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Spatial mapping of Pearl River Estuary surface sediment geochemistry: Influence of data analysis on environmental interpretation

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ABSTRACT

Distinguishing between natural and human-induced sources of estuarine sedimentary elemental concentrations often relies on mathematical normalisation (using geochemical or granulometric variables) and multivariate statistical techniques (e.g. Principle Component Analysis (PCA)). However, the extent to which these mathematical treatments can influence the interpretation of the data is not well constrained.

We report here the highest resolution mapping of surface sediment elemental concentrations in the Pearl River Estuary (PRE) to date ($n = 77$) and detail an investigation on the effect of "pre-defining" elements of interest before statistical analysis, a comparison of common normalisation techniques and discuss implications for the identification and interpretation of sediment elemental concentrations enriched by human activities.

Our analysis indentifies 4 distinct patterns of distribution in the PRE: North River, Western Shoal, Macau and Coastal Water distribution patterns. Mapping of these raw distribution patterns underpins a conceptual understanding of the interacting processes driving these patterns of deposition in the PRE, aiding the implementation of PCA and mathematical normalisation. However, we find evidence that (i) different normalisation elements/parameters can significantly alter the distribution patterns in elemental concentrations when applied across the entire PRE and may not reflect the true distribution (i.e. an artefact), and (ii) developing a reduced dataset for PCA can also alter the underlying trends in the spatial data; both of which significantly impact upon the subsequent environmental interpretation of source and human-induced pollution effects.

However, we demonstrate that through interpolation and mapping of raw geochemical data, zonation of the PRE can allow for much more accurate normalisation within discrete regions using the most appropriate conservative tracer element for each specific region identified.

1. Introduction

The concentration of elements in estuarine sediments broadly reflects natural background variability within the environment (e.g. catchment erosion, sediment grain size; mineralised/authigenic deposits) and human-induced pollution from industrial and urban activities (e.g. Schropp et al., 1990; Liu et al., 2003; Schrőder-Adams, 2006). Estuarine sediments are recognised as an important sink for heavy metals and other pollutants due to their affinity to fine-grained estuarine particles (e.g. silt- and clay-sized fractions; Loring, 1990; Covelli and Fontolan, 1997; Li et al., 2001; Liu et al., 2003; Ip et al., 2004). Although estuarine sediments may act as a sink for heavy metals, their removal from the water column may only be temporary due to remobilisation caused by changes in environmental conditions; such as water column oxygen concentrations which may remobilise elements (e.g., Fe, Mn, Cu; Edgington and Robbins, 1976; Davison, 1993; Lee and Cundy, 2000; Li et al., 2001). Additionally, the natural occurrence of elements within the environment makes an unequivocal investigation into elemental source difficult, with both natural and human-induced processes contributing to the geochemistry. The Pearl River Delta (PRD) has been subject to a number of studies aiming to quantify the extent of human-induced enrichment of elemental concentrations within; i) the sediments of the Pearl River Estuary (PRE) (Li et al., 2000, 2001; Zhang and Wang, 2001; Zhou et al., 2004; Wong et al., 2007); ii) agricultural soils (Wong et al., 2002); iii) the

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atmosphere (Wong et al., 2003; Siu et al., 2005; Lee et al., 2007); and iv) estuarine aquatic species (Liu and Deng, 2007; Cheung et al., 2008).

In an attempt to interpret this human-induced contribution to surface sediment elemental concentration(s), mathematical normalisation of the measured data to a "reference" element(s)/parameter(s) is commonly undertaken to account, for example, for grain size distribution and mineralogy (e.g. Loring, 1990; Schiff and Weisberg, 1999; Reid and Spencer, 2009). A number of "reference" element(s)/parameter(s) have been used in the literature, from which it is clear there is no uniform protocol (if even that can be realised in the context of spatial and temporal heterogeneity of elemental delivery and distribution within and between estuarine environments). For example, Fe (Van Alsenoy et al., 1993; Schiff and Weisberg, 1999; Liu et al., 2003), Li (Loring, 1990; Loring and Rantala, 1992; Aloupi and Angelidis, 2001), Ti (Loller, 2004), Al (Liu et al., 2003; Ho et al., 2010), Co (Matthai and Birch, 2001), grain size (Ip et al., 2004; Zhou et al., 2004), Rb (Grant and Middleton, 1990) and total organic carbon/matter (Dashkalakis and O'Conner, 1995; Zwolsman et al., 1996) have all been used to normalise for background environmental variability and subsequently enhance the human-induced signature.

Normalisation makes a series of important assumptions on the relationship between the measured elemental concentration and the chosen reference element/parameter (e.g. Luoma, 1990; Schiff and Weisberg, 1999): (i) proportional co-variability between the chosen reference element/parameter and natural background variability of the system being investigated (i.e. ideally representative of a single process, such as catchment erosion), (ii) the reference element/parameter is stable and not subject to variability under changing, non-linear environmental processes such as redox changes in the water column, diagenetic processes and adsorption/desorption, and (iii) there is no anthropogenic source for the chosen reference element/parameter. In addition, normalisation assumes (near) linearity between the measured elemental concentrations and normalisation element/parameter (i.e. the process it represents) and a negligible seasonal influence on elemental distributions and concentrations. Furthermore, we highlight an additional assumption that the most polluted areas are adjacent to predetermined pollution sources and that the effect of fluvial, tidal and mixing regimes on the redistribution of these metals across the estuary is negligible (i.e. permitting a holistic approach to normalisation). As a consequence of the diversity of estuarine systems in space and time, it can be difficult to determine a generic normaliser for a particular dataset, resulting in datasets being split and normalised to different elements (and potentially processes) based on an apparent linear relationship with proposed normalising elements (e.g. Sharma et al., 1999; Liu et al., 2003).

Whilst data normalisation has proved to be an important step for distinguishing natural background variability from (any) human-induced pollution signature, the potential for uncertainty (and misleading interpretations) in the resulting analysis is widely unrecognised (e.g. Reid and Spencer, 2009). In the first instance, the use of Fe as a normalisation element for changes in catchment influx, for example, is highly questionable in the context of its inherent sensitivity to changing water column oxygen conditions (changing redox potential). Fe, like Mn and Cu, is a redox sensitive parameter which forms oxide/oxyhydroxide precipitates under high oxygen concentrations in the water column (oxic), resulting in the deposition in the sediment. However, under low oxygen concentrations (anoxia in the water column/sediment pore water), these precipitates are diagenetically remobilised resulting in diffusion of Fe into the water column. This remobilisation can lead to its transportation away from the point of remobilisation and deposition elsewhere within the estuarine sedimentary record as a function of water column oxygen conditions (which can vary intra- and inter-seasonally) and estuarine circulation regime: this should preclude the consideration of Fe as a normalisation element. Similarly, total organic carbon can be influenced by changes in water column oxygen conditions (increased degradation during oxic conditions, and reduced degradation during anoxic conditions), sedimentary diagenetic processes, uncertainties linked to analytical methods (see Brodie et al., 2011a, 2011b), OM preservation linked to the elemental biochemical cycles (cf. Lalonde et al., 2012) and human influence (Dashkalakis and O'Conner, 1995) undermining its strength as a reliable normalisation parameter.

A recent investigation into the affect of normalisation procedures on estuarine sediment geochemical data revealed the potential for artefacts in the data distribution as a function of mathematical treatment (Reid and Spencer, 2009). Specifically, Al, grain size ($\leq$63 μm) and a $\log(x+1)$ transformation significantly skewed the data distribution and over emphasised the influence of grain-size in the subsequent PCA. More importantly, the degree with which these normalisation techniques highlighted a human-induced contribution to the concentration of heavy metals within the surface sediments was highly variable, indicating the real potential for deriving very different environmental interpretations of the measured data.

There has been a tendency to analyse the statistical relationships between various elements before understanding the raw distribution in the PRE (Li et al., 2000; Liu et al., 2003). In a heterogeneous estuary (e.g. bathymetry, freshwater influx, tidal influx, population centres), spatially mapping raw geochemical data provides an initial understanding of the processes that may not only be interacting in the estuary, but driving various patterns of elemental distributions.

Three studies have mapped raw trace metal concentrations within the PRE from a small number of sampling locations (Zhou et al., 2004 ($n = 12$); Ip et al., 2004, 2007 ($n = 39$); Yu et al., 2010 ($n = 46$)), each producing contradictory findings. Two of these studies reported that Co, Cr, Cu, Pb and Zn are most enriched along the Western Shoal (Zhou et al., 2004; Yu et al., 2010), whilst the other suggested these same metals are more enriched in the mouth of the PRE and in the adjacent coastal waters (Ip et al., 2007). However, commonalities are apparent between these studies. For instance these studies report Co, Cu, Pb and Zn are in higher concentrations across the estuary as the result of anthropogenic activities (Pb in particular). The Humen gate and mid-western section of the PRE have the highest concentrations of all heavy metals and are described as being the most polluted areas (Li et al., 2000; Zhou et al., 2004; Yu et al., 2010). Some of these interpretations are primarily based on the association of processes derived from the literature and *a priori* expectations which have led to a limited understanding of the physical connections between sources (natural and human-induced), transport pathways, estuarine mixing processes and deposition regimes, and the potential complexities in space and time within and between estuarine environments. These findings in themselves indicate that the human-induced and environmental processes contributing to the sedimentary elemental concentrations in the PRE are highly complex.

To better quantify elemental distributions in the PRE (and elsewhere), PCA has been employed to aid the identification of the associations between total surface sediment elemental concentrations and sources of human-induced pollution to surface sediment elemental concentrations (Liu et al., 2003; Zhou et al., 2004; Ip et al., 2007). However, and in addition to the potential artefacts introduced from normalisation, the final interpretation may be skewed through the reduction of the number of elements included in the PCA analysis (Liu et al., 2003; Zhou et al., 2004; Reid and