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# Magnetic approach to normalizing heavy metal concentrations for particle size effects in intertidal sediments in the Yangtze Estuary, China

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*Heavy metal concentration normalization for particle size effects by a magnetic approach facilitating sediment-based environmental monitoring.*

**Abstract**

In this study, mineral magnetic, particle size and geochemical analyses were conducted on intertidal sediments from the Yangtze Estuary to examine the feasibility of heavy metal concentrations normalization using magnetic techniques. Susceptibility of Anhysteretic Remanent Magnetization ($\chi_{ARM}$), the ratio of $\chi_{ARM}$ to SIRM (Saturation Isothermal Remanent Magnetization) and susceptibility ($\chi_{ARM}$/SIRM and $\chi_{ARM}/\chi$, respectively), and to a lesser degree, frequency dependent susceptibility ($\chi_{fd}$), displayed significant correlations with the fine sediment fraction (<16 μm). The strong relationships between $\chi_{ARM}$ and heavy metals can be explained by the role of particle size and iron oxides in controlling metal concentrations. This study demonstrates that $\chi_{ARM}$ can be used to normalize for particle size effects as efficiently as common reference elements such as Al. Furthermore, the rapid and non-destructive nature of mineral magnetic measurement technique means that $\chi_{ARM}$ has a considerable application value in environmental quality monitoring and related studies.


*Keywords:* Heavy metal; Particle size; Normalization; Magnetic method; Yangtze Estuary

## 1. Introduction

With the development of environmental magnetism, magnetic measurement is becoming an important means in particulate pollution study. Attention has been focused on identifying polluted sites, monitoring environmental quality and discriminating pollution sources, either independently or in combination with geochemical analysis (e.g. Oldfield et al., 1978; Scoullos et al., 1979; Hunt et al., 1984; Heller et al., 1998; Hoffmann et al., 1999; Matzka and Maher, 1999; Shu et al., 2000; Muxworthy et al., 2001; Jordanova et al., 2003; Lecoanet et al., 2003; Robertson et al., 2003; Plater and Appleby, 2004; Urbat et al., 2004; Shilton et al., 2005). The primary assumption has been that emissions from industrial and urban sources often include high concentrations of magnetic particles. Once they are deposited, the environments containing these anthropogenic particles will display distinctive magnetic properties such as magnetic enhancement (Thompson and Oldfield, 1986). Some studies have found good relationships between certain magnetic properties (e.g. magnetic susceptibility $\chi$) and heavy metal concentrations. This opens the possibility of using magnetic

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parameters as a proxy for pollutant concentrations (Williams, 1991; Clifton et al., 1999; Petrovský and Ellwood, 1999; Xie et al., 2001; Urbat et al., 2004; Schmidt et al., 2005; Shilton et al., 2005; and references therein).

Despite these advances, the approach of using mineral magnetic properties in the study of environmental pollution has not been fully explored. It is well documented that particle size plays a significant role in controlling pollutant concentrations in sediments whereby the concentrations tend to increase with declining particle size (Rae, 1997). Therefore in order to assess any anthropogenic influence on sediment properties, it is necessary to take into account the effect of particle size variations by granulometric or geochemical methods (Rae, 1997). Granulometric normalization normally analyses a specific particle size fraction of sediment, e.g. the <63 μm size (Salomons and Fornster, 1984). However, this method requires a laborious separation of the particular particle size fraction, and it is likely that pollutant concentrations in the separated fraction may not reflect the concentrations in the bulk sediments (Ravichandran et al., 1995). Geochemical methods involve the correction of pollutants against some conservative elements, such as Al, Li, Fe, Cs, Sc and Rb, which are considered to be proxies of the finer fractions of particle size (Daskalakis and O'Connor, 1995; Rae, 1997; Roussiez et al., 2005). Among these elements, Al is the most widely used geochemical normalizer, because it is the structural constituent of clays, the smallest sized particles and an important carrier phase for absorbed metals (Kersten and Smedes, 2002). Furthermore, Al has a high natural abundance and is not susceptible to anthropogenic contamination and diagenetic alteration. Recently, a magnetic approach has been suggested (Oldfield et al., 1993; Oldfield and Yu, 1994; Clifton et al., 1999). In the study of coastal sediments from the Irish Sea, Oldfield et al. (1993) found that Anhysteretic Remanent Magnetization (ARM, now often expressed in susceptibility form as $\chi_{ARM}$), which is sensitive to fine-grained single domain magnetite, correlated well with the finer fraction (<31 μm) of these sediments and the $^{241}$Am and $^{137}$Cs levels. Based on this finding, a method for reducing particle size effects on pollutant concentrations using their ARM value was proposed. By virtue of magnetic measurements being simple, quick and non-destructive, magnetic normalization could be a valuable tool for pollution assessment. Nevertheless, such studies are still relatively sparse (Clifton et al., 1999), and whether this finding holds true in other areas remains to be validated. Furthermore, there are other magnetic parameters that are sensitive to the presence of fine-grained magnetic minerals. For example, frequency dependent susceptibility ($\chi_{fd}$) is an indicator of fine viscous grains near the superparamagnetic (SP) and stable single domain (SSD) boundary, which is around 0.02 μm for isodiametric grains (Maher, 1988; Worm, 1998; Muxworthy, 2001). The potential use of this parameter for a normalization purpose has not been tested. In this paper, we present simultaneous magnetic, geochemical and granulometric analyses of intertidal sediments from the Yangtze Estuary, China. The purpose of the investigation is to examine the potential value of applying a mineral magnetic technique as means of normalizing pollutant concentrations for particle size effects.

## 2. Materials and methods

Shanghai, the largest industrial city in China with a population of ca. 13 million, is situated adjacent to the lower part of the Yangtze Estuary. Extensive intertidal flats have developed due to the huge flux of suspended materials ($4.6 \times 10^8$ t year$^{-1}$) carried by the Yangtze River (Chen, 1998). The intertidal sediments are predominantly composed of silts and clayey silts, and display substantial variations in particle size composition due to hydrodynamic and vegetation cover changes, both in the direction along the coast as well as perpendicular to the coast (Zhang et al., 2001a). Coastal sewage discharge has resulted in elevated, but localized heavy metal concentrations in parts of the intertidal zone (Zhang et al., 2001a; Feng et al., 2004).

Eighteen sites, covering most areas of well-developed intertidal zone, were selected for sampling in 2001 (Fig. 1). At each site, depending on the width of intertidal zone, two to three surface (0–5 cm) samples were taken along a transect from the upper, vegetated marsh zone to the lower, bare mudflats. In addition, three short cores (20 cm in length) were recovered from higher, middle and lower tidal flat near the Bailonggang sewage outlet, and each of the cores was sectioned at 0.5–5 cm intervals (Feng et al., 2004). A total of eighty five samples were obtained, and each sample was dried at a low temperature of 40 °C. Previous studies have indicated that sulphide content of these sediments is quite low (Han, 2002), and detrital magnetite of pseudo-single domain (PSD)/multi domain (MD) magnetite dominates the magnetic properties of the sediments (Zhang and Yu, 2003). In comparison with lyophilization, such pre-treatment of samples causes no significant alternation of magnetic minerals (Chen et al., 2001). A mixture of concentrated $HF-HClO_4-HNO_3$ was employed for the total digestion of the sediments (NEB, 1998). Cu, Zn, Pb, Ni, Li, V, Mn, Fe and Al were determined using ICP-AES (Perkin Elmer Plasama 2000). Quality assurance techniques included the use of a certified reference material (GSD9, China National Standard) and replicate analysis of each batch of samples. The results for the standard were within ±10% of the certified values.

Particle size was determined using a Coulter Laser Granulometer (LQ-100). For the mineral magnetic measurements, we focused on parameters sensitive to fine-grained magnetic minerals ($\chi_{ARM}$ and $\chi_{fd}$) or commonly used as magnetic grain size indicators, e.g. ratio of $\chi_{ARM}$ to SIRM (Saturation

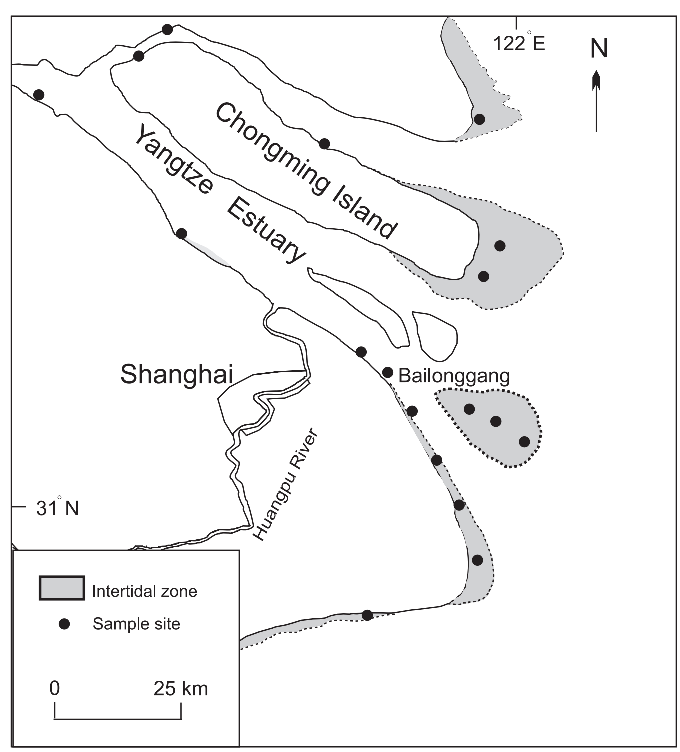


Fig. 1. The Yangtze Estuary showing the intertidal zone and the sample sites.