Science of the Total Environment 612 (2018) 26–38

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Metal pollutants in Indian continental coastal marine sediment along a 3700 km transect: An electron paramagnetic resonance spectroscopic study

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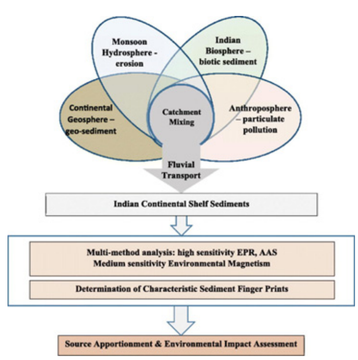
HIGHLIGHTS

- 3500 km coastal transect mapping Indian continental shelf marine pollution.
- Monsoon meteorology/hydrosphere pollution coupling in geo- and anthropo-spheres
- Monsoons flush bio-toxic anthropogenic sediment into coastal ecosystem.
- Modelling of EPR spectra enables analytical environmental magnetic analysis.
- EPR and environmental magnetism enable geospatial marine sediment fingerprinting.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 May 2017
Received in revised form 7 August 2017
Accepted 7 August 2017
Available online 1 September 2017

Editor: Jay Gan

Keywords:
EPR
Environmental
Fingerprint
Geo-spatial
Modelling
Bio-toxicity

ABSTRACT

We report the analysis and geographical distribution of anthropogenically impacted marine surficial sediments along a 3700 km transect around the continental shelf of India. Sediments have been studied using a mixed analytical approach; high sensitivity electron paramagnetic resonance (EPR), chemical analysis and environmental magnetism. Indian coastal marine deposits are heavily influenced by monsoon rains flushing sediment of geological and anthropogenic origin out of the subcontinental river systems. That is, climatic, hydro-, geo- and anthropogenic spheres couple strongly to determine the nature of Indian coastal sediments. Enrichment of Ni, Cu and Cr is observed in shelf sediments along both east and west coasts associated with industrialised activities in major urban areas. In the Gulf of Cambay and the Krishna and Visakhapatnam deltaic regions, levels of Ni and Cr pollutants (≥80 and ≥120 ppm respectively) are observed, sufficient to cause at least medium adverse biological effects in the marine ecosystem. In these areas sediment EPR spectra differ in characteristic from those of less impacted ones. Modelling enables deconvolution of EPR spectra. In conjunction with environmental magnetism techniques, EPR has been used to characterise species composition in coastal depositional environments. Paramagnetic species can be identified and their relative concentrations determined. EPR g-values provide information about the chemical and magnetic environment of metals. We observe g-values of up to 5.5 and large g-shifts indicative of the presences of a number of para and ferrimagnetic impurities in the sediments. EPR has enabled the characterisation of species composition in coastal depositional environments, yielding marine sediment environmental 'fingerprints'. The approach demonstrates the potential of EPR spectroscopy in the mapping and

Abbreviations: ASA, absorption spectral area; EC, east coast; EPR, electron paramagnetic resonance; ESR, electron spin resonance; FMR, ferri magnetic resonance; HF, high frequency; ICP, inductively coupled plasma; IRM, Isothermal Remanent Magnetisation; LF, low frequency; PtP, peak to peak; SIRM, saturation IRM; WC, west coast.

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http://dx.doi.org/10.1016/j.scitotenv.2017.08.065

evaluation of the concentration and chemical speciation in paramagnetic metals in sediments from marine shelf environments and their potential for source apportionment and environmental impact assessment.

1. Introduction

Elevated levels of Co and Zn indicative of anthropogenic input have been observed in Indian rivers (Alagarsamy and Zhang, 2005). Thus, it is unsurprising that metal enrichment of Co and Cu associated with industrial activities occurs in Indian continental shelf sediments along both east and west coasts proximal to major urban areas (Alagarsamy and Zhang, 2010). Indian coastal marine deposits are heavily influenced by monsoon rains flushing sediment out of the river systems, sediments both geological and anthropogenic in origin. That is climatic, hydro-, geo- and anthropogenic spheres couple strongly to determine the nature and biological impact of these sediments. Techniques commonly employed in the analysis and detection of trace metals in the marine environment include atomic absorption spectroscopy, emission spectroscopy and neutron activation. Whilst these techniques give qualitative and quantitative information, they do not yield information on the trace metal micro-environment. In contrast, the high sensitivity of electron paramagnetic resonance (EPR) spectroscopy, also known as electron spin resonance (ESR) spectroscopy, provides additional information on metallic oxidation states and the chemical environment of magnetically active minerals whether of geological or anthropogenic origin. That is, EPR has the capacity to yield quantitative and qualitative data that is complementary to that obtained from other bulk chemical and magnetic techniques. This is demonstrated here in a study of anthropogenically impacted Indian coastal marine sediments along a 3700 km transect.

EPR has been used to investigate the behaviour of paramagnetic particulate species in marine (Wakeman and Carpenter, 1974, Crook et al., 2002,) and anoxic sediments (Billon et al., 2003), rivers (Boughriet et al., 1992), estuaries (Ouddane et al., 2001) and terrestrial (Küçükuysal et al., 2011) materials. Otamendi et al. (2006) have employed EPR to study the stratigraphy of geological marine sediments in southwestern Venezuela. EPR has also been used quantitatively to determine trace levels of Cu in seawater (Virmani and Zeller, 1974) and to monitor low concentrations of Mn and other heavy metals in natural water systems (Angino et al., 1971). Sun et al. (2008) have proposed the use of EPR to detect organic free radicals and trivalent iron pollution in mangrove swamps. Heise (1968) investigated the variation of transition metal EPR spectra with sediment depth in marine sediments although without detailed analysis of sediment composition. Violante et al. (2010) have used EPR to complement other spectroscopic techniques in the identification of terrestrial metal complexes at the surfaces of Al, Fe and Mn oxides in silicate clays and soil organic matter. Espinosa et al. (2001) have employed EPR in the analysis of V(IV) porphyrins in petroleum products. Guedes et al. (2003) employed EPR in the characterisation of the molecular structure of asphaltenes in Brazilian oil whilst multicomponent systems have been studied in the laboratory by Guilbault and Misel (1969, 1970), Guilbault and Moyer (1970). Mangrich et al. (2009) have used EPR to trace the provenances of dusts by studying sunlight bleaching of Ti E_1' electron trap centres in quartz which are induced by natural radiation (Gao et al., 2009). Nagashima et al. (2012) have used variation in the EPR signal intensity of E_1' centres to assess the contribution of detrital materials from the Yukon River to continental shelf sediments in the Bering Sea. Bahain et al., 2007 have used the EPR response of E_1' centres in quartz and carbonates to date archaeological deposits buried in river sediments and Tissoux et al., 2008 have used active E_1' centres to date Pleistocene deposits.

Although EPR has been applied to geochemical and terrestrial systems it has found more limited application to the analysis of marine systems. This is surprising as its detection limit is comparable to the techniques more commonly used for the chemical analysis of sediments. We believe that the present study is the first of its kind to apply EPR analysis combined with detailed modelling of para- and ferri-magnetic components to marine continental shelf sediments along the east and west coasts of India providing better understanding of the status of sediment pollution. Our integrated EPR, chemical and environmental magnetic methodology also enables the determination of a suite of parameters that yield a 'fingerprint' for these surficial coastal sediments with the potential to enable source apportionment.

2. Study area

2.1. Geographic and climatic setting

Geographically the subcontinent of India (Fig. 1) embraces tropical and subtropical climatic zones which are dominated by monsoon systems. These are characterised by strong seasonal variations alternating between warm-humid to cold-arid conditions resulting in wet and dry seasons alone and significant seasonal variation in rainfall and temperature. The gradient of these climatic zones is affected predominantly by the sharp altitudinal changes in the northern half of the subcontinent where the Himalaya form the major relief. The Himalaya act as a barrier to the cold northerly winds from Central Asia maintaining the pattern of the Indian Ocean monsoon circulation. The Thar Desert in the north west of India allows oceanic atmospheric circulation and promotes sediment dust-aerosol influx deep into the continent. The southwest monsoon is divided west and east of the Indian peninsular into the Arabian Sea and weaker Bay of Bengal branches, respectively. The latter results in regional turbulence due to the rapid altitudinal differences and narrowing orography. The former branch moves northwards along the Western Ghats giving rain predominantly to the west coast. These complex weather patterns cause large-scale climate-induced coastal sedimentation during monsoon cyclones (Sangode et al., 2007). The large volumes of water flushing rivers during the monsoon purge and dilute anthropogenic pollution affecting the composition of sediment in the deltas of rivers that run through industrial areas (Alagarsamy and Zhang, 2010).

2.2. Coastal-geological setting

Source bedrock and their specific weathering mechanisms control the distinct geochemical compositions of Indian coastal sediments (Alagarsamy and Zhang, 2005). The outer limit of the eastern continental shelf lies at *c.* 200 m depth (Fig. 1) covered by calcareous relict sediment whilst the inner shelf and continental slope are covered by clastic sediments (Rao, 1985). Away from river mouths the shelves are covered by fine-grained terrigenous sediment. Sedimentation rates vary around the continental shelf, decreasing southwards along the WC. Deorukhakar (2003) observes 14 mm/yr in the Mumbai basin. Clay accumulation rate for the Gulf of Cambay are between 1.8 mm/yr and 19 mm/yr decreasing southwards from the confluence of the Tapti and Narbarda rivers (Borole, 1988) to 0.01–2.6 mm/yr further southwest (Pandarinath et al., 2004), consistent with sediment dispersal being regulated by monsoon dominated littoral currents. Low clay accumulation rates (1.8–2.5 mm/yr) on the outer shelf suggest that transport of suspended matter across the shelf is low (Borole, 1988). Very low sedimentation rates of 0.72 and 0.56 mm/yr at water depths of 35 and 45 m respectively have been determined by Manjunatha (1992) in the shelf region off Mangalore. The shelves formed at the mouths of