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Use of spatial factors in the analysis of heavy metals in sediments in a Brazilian coastal region

T. C. Bailey[1,*,†], C. Barcellos[2] and W. J. Krzanowski[1]

[1]*Department of Mathematical Sciences, University of Exeter, Laver Building, North Park Road, Exeter, EX4 4QE, U.K.*
[2]*Fundação Oswaldo Cruz, Rio de Janeiro, Brazil*

SUMMARY

Environmental phenomena often generate complex data which are not only multivariate, but where spatial structure and dependency may also be important. One potential area of interest is that of identifying combinations of variables which exhibit distinctive spatial structure in a set of multivariate and geographically indexed observations, e.g. long, as opposed to short, range spatial contiguity. Such components may serve not only to characterize the main determinants in the geographical distribution of a set of environmental measurements, but may also provide useful insight into the physical or environmental processes underlying and governing that distribution. This article suggests one form of multivariate technique which may be useful in such a context. We demonstrate the method in relation to data comprising measures of various heavy metals in sediments in a Brazilian coastal region. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS: multivariate spatial analysis; spatial factors; environmental statistics; heavy metals

1. INTRODUCTION

Assessment and modelling of the spatial or spatio-temporal distribution of environmental phenomena is a complex task which involves a blend of both appropriately sophisticated mathematical or statistical methodology, and a good scientific understanding of the underlying physical processes relating to the phenomena studied. One statistical challenge often faced is that environmental phenomena may generate data in which both multivariate and spatial considerations are important. There is then a need to simultaneously handle both correlation between the multivariate measurements, and also spatial autocorrelation within each variable, or spatial cross-correlation between pairs of variables.

Multivariate techniques which are explicitly designed for spatial data are relatively undeveloped when compared to other methods in spatial statistics. Many of the developments in multivariate spatial methods which do exist have so far been confined to rather specialized fields, notably image processing and geostatistics. There is therefore an important requirement to develop, extend, and

*Correspondence to: T. C. Bailey, Department of Mathematical Sciences, University of Exeter, Laver Building, North Park Road, Exeter, EX4 4QE, U.K.
†E-mail: T.C.Bailey@exeter.ac.uk

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more widely disseminate multivariate spatial methods. This article describes one form of analysis which is designed to identify combinations of variables in a multivariate spatial data set which exhibit distinctive spatial structure, e.g. long, as opposed to short, range spatial correlation. Such 'spatial factors' may be a particularly useful adjunct in studying multivariate environmental phenomena since they may serve not only to characterize the main determinants in the geographical distribution of a group of measurements, but may also provide useful insight into the physical or environmental processes underlying and governing that distribution.

We investigate use of this spatial factor methodology for analysing measures of various heavy metals in sediments in a Brazilian coastal region. In Section 2 of the article we discuss some background to the study of the spatial distribution of heavy metals in the environment and introduce the specific Brazilian coastal region and data set relevant to later sections of the article. Section 3 then describes the relevant multivariate spatial methodology, and results of applying that technique to the data on heavy metal concentrations are given in the subsequent section. The article concludes with a brief discussion.

2. HEAVY METAL CONCENTRATIONS AND SEPETIBA BAY

A knowledge of the distribution of heavy metals at the regional scale is useful in the design of environmental monitoring programmes and the identification of sources of risk to human health that may arise from such pollutants. The distribution of heavy metals in sediments is controlled both by the presence of local sources and by relevant environmental behaviour (Hornberger *et al.*, 1999). Natural and anthropogenic sources of metals are rarely specific. For instance, soil erosion is a major natural source, which releases to the aquatic environment a range of metals and other mineral content. Industries also use and release metals in different proportions depending on their production objectives and availability of technology. Once discharged into the environment, heavy metals are influenced by a range of physical, chemical and biological processes which affect their behaviour and facilitate their accumulation or dispersion. Coastal regions are especially complex environments where several processes occur simultaneously due to the mixture of oceanic and continental waters, the high organic matter production, and the existence of intensive sedimentation and re-suspension forces.

These processes can affect each metal to different degrees because of intrinsic metal affinity to organic matter binding, clay adsorption and sensibility to redox and PH conditions. For instance, iron (Fe) is commonly found in the crystal structure of clays, and physical or chemical environmental changes can rarely mobilize the element from this geologic matrix. Therefore, Fe behaviour is mainly affected by sedimentation, and has been considered as a tracer of terrigenous matters (Salomons and Forstner, 1984). Manganese (Mn) is also a natural component of terrigenous sediments, but can be mobilized from sediments to the water column in low oxigen micro-environments (Thandrup *et al.*, 1994). On the other hand, cadmium (Cd) and copper (Cu) can be cycled in estuaries similarly to organic matter due to affinity to the organic coating of sediments (Helland and Bakke, 2002).

In summary, metal concentration in sediment is a dependent function of local environmental conditions and the distance from main sources. Since these variables affect all metals, the study of metal distribution in sediments should ideally adopt a multivariate approach. Several studies have been carried out in coastal areas aiming to map heavy metal distribution in sediments (Pavoni *et al.*, 1988; Shine *et al.*, 1995; Liu *et al.*, 2003). Conclusions often point out hot spots where metals accumulate in sediments, situated in the main river estuaries, but such trends can also result from important adsorption and sedimentation processes, as well as being a simple consequence of the proximity to

pollution sources. Metal concentration in any sampling site is potentially related to concentration of the same metal in the vicinity of that site (spatial autocorrelation), and also concentrations of other metals, both in the same sampling site (inter-variable correlation) and in the vicinity of that site (spatial cross-correlation). There is therefore value in studying the spatial distribution of heavy metals as a single phenomenon, in which each metal is directly or indirectly affected by environmental characteristics, therefore presenting a strong inter-metal correlation structure. In subsequent sections of this article we demonstrate how a multivariate spatial approach to the analysis of heavy metal concentrations in a coastal region of Brazil can potentially contribute to the understanding of environmental processes rather than just the distribution of individual metals.

Sepetiba Bay is a semi-enclosed lagoon, with an area of 447 km^2 located about 60 km west of the city of Rio de Janeiro (Figure 1). Its drainage basin comprises the western Rio de Janeiro metropolitan area, with around 1 million inhabitants, and also that of over 400 important manufacturing activities throughout a wider region with a total area of 2065 km^2. Water depth in the bay ranges from 2 m in the inner zone to 20 m at the broad sea interface. A clockwise circulation pattern promotes the permanent exchange of water with the sea (Signorini, 1980) but also creates extensive mud flats along the northern coast of the bay. The northern bay shore region acts as a sink for river transported sediments and antigenic organic matter (Argento and Vieira, 1989).

The bay's sediment and biota have been studied for heavy metal contamination and a high contamination of cadmium (Cd), lead (Pb) and zinc (Zn) has been identified through sediment analysis. A major source of metals resides in two important industrial centres, with major influence from metallurgic plants that produce and use aluminium (Al), Fe and Zn (Barcellos *et al.*, 1991). Fish contamination by heavy metals has been assessed by comparing observed concentration in the biota in Sepetiba Bay with other regions that are not affected by pollution activities (Lacerda *et al.*, 1987; Carvalho *et al.*, 1991; Pfeiffer *et al.*, 1988; Junior *et al.*, 2002). Although measurements rarely exceed the maximum allowable values for human consumption under Brazilian regulations, metal concentrations do show evidence of fish and crustacean contamination when compared with levels observed in

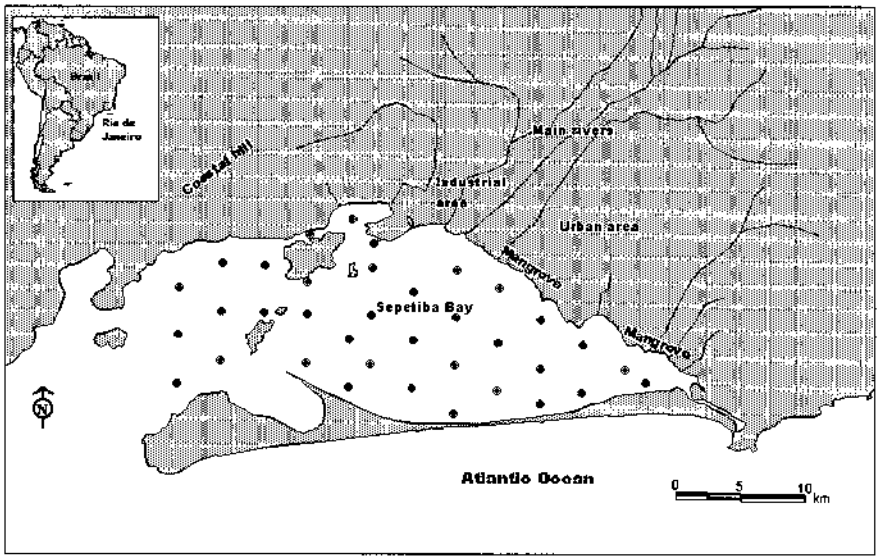

Figure 1. Sampling locations in Sepetiba Bay

other areas. Consumption of contaminated fish has been suggested as an important factor in exposure of the local population to heavy metals such as Cd, Zn and chromium (Cr) (Pfeifer *et al.*, 1983).

Analyses reported subsequently in this article, concern a particular data set on metal distribution in Sepetiba Bay previously analysed by Barcellos (1995) and collated from previously published work (Dib and Argento, 1989; Watts, 1990; Rezende, 1993; Leitao-Filho, 1995). The criteria for the inclusion of sample observations in the collated data set were common field and laboratory procedures combined with adequate spatial localization of samples (Barcellos, 1995).

The resulting data set consists of 36 bottom sediment samples at irregularly spaced points covering Sepetiba Bay and collected between 1988 and 1990, a period in which metal releases from industrial activities were acknowledged to have been at high levels (IFIAS, 1988; Barcellos *et al.*, 1991). Sediment samples were sieved and total metal concentrations of iron (Fe), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni), cadmium (Cd), manganese (Mn) and copper (Cu) in each sample were obtained by standard techniques using acid extraction followed by atomic absorption spectrometry. Approximate sample locations are shown in Figure 1 and were obtained by digitizing sampling points from a hard copy 1:50000 scale map. Standard GIS software was then used to compute associated UTM grid references. This process results in the locations of sampling points being subject to a spatial accuracy of around 100 m.

3. STATISTICAL METHODOLOGY

Given a multivariate spatial data set, Bailey and Krzanowski (2000) proposed methods for identifying linear combinations of variables (components) that have potentially interesting spatial structure. Their techniques are broadly related to a group of methods, sometimes referred to as 'spatial factor analysis', which have been employed in geostatistics and in some forms of image processing (e.g. Switzer, 1985; Grunsky and Agterberg, 1992; Bailey and Krzanowski, 2000). There are also conceptual links to the linear model of coregionalization employed in geostatistics and to related techniques such as factorial kriging (e.g. Goovaerts, 1992; Wackernagel, 1995).

One of the spatial factor techniques suggested by Bailey and Krzanowski (2000) is of particular interest in analysing data such as that concerning heavy metal distribution in Sepetiba Bay. Given a set of geographically indexed, multivariate measurements, this technique determines a set of uncorrelated linear combinations of the variables such that the spatial autocorrelation structure of each of these components operates over a distinct spatial range. So that, for example, we might identify linear combinations of a set of multivariate environmental measures which best relate to short, medium or longer range spatial structure. The components and their corresponding spatial autocorrelation structures are simultaneously derived, so the technique determines what scales of spatial variation are present in the data, as well as what linear combinations of variables correspond to those scales.

Full mathematical details of the method are given in Bailey and Krzanowski (2000), but we summarize the key aspects here. Suppose $\boldsymbol{y}(s) = (y_1(s), \ldots, y_p(s))'$ is a p-variate, second-order stationary, spatial process, defined over point locations, s, within some spatial domain or region. Let $\boldsymbol{\Sigma} = \mathrm{var}(\boldsymbol{y}(s))$ be the overall dispersion matrix; let $\boldsymbol{C}(\boldsymbol{d}) = \mathrm{cov}(\boldsymbol{y}(s), \boldsymbol{y}(s+\boldsymbol{d}))$ be the matrix of auto-/cross-covariances of the p variables at sites a vector separation $\boldsymbol{d}$ apart; and let $\boldsymbol{\Gamma}(\boldsymbol{d}) = \frac{1}{2}\mathrm{var}(\boldsymbol{y}(s+\boldsymbol{d}) - \boldsymbol{y}(s))$ be the corresponding matrix of semi-variances. Then the spatial autocorrelation of a linear combination of the original variables, $u(s) = \boldsymbol{a}'\boldsymbol{y}$, at sites a vector separation $\boldsymbol{d}$ apart, is given by $\mathrm{corr}(u(s), u(s+\boldsymbol{d})) = \frac{\boldsymbol{a}'\boldsymbol{C}(\boldsymbol{d})\boldsymbol{a}}{\boldsymbol{a}'\boldsymbol{\Sigma}\boldsymbol{a}}$. Alternatively, we may rewrite this as $\mathrm{corr}(u(s), u(s+\boldsymbol{d})) = 1 - \frac{\boldsymbol{a}'\boldsymbol{\Gamma}(\boldsymbol{d})\boldsymbol{a}}{\boldsymbol{a}'\boldsymbol{\Sigma}\boldsymbol{a}}$, since the variogram of a stationary process is related to its covariogram via $\boldsymbol{\Gamma}(\boldsymbol{d}) = \boldsymbol{\Sigma} - \boldsymbol{C}(\boldsymbol{d})$.

As outlined earlier, the objective of the spatial factor technique is to find coefficients $\boldsymbol{a}_1, \ldots, \boldsymbol{a}_K$, for a set of K uncorrelated factors, $u_k(\boldsymbol{s}) = \boldsymbol{a}_k' \boldsymbol{y}(\boldsymbol{s})$, $k = 1, \ldots, K$, such that each such factor has a distinct spatial autocorrelation structure. To do that, a suitable general family of spatial autocorrelation functions, $\rho(\boldsymbol{d}; \boldsymbol{\beta})$, is chosen (where $\boldsymbol{\beta}$ is a set of parameters indexing members of this family), and then, using a least squares criterion, we successively determine pairs $\boldsymbol{a}_k$ and $\boldsymbol{\beta}_k$ for $k = 1, \ldots, K$, so that $u_k(\boldsymbol{s})$ are uncorrelated and $\mathrm{corr}(u_k(\boldsymbol{s}), u_k(\boldsymbol{s} + \boldsymbol{d}))$ best fits $\rho(\boldsymbol{d}; \boldsymbol{\beta}_k)$ over a suitable range of values of $\boldsymbol{d}$. More specifically, and using the derivations given earlier, we first consider the optimization:

$$\min_{\boldsymbol{a},\boldsymbol{\beta}} \left\{ \frac{\sum_i \left(\rho(\boldsymbol{d}_i; \boldsymbol{\beta}) - \left(1 - \frac{\boldsymbol{a}' \boldsymbol{\Gamma}(\boldsymbol{d}_i) \boldsymbol{a}}{\boldsymbol{a}' \boldsymbol{\Sigma} \boldsymbol{a}} \right) \right)^2}{\sum_i \left(1 - \frac{\boldsymbol{a}' \boldsymbol{\Gamma}(\boldsymbol{d}_i) \boldsymbol{a}}{\boldsymbol{a}' \boldsymbol{\Sigma} \boldsymbol{a}} \right)^2} \right\}$$

where $\{\boldsymbol{d}_i\}$ are a set of spatial separations or lags appropriately chosen to cover the full distance over which one would expect the spatial correlation of any component to act. We then denote the resulting optimizing parameters as $\boldsymbol{a}_1, \boldsymbol{\beta}_1$ and then project the original data into the subspace orthogonal to this component and repeat the minimization. Iterating this process K times we obtain coefficients, $\boldsymbol{a}_1, \ldots, \boldsymbol{a}_K$, for the required uncorrelated spatial factors, $u_1(\boldsymbol{s}), \ldots, u_K(\boldsymbol{s})$, and their corresponding best fitting autocorrelation functions, $\rho(\boldsymbol{d}, \boldsymbol{\beta}_1), \ldots, \rho(\boldsymbol{d}, \boldsymbol{\beta}_K)$. Note that the denominator in the above optimization is present simply so that successive factors will be extracted in order of decreasing range of spatial autocorrelation.

Clearly, practical application of the method requires estimates of $\boldsymbol{\Sigma}$ and of $\boldsymbol{\Gamma}(\boldsymbol{d})$ at any given spatial separation $\boldsymbol{d}$. $\boldsymbol{\Sigma}$ is estimated by the conventional sample covariance matrix for the p variables. Estimation of $\boldsymbol{\Gamma}(\boldsymbol{d})$ is achieved using standard variogram estimation techniques commonly employed in geostatistics. $\boldsymbol{\Sigma}$ and $\boldsymbol{\Gamma}(\boldsymbol{d})$ in all the above expressions are then replaced by their estimates $\hat{\boldsymbol{\Sigma}}$ and $\hat{\boldsymbol{\Gamma}}(\boldsymbol{d})$. Note that formulation of the optimization in terms of $\boldsymbol{\Gamma}(\boldsymbol{d})$, rather than $\boldsymbol{C}(\boldsymbol{d})$, is deliberate since direct estimation of $\boldsymbol{C}(\boldsymbol{d})$ will usually require corrections to achieve a symmetric and positive definite estimate, whereas this is not a problem with direct estimation of $\boldsymbol{\Gamma}(\boldsymbol{d})$.

In summary, this spatial factor technique potentially allows us to explore a multivariate spatially indexed data set for the presence of distinctive scales of spatial variation and at the same time identifies those components in the data which exhibit a spatial autocorrelation structure corresponding to each such scale. Interpolated maps of the scores for each such component can then be used to highlight distinctive spatial trends or patterns inherent in the multivariate responses, but ones which are perhaps not obvious in any of the original variables taken in isolation. When these factor maps are interpreted in terms of the factor coefficients, i.e. the loadings of each of the original variables, they potentially provide interesting insight into the main characteristics of the geographical distribution in the multivariate responses and possibly contribute to a better understanding of the environmental processes underlying that distribution (atmospheric deposition, river transport, industrial waste disposal, etc.).

4. RESULTS

Returning to the Sepetiba Bay data set introduced in Section 2, the observed correlation matrix for variable values at the same site shows significant correlation between Fe and a range of other metals affected by sedimentation: Zn, Pb, Cr, Cd, Mn and Cu. The correlations of Fe with other heavy metals

Table 1. Observed correlation matrix between variables (bold typeface indicates statistically significant values)

	Fe	Zn	Pb	Cr	Ni	Cd	Mn	Cu
Fe	1.000							
Zn	**0.596**	1.000						
Pb	**0.581**	**0.636**	1.000					
Cr	**0.651**	**0.511**	0.419	1.000				
Ni	0.019	0.239	**0.347**	0.205	1.000			
Cd	**0.442**	**0.737**	**0.525**	0.258	**0.389**	1.000		
Mn	**0.461**	0.041	0.203	0.135	−0.136	−0.005	1.000	
Cu	**0.629**	**0.721**	**0.678**	**0.450**	0.225	**0.619**	0.159	1.000

might be a consequence of 'grain size effect' in which fine sediments tend to concentrate all heavy metals, mainly Fe, due to the wider adsorption surface, sedimentation velocity and organic matter affinity (Salomons and Forstner, 1984). Other strong correlations exist among typically industrial and urban released metals such as Pb, Cd, Zn and Cu. The strong correlations among these metals indicate common sources in the bay (see Table 1).

Auto-/cross-correlation matrices for increasing spatial lags between sites (2000 m, 4000 m, 6000 m and so on), show observed cross-correlations decreasing with the increase of spatial lag, implying a weakening of the main driving forces in the bay (sedimentation, oxi-reduction and organic matter cycling). This indicates the presence of local processes, acting within limited ranges of space.

The spatial factor technique described in the previous section was then applied to identify factors acting at different spatial scales. In this case we characterized the maximal spatial separation range to be 25 000 m and so set $\{\boldsymbol{d}_i\}$ to correspond to spatial separations from 2500 m to 25 000 m in steps of 2500 m. The choice for $\rho(\boldsymbol{d};\boldsymbol{\beta})$ was taken to be the simple, isotropic exponential form, $e^{-\beta d}$, where d denotes the length of the spatial separation $\boldsymbol{d}$, and the single parameter, β, essentially reflects the range of spatial correlation.

Table 2 reports results for the first four factors extracted. Factors are denoted $F1,\ldots,F4$ and the columns of this table give the four sets of factor coefficients $\boldsymbol{a}_1,\boldsymbol{a}_2,\boldsymbol{a}_3,\boldsymbol{a}_4$ and the corresponding four best fitting autocorrelation parameters, $\beta_1,\beta_2,\beta_3,\beta_4$ (with distance units assumed measured in metres).

The spatial range of each factor in the bay can be inferred from the corresponding β coefficient in Table 2. This can be seen more directly in Figure 2 which shows the observed autocorrelations of factor scores at spatial lags between zero (maximum auto-correlation) and 25 000 m.

Table 2. Spatial factor loadings and corresponding spatial autocorrelation parameter values

	F1	F2	F3	F4
Fe	0.388	−0.118	0.796	−0.262
Zn	−0.442	0.060	0.460	0.649
Pb	0.421	−0.030	−0.327	0.257
Cr	−0.434	0.358	−0.097	−0.048
Ni	−0.214	−0.445	0.042	−0.086
Cd	0.384	−0.224	−0.072	0.615
Mn	−0.009	0.160	0.150	0.236
Cu	0.306	0.761	0.092	0.022
β	0.000645	0.000541	0.000403	0.000323

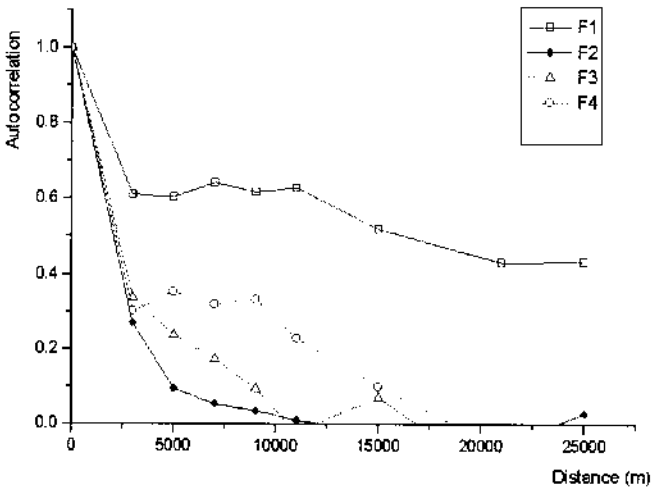

Figure 2. Spatial autocorrelation of factors in Sepetiba Bay sediments

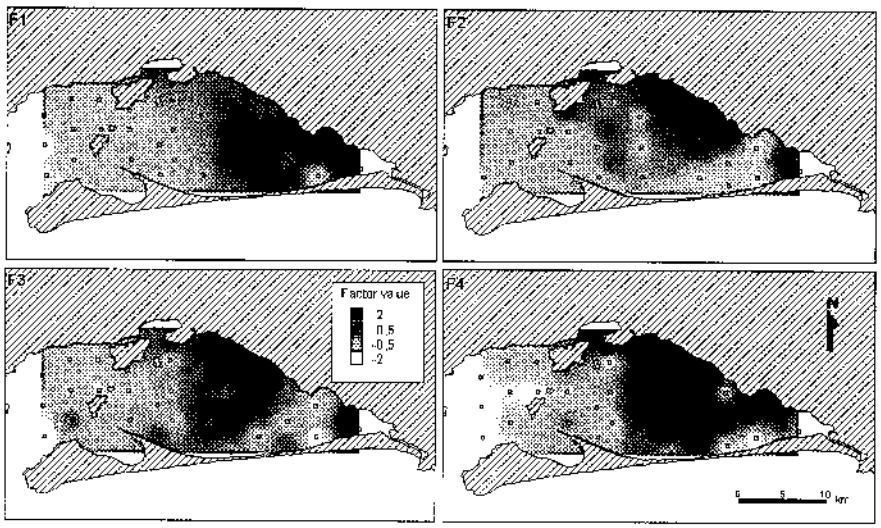

Figure 3. Spatial distribution of factors in Sepetiba Bay

Figure 3 shows interpolated maps of each factor score, based on localized regression using the loess function in SPlus with an appropriately chosen smoothing parameter (see, for example, Cleveland *et al.*, 1992). This serves to provide a basic exploratory analysis of the observed spatial variations and trends in each factor over the bay.

From the loadings in Table 2, Factor 1 has important contributions of Pb and Cd, which are recognized to be local pollutants, and Fe, which is a natural content of river transported fine sediments. This factor therefore relates to total terrigenous inputs to the bay. The spatial distribution of F1 (Figure 3) shows higher values in the eastern portion of the bay, decreasing towards the bay's entrance.

The decrease of factor values in the western area may be explained by the major influence of the sea in the broad bay entrance. Sea influence in the western area may act to dilute these metals in sediments as well as change their proportionality.

Factor 2 presents higher loadings for Cr and Cu, which are recognized as metals affected the general pH and Eh conditions of water column. Sea influence acts as a buffer by maintaining high pH and Eh values in the water column. However, in restricted areas of the bay these values may decrease due to organic matter accumulation and oxygen consumption in the water column. The distribution of this factor in the bay, shown in Figure 3, indicates values increasing from south to north, where restricted circulation of water and the presence of a mangrove belt promote organic matter accumulation in sediments (Argento and Vieira, 1989).

Factor 3 has strong Fe and Zn loadings, which are typical metals from river origins. The presence of siderurgical plants and urban sources in the river basins promotes the release of these metals in rivers and subsequently in the bay. Higher values for this factor follow the expected river plume in the bay, as shown in Figure 3. The easternmost area is not directly affected by this riverine influence.

Cd and Zn dominate the composition of factor 4. These metals are the most important pollutants in the bay sediments and are directly released into the bay by the erosion and leaching of industrial tailings located on the northern coast. The distribution of factor 4 in the bay shown in Figure 3 may indicate the dispersion of contaminated sediments in the bay, following a clockwise circulation of water.

It is important to notice that some metals, like Zn, Cd and Fe, are important components of more than one factor. This may indicate that these metals are involved in more than one environmental process acting in the bay. On the other hand, Mn and Ni do not contribute significantly to any observed factor, possibly indicating that these metals are influenced by several environmental processes but not one in particular.

As noted earlier in relation to Figure 2, the four factors have different ranges in the bay. Factor 1 shows a high autocorrelation plateau across the bay. This long range pattern may indicate that the component dominates a large portion of the bay's area and is only disturbed by the sea influence in the western area. Other factors present a short range in the bay, indicating the restricted influence of local processes. Organic matter production and consumption (F2) and riverine sediment discharge (F3) tend to a zero autocorrelation value around 5000 m. The fourth factor, representing the spread of Cd and Zn as local pollutants, has an intermediate range in the bay, maintaining some larger autocorrelation values till 15 000 m.

5. DISCUSSION

Metals in estuarine environments derive from a variety of sources and are involved in a number of geochemical processes, which affect their accumulation in sediments. One of the problems involved in studying metal contamination in those environments is to assess the contribution of each source in the overall distribution of metal concentrations. Empirical data can reveal the magnitude and location of sources by evaluating the release due to human activities (e.g. WHO, 1982). Overall metal accumulation is also relatively easily evaluated by sampling and analysing metal contents in sediments (Salomons and Forstner, 1984). However, environmental processes are more difficult to measure and trace. The spatial factor methodology discussed in this article provides a useful additional tool to assist in identifying and mapping these processes by relating them to a composite of metal concentration values and spatial structure.

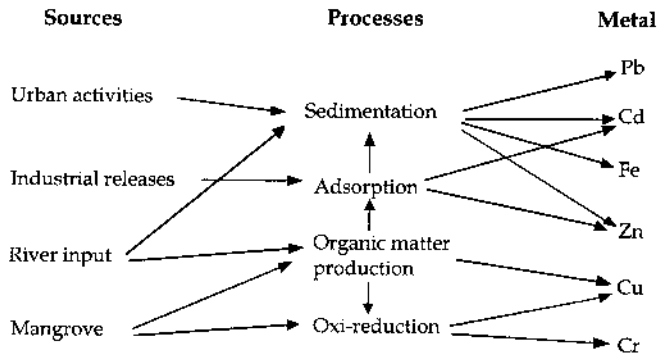

Figure 4. Proposed links among metal behaviour and related sources and environmental processes in Sepetiba Bay

For example, based upon the results obtained in the previous section, a useful general structure can be proposed to link possible sources and processes that affect metal accumulation in the Sepetiba Bay sediments as shown in Figure 4.

Clearly, the ultimate justification for any statistical methodology is the extent to which it assists in a meaningful and useful analysis of data in practice. In that context, the spatial factor technique discussed in this article should be viewed primarily as an exploratory, or descriptive, methodology. In general, the spatial factors derived cannot be guaranteed to be informative and to relate to known environmental processes. In some cases they may arise as artefacts of the particular data set under consideration and not be so useful as in the application presented in this article. Despite this proviso, the method discussed in this article provides a potentially useful addition to the relatively undeveloped range of methods which are available to assist in the study of environmental phenomena where both multivariate and spatial considerations are important.

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