury concentrations were reduced in the period of 1984-1986, attenuation is rigorously the same. The reduction in sedimentary concentration is probably attributed to the reduction in mercury dumping from a chlor-alcali plant, however, this reduction is far from being proportional to the reduction of the effluent (FEEMA, 1985, claims a reduction of 1.4 tones year^{-1} to 20 kg year^{-1}). Measurements performed in the nineties indicate that, on the contrary, concentrations increased with time (Rego et al., 1993; Barrocas, P.R.G et al., 1995; Wasserman et al., 2000), showing that other sources are also important or the reduction in mercury dumping from the plant was not as important as claimed. On the other hand attenuation of mercury concentrations remains the same in both segments because the geochemistry of did not changed with time.

Lead concentrations in the Guanabara Bay presented in figures 2E and 2F show that the sediments are not excessively contaminated with this pollutant. It is clear From Table 1 that lead attenuation of concentrations is considerably higher than those of mercury and cadmium, due to the fact that this element is less mobile than the others (Carruesco and Lapaquellerie, 1985).

A multi-hot spot model could be applied for lead because in both periods two important dispersion sources could be identified, the first in the Northwest of the bay (point A_{pb}) and the second in Southwest part of the bay (point D_{pb}). The first point is associated with the majority of the sources of the bay, located in the drainage basin of the São João de Merití River and the second is a rushed ferry boat harbor and the head of an airport landing-strip (Santos Dumont Airport). Attenuation of concentrations in the segment A-B is always lower than attenuation in the segments A-C, indicating that lead (and also mercury) tend to disperse more easily in the Northeast direction than to the South. The fact that metals (lead and mercury) are more mobile in the Northeast path is contradictory with general circulation pattern as described by Amador (1980). who established stronger currents between Governador Island and the continent (segment A-C). In the Southern hot spot (D) there is a tendency of dispersion in the Northeastern direction (D-F).

CONCLUSIONS

The study shows that the model of attenuation of concentrations can provide important informations concerning metals mobility. The model is based on the dispersion of the metals, that is controlled by hydrodynamic factors combined with chemical factors. Since these two factors are extremely difficult to be modeled separately or gathered, the attenuation model should be an easy way to describe metallic behavior. The problem is that attenuation model can not be applied as a prevision model, for it is based on the dispersion metals have already performed. Nevertheless, it can be useful in the prevision of impacts on the biota from metallic effluents in sedimentary systems

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