

## **Metal pollutants in Indian continental coastal marine sediment along a 3,700 km transect: An Electron Paramagnetic Resonance spectroscopic study**

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### **Abstract**

We report the analysis and geographical distribution of anthropogenically impacted marine surficial sediments along a 3,700 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 ( $\geq 80$  and  $\geq 120$  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 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.

**Key words:** EPR, Environmental, Fingerprint, Geo-spatial, Modelling, Bio-toxicity.

## 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 & 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 3,700km 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.

Acronyms: 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.

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<sub>1</sub>' 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<sub>1</sub>' 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<sub>1</sub>' centres in quartz and carbonates to date archaeological deposits buried in river sediments and Tissoux et al. (2008) have used active E<sub>1</sub>' centres to date Pleistocene deposits.

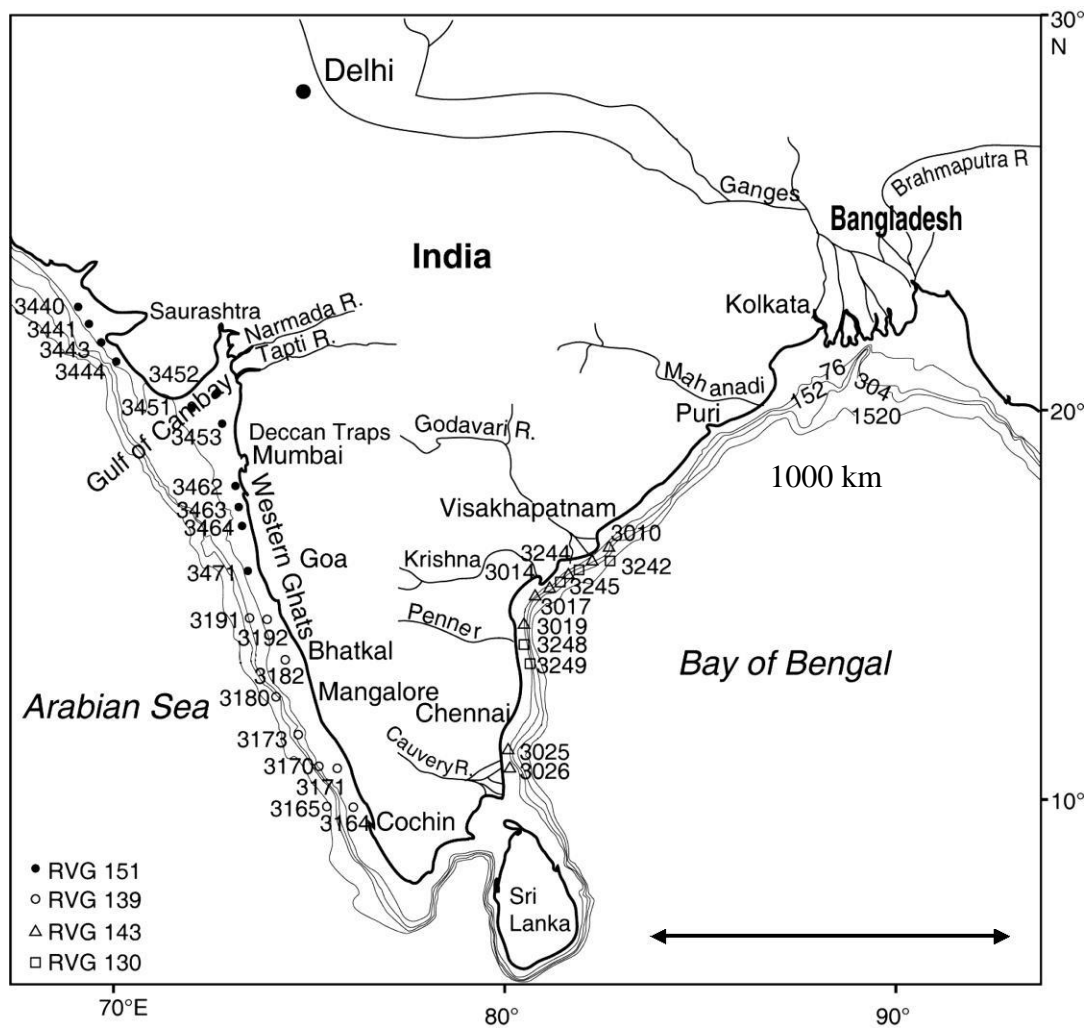
Although EPR has been applied to geochemical and terrestrial systems it has found more limited application to the analysis of marine systems. This is surprising as its detection limit is comparable to the techniques more commonly used for the chemical analysis of sediments. We believe that the present 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).



**Fig. 1.** Location of the principal rivers in the Indian peninsular and principal\* sediment sampling stations on the Indian east and west coast during cruises RVG 130, 139, 143 and 151, see text, (some site labels omitted for clarity).

## 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 Tapi and Narmada 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 northern east coast (EC) rivers receive a large part of their sediment from the Ganges, Brahmaputra and Mahanadi. Coastal sediments of the central EC region derive from the Godavari and Krishna. All these rivers form fertile deltas, which in turn, are heavily populated. These rivers have reduced the salinity of surface waters along the shore and, over time, their sediment load has resulted in shallow seas. Sediment input and annual discharge in the south is less from smaller rivers such as the Pennar and Cauvery (Rao, 1985). The Mahanadi, Godavari and Cauvery river systems discharge basaltic deposits into the EC Bay of Bengal due to the prevalence of Deccan Basalt within their catchments (Sangode et al. 2007). Sediments from rivers originating in the western part of India are derived from black “cotton soils” which cover the western Deccan Traps. In their lower reaches these rivers drain through Precambrian formations containing kaolinite rich soils. Black cotton soils are of secondary significance in the shelf sediments derived from the Godavari and Krishna rivers (Rao, 1991). The Indus is the largest source of sediment in the western Arabian Sea, extending outward from the coast to a distance of *c.* 1000 – 1500 km (Rao and Rao, 1995) to the north west of the current study area. The Indus predominantly drains the Precambrian metamorphic rocks of the Himalayas and to a lesser extent the semiarid and arid soils of West Pakistan and NW India (Krishnan, 1968). Deccan Trap basalts are the predominant rock types in the Saurashtra and drainage basins of the west coast (WC) Narmada and Tapi rivers. These rivers discharge  $\sim 60 \times 10^6$  tonnes of sediment

annually through the Gulf of Cambay (Rao, 1975). The northern Western Ghats are composed of basalts between Mumbai and Goa, and further south, between Goa and Cochin, of Precambrian granites, gneisses, schists and charnockites (Krishnan, 1968).

Alagarsamy and Zhang (2005, 2010) have studied the occurrence of trace metals (e.g. Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Ba, Pb) in suspension and sediment in the river mouths of major Indian rivers (e.g. Brahmaputra, Ganges, Narmada, Tapti, Krishna and Cauvery). They find that the average particulate trace metal concentration ( $\sim 300 - 1000 \text{ mg g}^{-1}$ ) to be higher than the global average ( $\sim 170 - 350 \text{ mg g}^{-1}$ ). Regional and watershed differences in segregation factors are observed, reflecting variable weathering rates due to differing mineralogy, preferential removal of alkaline and alkaline-earth metals relative to oxide-forming elements (e.g. Fe and Al), and a regional climatic shift from northern temperate to southern subtropical conditions. A study by Alagarsamy (2006) of the variation in anthropogenic input of trace metals (Fe, Mn, Co, Cu, Zn and Pb) into the industrialised lower Mondovi River and estuary shows that the seasonal influence (pre, during and post monsoon) upon metal concentration in the continental shelf is relatively small. Additional geographical, geological and climatic details of the Indian sub-continent may be found in Alagarsamy (2009).

### **3. Materials and methods**

#### **3.1. Sampling and Analysis**

Surface sediments from the east and west coasts of India were collected over a period of 14 months both before and after monsoon seasons along western and eastern portions of the Indian continental shelf during four cruises (130, 139, 143 and 151) of the R.V. Gaveshani (Table S1 in supporting information). The four digit station numbers in Table 1 (and Table S1), prefixed in the text and figures by S, are cross referenced in Fig. 1. Chronologically, sampling was undertaken along (i) EC in early January, post-Monsoon cruise 130, N to S, S3010 – S3026, (ii) WC late May / early June, pre-Monsoon, cruise 139, S to N, S3164 – S3192, (iii) EC early November, post-Monsoon, cruise 143, N to S, S3242 – S3249, (iv) WC March, pre-Monsoon, cruise 151, N to S, S3440 – S3471. Sediment samples were collected from the uppermost layer of the continental shelf at depths of between 30 and 700 metres using a deep-sea Van Veen Grab / Snapper. This sampled the surface layer to between 100 and 200 mm over an area of *c.*  $1.2 \text{ m}^2$ . Given the 0.56 to 19 mm/yr range of average sedimentation rates (Manjunatha 1992, Borole 1988, Deorukhakar 2003) this sample thickness represents the net sediment deposition at any given site of between two to ten years or so, which is longer than the experimental campaign period. As noted above, Alagarsamy (2006) found seasonal differences in anthropogenic trace metals in coastal sediments to be small. Thus the extended period of the

sampling campaign is not expected to unduly bias the data set. Samples were bagged and frozen after collection to avoid cross contamination. After thawing and oven drying in the laboratory at 50 – 60°C samples were disaggregated using an agate mortar. Bulk sediment samples were homogenised before subsampling for analysis. Nondestructive environmental magnetism measurements (using *c.* 15g) and EPR spectral measurements (using *c.* 0.01g) were undertaken prior to metals analysis by acid digestion (as detailed in supporting information). Environmental magnetism measurements were made on a subset of EC and WC samples. EPR spectra were subsequently modelled to elucidate the key magnetic components.

### 3.2. EPR Spectral analysis

EPR spectra were obtained at room temperature in magnetic fields of 250±250 mT using a JEOL JES-TE100 spectrometer operating at a nominal frequency of 9.7 GHz with 100 kHz RF cavity modulation and digitised for analysis. Microwave power and modulation amplitude were adjusted to avoid saturation. Cavity modulation enables phase sensitive detection. This enhances the signal to noise ratio and results in spectra being detected as the differential of the absorption spectrum. Thus, symmetric Lorentzian or Gaussian resonances are displayed as anti-symmetric spectra with positive and negative peaks, their spectral *g* values determined from the baseline crossover field. The mean microwave frequency after cavity tuning was similar for all samples (9.355GHz ±0.056%) resulting in base-line crossover for DPPH (*g* = 2.0036, *S* = ½) at 0.333T. DPPH was used as the standard for *g*-factor calculations. EPR spectra can be determined for a few milligrams or less of sample bestowing high sensitivity upon the technique. Spectra were normalised to experimental conditions (gain, microwave power and sample weight) permitting quantitative and qualitative comparison. Variations in the EPR differential signal intensity calculated by multiplying the line width, determined as the distance between the principle absorption maximum and minimum fields,  $\Delta H$ , by the peak to peak (PtP) signal amplitude, are often used as a proxy proportional to variations in relative concentration. This proxy has been compared to the total area of EPR absorption spectra, likewise proportional to the paramagnetic content of samples (see results and discussion). The total area of the EPR spectrum is a measure of the para and ferri magnetic content of the samples contributed by magnetic particles and impurities. The intensity of six-line hyperfine Mn<sup>2+</sup> EPR spectra was determined using the strongest low field resonance line (at ~ 325 mT) to minimise the effects of superposition from other spectral components around *g* ~ 2.00. When present in dilute samples, the Mn<sup>2+</sup> hyperfine spectrum can be used as a secondary field calibration between spectra.

### 3.3 EPR applied to environmental sediments

EPR is sensitive to paramagnetic ions with odd numbers of unpaired electrons. Zero field splitting appears in complexes which have more than one unpaired electron. Complexes with an odd number of electrons always give rise to an EPR spectrum (Abragam and Bleaney, 1970). Conversely, diamagnetic ions with even number of unpaired electrons do not exhibit EPR spectra. Classically, electron spins precess in a magnetic field at the Larmor frequency determined by their spin and the field's magnitude. Resonance occurs when the simultaneous application of microwave photons of frequency,  $f$ , provides sufficient energy,  $E$ , to enable spin transitions between the Zeeman energy states. That is when the microwave and Larmor frequencies are equal such that  $hf = g\mu_B B$  where  $\mu_B$  and  $g$  are the electronic Bohr magneton and  $g$ -value respectively. For dilute spin  $\frac{1}{2}$  ions a single resonance is observed with a  $g$ -value close to that of a free electron ( $g_e = 2.0023$ ). Resonance can then be characterised by an effective  $g$ -value and its variation from that of a free electron by the shift in  $g$ ,  $\Delta g = g_{\text{observed}} - g_e$ .  $g$ -shift is also a measure of the variation in the local field experienced by and perturbing the magnetic spin centres i.e. their magnetic and chemical environment. In strongly para- or ferri- magnetic sediments  $g$ -values can shift significantly above 2.00 as the sample magnetisation enhances the local field. The local field, however, only has limited capacity to move the resonance position of an EPR active species. Thus, resonances remote from  $g \sim 2$  are more likely to be due to non  $s = \frac{1}{2}$  species. At constant (microwave) frequency the apparent  $g$ -value for dilute samples is inversely proportional to the resonance field, i.e. the EPR differential spectrum cross-over field. However, in more concentrated and multi-component samples the cross-over field approach to sediment impurity classification is naive as it cannot account for an admixture of several EPR active components or samples may be insufficiently dilute for the pure elemental  $g$ -value to be observed. Thus, spectral cross-over  $g$ -values may not be characteristic of all metals within a sediment and modelling of spectra is necessary if quantitative measurements are to be made. Further, for ferro- ferri- and anti- ferromagnetic particulate materials in sediments, the line width, and hence signal intensity, is dependent on particle size, shape and concentration. When even low concentrations of single, pseudo single domain or polydomain ferri or ferromagnetic minerals are present, dipolar magnetostatic fields can cause line broadening of several hundreds of mT and consequently very broad and displaced EPR spectra (e.g. Crook et al. 2002). This is because intra- and inter-particle demagnetising and dipole-dipole fields perturb the high homogeneity EPR spectrometer field. Hence, in strongly magnetic environmental samples a linear relationship between magnetic susceptibility and EPR intensity cannot be assumed.

The microwave EPR magnetic susceptibility, DC, low (0.465kHz) and high (4.65kHz) RF magnetic susceptibilities measured using environmental magnetism methods (see sec.3.5 later) are all related by the sample's magnetic susceptibility tensor. Thus, taken together, these



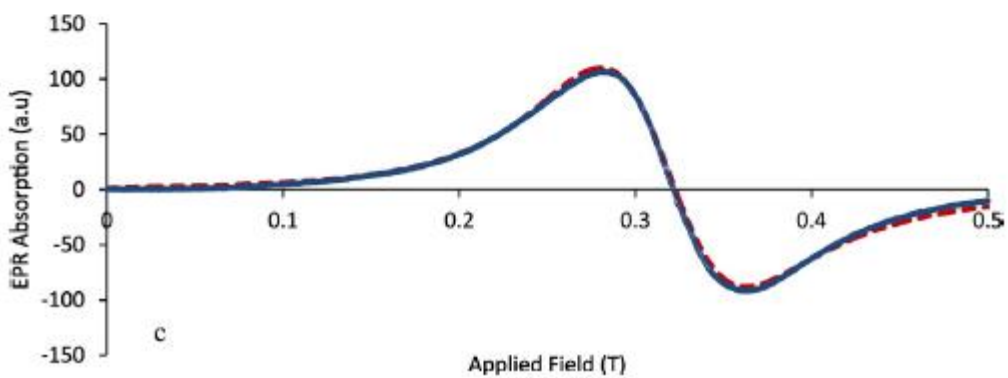
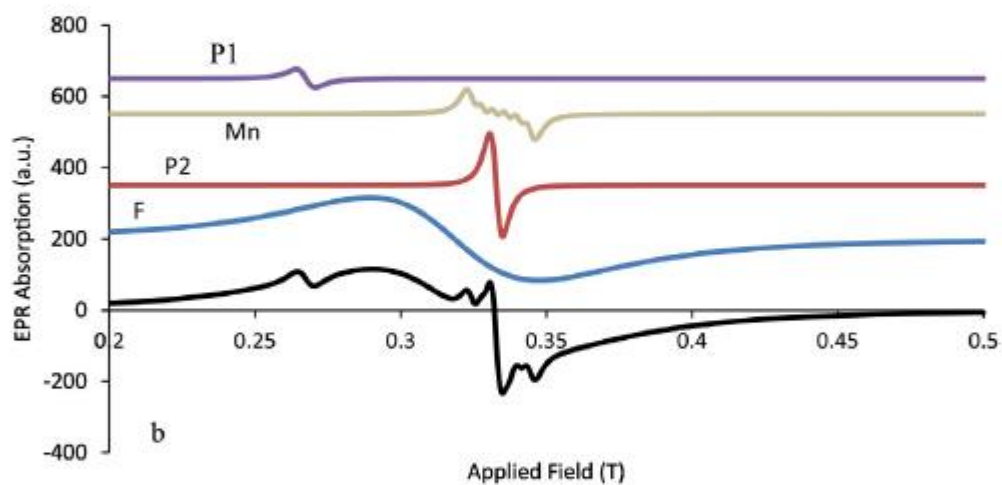
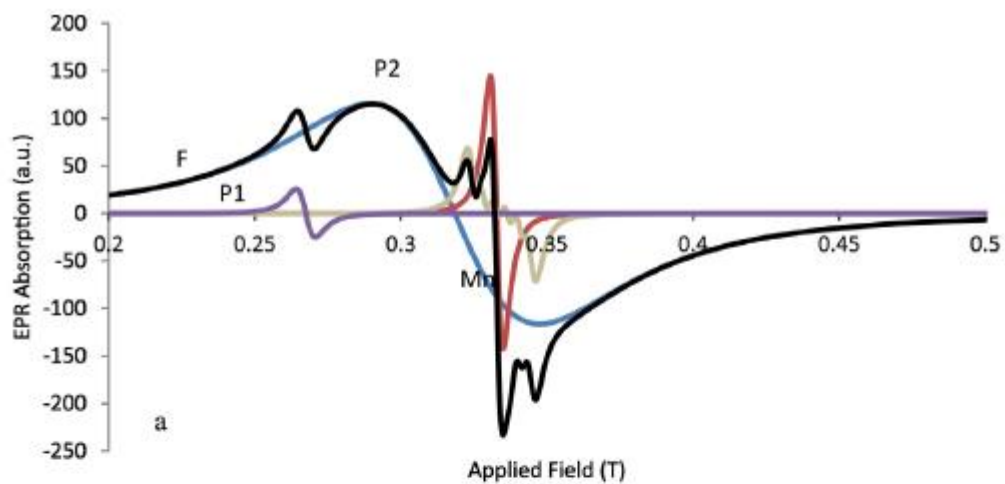
measurements have the potential to yield a characteristic ‘fingerprint’ of environmental sediments and contribute to source apportionment in sediment un-mixing models.

### 3.4. EPR Modelling

Sediment EPR spectra have been modeled from first principles using a graphical user interface package developed at MMU, see supporting information for more detailed information. This enables the relative contribution from constituent components to be fitted and determined generating an EPR ‘fingerprint’. This approach is more subtle and distinctive than using bulk environmental magnetism parameters alone. EPR spectrometer settings and sediment parameters comprise optimisable input (and consequently ‘fingerprint’) model parameters. Parameters include, for example, magnetic susceptibility and volume fraction, g-values and spin-lattice relaxation time,  $\tau_1$ , of the para- and ferri-magnetic components. Hyperfine splitting and line broadening due to magnetostatic interactions, can be modelled using a number,  $n$ , of field-displaced resonances and optimising  $\tau_1$  such that the line widths overlap. The model outputs the computed field dependent EPR absorption curve along with each resolvable magnetic component, determined on the basis of materially relevant sample characteristics. A model spectrum and its constituent components is shown in Fig. 2.

**Fig. 2:** a) An indicative composite model spectrum showing a broadline width particulate ferrimagnetic (magnetite) component (F), a six fold hyperfine paramagnetic ( $\text{Mn}^{2+}$ ) and two paramagnetic components (P1, P2) of differing g- values, susceptibilities and volume fractions a) overlain spectrum, b) EPR spectrum components displaced for clarity, c) Experimental (solid line) and model fit (dashed line) for station R7-S3453 in the Gulf of Cambay.

Fig 2



### 3.5 Environmental Magnetic Methods

Only a summary of the environmental magnetic measurements and properties of these sediments sufficient to support the context and discussion of this EPR study is given here. For a detailed environmental magnetism study see Alagarsamy (2009), Alagarsamy and Zhang, (2010). Sample sizes for environmental magnetism measurements tend to be of the order of several grams or tens of grams rather than a few milligrams as for EPR. In environmental magnetism, determination of the so called Low Frequency (LF) 0.465kHz and High Frequency (HF) 4.65kHz RF susceptibilities and their difference ratio,  $\chi_{fd}$  (%), are used as a measure of the presence of superparamagnetic mineral grains. High LF and HF susceptibility, suggests the presence of significant ferri- or para- magnetic content. Paramagnetic  $Fe^{3+}$  and  $Mn^{2+}$  ions, which result in high environmental magnetism susceptibility are expected to show strong EPR spectra. Increased LF and HF susceptibility is associated with discharge from the Krishna and Visakhapatnam delta. Alagarsamy (2009) observed that magnetic susceptibility had a more significant coefficient of determination ( $R^2 = 0.91 - 0.98$ ) with the concentration of transition metals Fe, Cr, Cu and Ni in EC sediments which also have higher concentration of ferrimagnetic minerals. EC samples showed higher values of  $\chi_{fd}$ (%) consistent with the presence of finer ferrimagnetic grains and enrichment of ferrimagnetic minerals also resulting in higher values of Isothermal Remanent Magnetisation (IRM), Saturation IRM (SIRM) and magnetic susceptibility suggesting the presence of higher ferrimagnetic minerals possibly derived from the weathering of Deccan Basalts (Alagarsamy 2009). EC samples also show greater correlation between and the magnetic susceptibility parameters ( $\chi$ ,  $\chi_{ARM}$ ,  $IRM_{20\text{ mT}}$  and SIRM) and Fe, Cr, Cu and Ni concentration (Alagarsamy, 2009).

## 4. Results and discussion

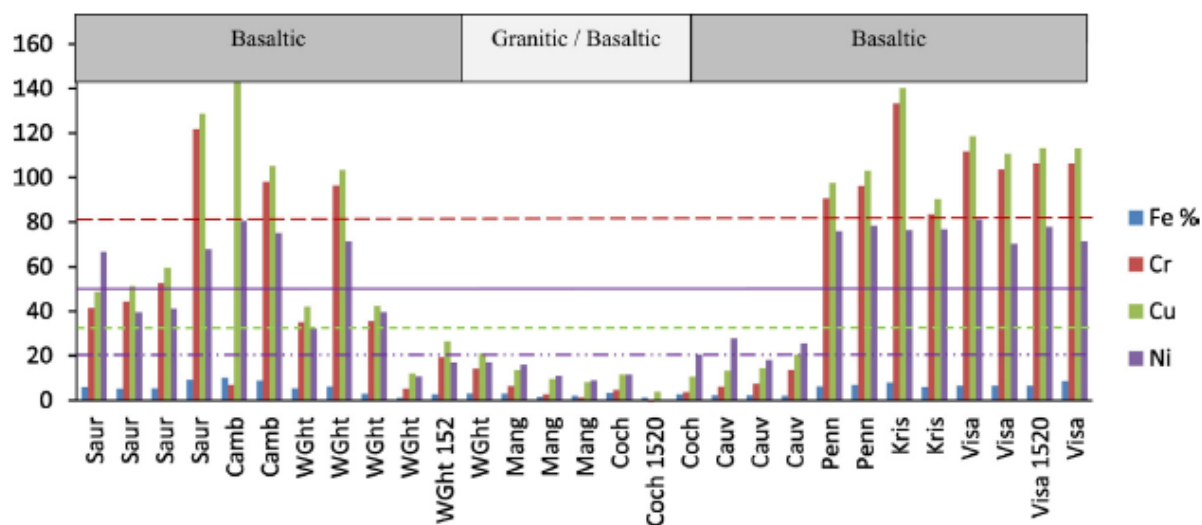
### 4.1 Metal concentrations

A detailed study of the geochemical distribution of the major and minor trace elements in these sediments (as listed in Sec.2.2) may be found in Alagarsamy and Zhang (2010). Here we report the IAS data of the paramagnetic elements relevant to EPR (i.e. Fe, Cu, Cr and Ni) in order to place the EPR spectra and environmental magnetic measurements in context. Of these four paramagnetic impurities Fe dominates the sediments at concentrations between 1 and 10 wt%, followed by Cu (4 – 140 ppm), Cr (1 – 130 ppm) and Ni (0.3 – 80 ppm), Fig. 3, Table S2. Fig. 3

displays the coastal metal concentrations geographically at survey stations along the continental shelf. Correlation between Cr, Ni, Cu and Fe are visually striking and statistically highly significant (Pearson correlation coefficients between 0.776 and 0.936, Fig. S1) consistent with entrainment of Cr, Ni, Cu with Fe in all sediments. Enhanced metal concentrations indicative of anthropogenic pollution (e.g. Cr, Ni) are observed in both western and eastern deltaic and coastal regions of the major river systems draining from the major basaltic rich catchments, Fig. 3. The broken horizontal lines in Fig. 3 correspond to the threshold concentration ranges for 'low' / 'medium' biological effects for Ni (20.9 / 51.6 ppm), Cu (34 / 270 ppm) and Cr (81 / 370 ppm) as defined by Long et al. (1995). Whether using the 'low' or 'medium' threshold concentration levels for Ni as a proxy for biologically significant levels of anthropogenic pollution, it is seen from Fig. 3 that the most biologically polluted sediment systems lie on the WC between the Saurashtra and northern Mid-Western Ghats and on the EC from the Penner to the Krishna and Visakhapatnam. Distal from these large river catchments (i.e. from the Western Ghats, through Mangalore, to Cochin and to the eastern Cauvery catchment) the sediments are generally far less impacted with Ni levels below the 'low' biological impact threshold. In the region of the Visakhapatnam Deltaic the high trace metal concentrations are almost identical for shallow (76 m and 152 m) and deep (1520 m) stations implying extensive sediment dispersal down the steep continental shelf. That is, bio-toxic concentrations of metals of anthropogenic origin impact well beyond the shallow coastal margin. In contrast, neither shallow nor deep station sites in the non-deltaic Cochin region on the SW coast, are significantly impacted, exhibiting only very low levels of Ni (0.32ppm).

**Fig. 3:** Coastal sediment distribution of Fe (wt%), and Cr, Cu and Ni (ppm). Horizontal lines, in ascending order, correspond to i) low biological effect for Ni(- - 20.9ppm), Cu(- - 34ppm) and Cr(- · - 81ppm), and ii) the medium effect range (solid line) for Ni (51.6ppm).

**Fig 3**



#### 4.2 EPR spectral characteristics and parameters

Differences in EPR spectra can be associated with the presence, oxidation state and concentration of para- and ferri- magnetic impurities. The impurities observed in the EPR spectra are mainly paramagnetic  $Mn^{2+}$  and  $Fe^{3+}$ , (Fig. 4). Fig. 4a shows the distinctive  $Mn^{2+}$  six line hyperfine resonance spectrum taken from an expanded central section of the EPR trace for SW Ghats station R12-S3191. Compared to pure  $Mn^{2+}$  the spectrum is displaced vertically and horizontally by other (e.g. Fe) components in the sample. As the spectra have been normalised, then for paramagnetic ions of similar line widths, peak intensity roughly corresponds to the relative concentration of the impurity. The paramagnetic components centered at  $g \sim 2.00$  are primarily indicative of  $Mn^{2+}$  although spectral contributions from any  $Fe^{3+}$ , free radicals in organic carbon or free electron centres in carbonates also occur at  $g \sim 2.00$ . The difference between  $Mn^{2+}$  and  $Fe^{3+}$  is that the latter has a broad resonance peak without any hyperfine resonances. This general information, enables the classification of the magnetically active transition metal centres as indicated in Table 1. Of the metal ions present in these samples only  $^{55}Mn$  and  $^{63,65}Cu$  have non-zero nuclear spins (5/2 and 3/2 respectively) and sufficient magnitude to provide hyperfine coupling splitting of the EPR spectrum resulting in 6 and 4 hyperfine resonance lines respectively. Due, however, to dipole-dipole interactions from Fe, hyperfine

resonance structure tend to occur as broad resonance lines. Similarly we do not expect to detect weak  $E_{1'}$  centres above the general broadline background in these light exposed samples measured at room temperature. Table 1a shows the relatively small variation in spectral g-values ( $\delta g < 0.294$ ) determined from the cross-over field as well as the concentration of metal ions present in the sediments. No simple correlation is observed in these complex sediments between the concentration of elemental iron, for example, and the corresponding magnitude of distinctive  $Fe^{3+}$  absorption lines, nor between g-value (shift) and elemental concentration.

Table 1: EPR model parameter values for reported spectra. a)  $K$  is the principal uniaxial anisotropy constant ( $\text{kJm}^{-3}$ ),  $\alpha$  the ferrimagnetic damping constant,  $\tau_{1n}$  ( $n = 1$  to  $3$ ) are paramagnetic spin-lattice damping times, EPR  $g$ -factors  $g_n$ , b) ferri- and para- magnetic volume / susceptibility products  $V_f \cdot \chi_f$  and  $V_{pn} \cdot \chi_{pn}$ , respectively, ( $n = 1$  to  $3$ ) are the number and splitting,  $\mu_0 H_{fn}$  (mT) of the hyperfine fields. Not detected (n.d.).

a)

S-E													
Rank													
index	Station	Coastal	Dominant Spectral Shape	spectral		K		$\tau_{1.1}$	$\tau_{1.2}$	$\tau_{1.3}$			
R	ID S	Region	& Strength	g-value	Ion	( $\text{kJ/m}^3$ )	$\alpha$	(mS)	(mS)	(mS)	$g_1$	$g_2$	$g_3$
1	3440	Saur.	Single, broad, weak	2.119	$\text{Fe}^{3+}$	1.00	0.23	0.100	4.000	0.200	5.500	1.980	4.000
2	3441	Saur.	Single, broad, weak	2.067	$\text{Fe}^{3+}$	1.00	0.23						
3	3443	Saur.	Single, broad, medium	2.128	$\text{Fe}^{3+}$	2.50	0.23	0.100			2.500		
4	3444	Saur.	Single, broad, strong	2.100	$\text{Fe}^{3+}$	2.00	0.20						
6	3452	Camb.	Single, broad, strong	2.097	$\text{Fe}^{3+}$	1.00	0.20	0.100			2.150		
7	3453	Camb.	Single, broad, strong	2.074	$\text{Fe}^{3+}$	1.30	0.19	0.100			2.000		
8	3462	Mumb.	Single, broad, strong	2.086	$\text{Fe}^{3+}$	1.90	0.19						
9	3463	Mumb.	Single, broad, medium	2.127	$\text{Mn}^{2+} \text{Fe}^{3+}$	2.00	0.23	0.100			2.500		
10	3464	WGha.	Single, broad, medium	2.059	$\text{Fe}^{3+}$	0.60	0.23	0.100	0.200		2.000	4.050	
12	3191	WGha.	V Weak, Weakly resolved	2.271	$\text{Mn}^{2+}$	0.02	0.10	0.080	8.000	0.060	2.350	2.005	2.000
13	3192	WGha.	Single, Weak	2.254	$\text{Mn}^{2+} \text{Fe}^{3+}$	7.00	0.14	0.080	1.000		2.350	2.900	
14	3182	Bhatkal	Weak, Weakly resolved	2.135	low $\text{Fe}^{3+}$	8.00	0.23	0.100	0.400		2.000	2.600	

15	3180	Mang.	multi, broad	2.025	low Fe <sup>3+</sup>	0.10	0.23	0.100	4.000	0.200	2.200	1.980	4.000
16	3173	Mang.	Weak, Weakly resolved	n.d.	n.d.	0.02	0.19	0.075	0.175		2.600	2.800	
17	3170	Cochin	Multi, weak	2.251	Mn <sup>2+</sup>	0.02	0.19	0.075	0.175		2.600	2.800	
19	3165	Cochin	Multi, v. weak	2.050	low Mn <sup>2+</sup> Fe <sup>3+</sup>	0.02	0.22	1.000	0.300	0.180	2.230	2.200	2.250
20	3164	Cochin	Weak, Weakly resolved	n.d.	n.d.	1.00	0.25	0.100	8.000	0.475	2.300	2.005	3.700
21	3026	Cauv.	Multi, weak	2.115	Mn <sup>2+</sup> Fe <sup>3+</sup>	0.80	0.23	0.100	0.060		3.100	4.800	
22	3025	Cauv.	Multi, weak	2.195	low Fe <sup>3+</sup>			0.170			4.600		
23	3024	Cauv.	Multi, v. weak	n.d.	n.d.	10.00	0.23	0.080	0.050	0.100	2.050	5.200	3.800
24	3249	Penner	Single, broad, weak	2.102	Fe <sup>3+</sup>	1.00	0.23						
25	3248	Penner	Single, broad, medium	2.089	Fe <sup>3+</sup>	1.00	0.21						
26	3019	Penner	Single, broad, medium	2.093	Fe <sup>3+</sup>	0.02	0.18	0.080	0.060		2.200	2.600	
28	3014	Krishna	Single, broad, medium	2.296	Fe <sup>3+</sup>	6.00	0.23	0.100			2.600		
29	3245	Visa.	Single, broad, medium	2.119	Fe <sup>3+</sup>	2.00	0.23	0.100	8.000	0.475	2.300	2.005	3.700
30	3244	Visa.	Single, broad, medium	2.038	low Fe <sup>3+</sup>	0.07	0.19	0.150			2.000		
32	3013	Visa.	Single, broad, medium	2.092	Fe <sup>3+</sup>	0.02	0.20	0.080	0.060		2.200	2.600	
33	3012	Visa.	Single, broad, medium	2.119	Fe <sup>3+</sup>	0.02	0.18	0.080	0.060		2.250	2.600	
34	3010	Visa.	Single, broad, medium	2.044	Fe <sup>3+</sup>	0.02	0.19	0.150			2.000		

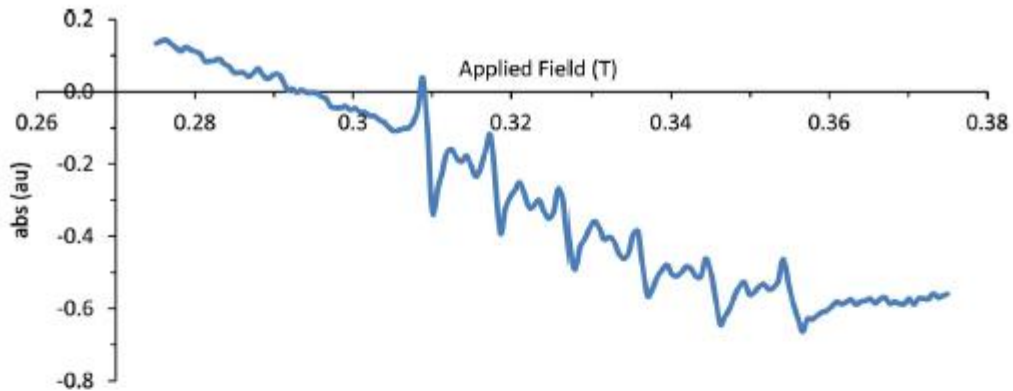


b)

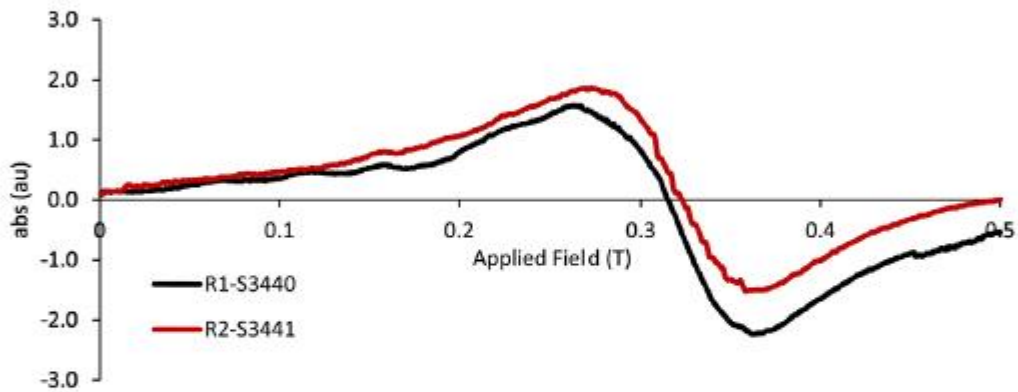
N-S-E												
Rank	Station	Coastal								$\mu\text{Hf}_1$	$\mu\text{Hf}_2$	$\mu\text{Hf}_3$
index R	ID S	Region	$V_f \cdot \chi_f$	$V_{p1} \cdot \chi_{p1}$	$V_{p2} \cdot \chi_{p2}$	$V_{p3} \cdot \chi_{p3}$	$n_1$	$n_2$	$n_3$	(mT)	(mT)	(mT)
1	3440	Saur.	4.0E-04	4.8E-07	2.0E-09	1.5E-07	1	6*	1		10	
2	3441	Saur	3.7E-04									
3	3443	Saur.	3.6E-03	3.2E-05			25			9		
4	3444	Saur.	7.2E-03									
6	3452	Camb.	3.1E-02	3.2E-03			7			10		
7	3453	Camb.	8.4E-03	9.0E-05			1					
8	3462	Mumb.	6.0E-03									
9	3463	Mumb.	7.6E-04	3.2E-05			25			9		
10	3464	WGha.	1.1E-03	1.3E-05	1.5E-07		1	1				
12	3191	WGha.	1.0E-05	1.5E-05	1.0E-10	5.0E-06	5	6*	7	30	10	40
13	3192	WGha.	4.0E-05	2.5E-05	1.0E-08		5	1		30		
14	3182	Mang.	6.0E-05	9.6E-06	1.0E-07		7	1		10		
15	3180	Mang.	6.0E-05	9.6E-06	3.0E-09	1.0E-07	11	6*	1	15	10	
16	3173	Mang.	4.0E-05	4.0E-06	2.5E-07		1	1				
17	3170	Cochin	4.0E-05	4.0E-06	2.5E-07		1	1				
19	3165	Cochin	1.0E-04	5.0E-08	4.0E-07	5.0E-06	4	1	1	10		
20	3164	Cochin	3.0E-05	1.6E-06	1.0E-10	5.0E-08	7	6*	1	10	10	

21	3026	Cauv.	4.6E-04	3.2E-06	1.5E-05		1	1			
22	3025	Cauv.	0.0E+00	2.0E-06			1				
23	3024	Cauv.	1.0E-05	1.6E-05	1.0E-05	1.0E-06	1	15	1		10
24	3249	Penner	1.0E-03								
25	3248	Penner	5.0E-03								
26	3019	Penner	1.4E-03	1.3E-04	3.0E-05		1	1			
28	3014	Krishna	4.0E-03	1.6E-04			25			9	
29	3245	Visa.	7.0E-03	1.6E-06	1.0E-10	5.0E-08	7	6*	1	10	10
30	3244	Visa.	2.0E-03	4.5E-05			1				
32	3013	Visa.	2.7E-03	2.0E-04	1.0E-04		1	1			
33	3012	Visa.	1.6E-03	1.7E-04	5.0E-05		1	1			
34	3010	Visa.	8.0E-04	5.0E-06			1				

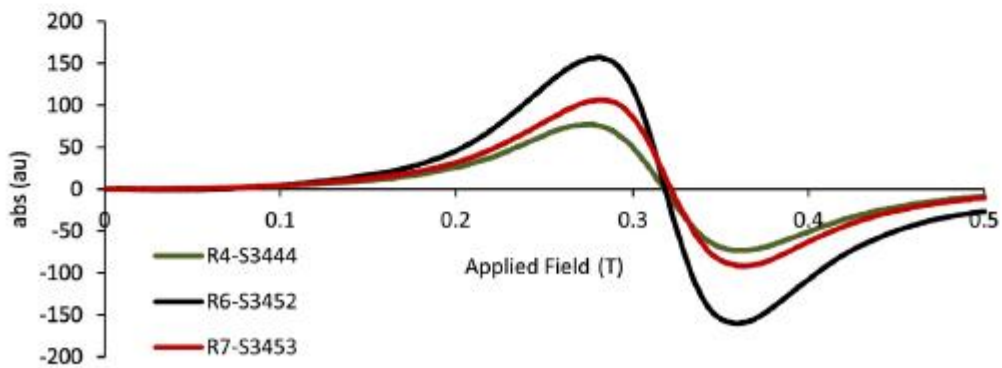
**Fig 4**



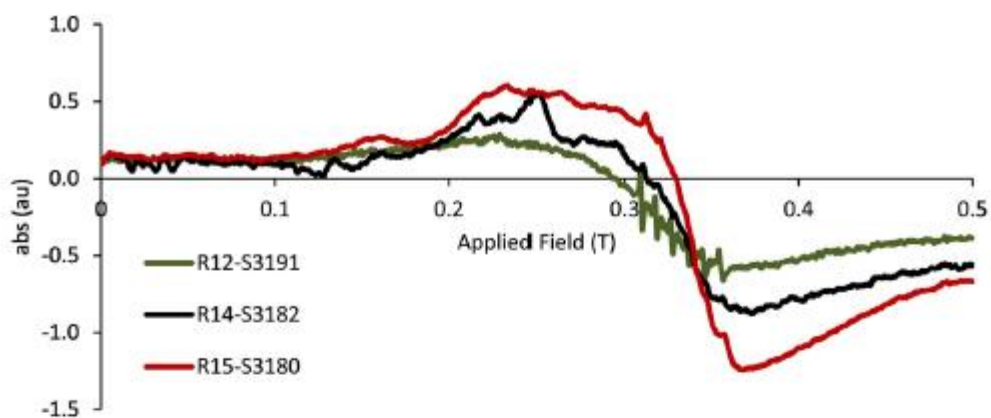
a:  $Mn^{2+}$  hyperfine absorption component, an expanded central section of S 3191.



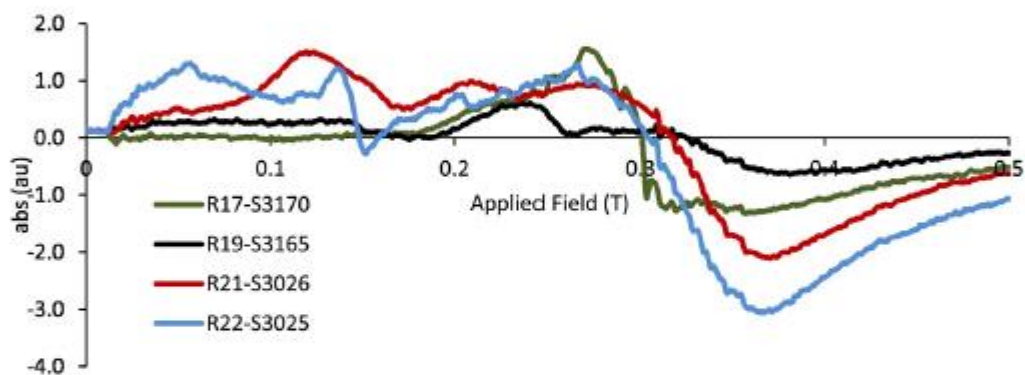
b: Proximal R1-S3440 & R2-S3441, N Saurashtra Basin, with low PtP values  $\sim 3.5$  a.u.



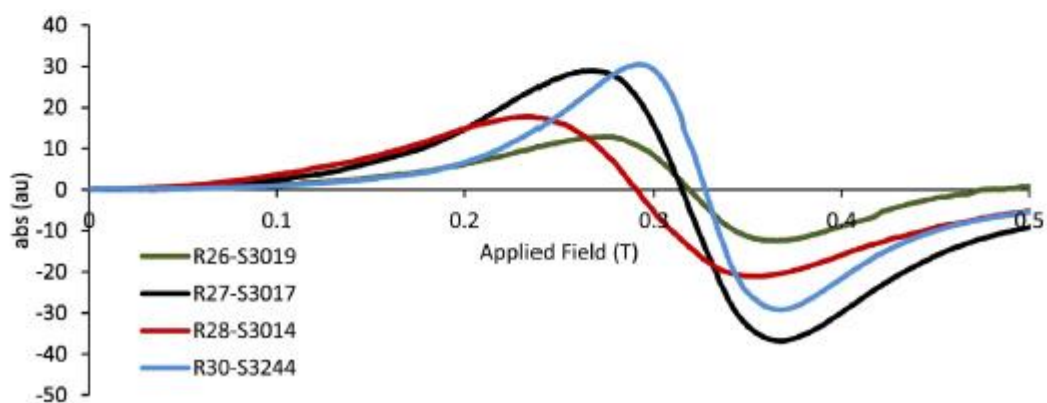
c: R4-S3444: S Saurashtra Bay, and 400km distant R6-S3452, R7-S3453 N & S Gulf of Cambay, respectively. Strong PtP  $\sim 200$  a.u., broadline spectra, similar spectral g-values.



d: R12-S3191, SW Ghats, R14-S3182 Bhatkal & R15-S3180 Mangalore, low PtP values  $\sim 1.0$  a.u., unimpacted sites. Note  $Mn^{2+}$  hyperfine spectrum in R12-S3191.



e: Multicomponent WC R17-S3170, R19-3165 N & Central Cochin resp., EC R21-S3025 & R22-S3026 N Cauvery delta spectra, low PtP, between 1 & 4 a.u.



f: EC R26-S3019 N Penner, R28-S3014 & R27-3017 Krishna, R30-3244 S Visa delta, moderate strength broadline spectra (25 to 65 a.u.) and significant spectral g-shifts.

Fig. 4 (continued).

In Fig. 4b-f indicative spectra have been grouped broadly by station coastal location. For visual clarity not all spectra are included. The spectra exhibit a variety of visual forms and amplitudes reflecting potential variation in the total concentration of para-, ferri- and canted antiferro- magnetic components. In some samples strong fairly uniform, weakly field dependent spectra are observed, e.g. Fig. 4e. Commonalities in the gross spectral characteristics, and thus by implication the sediment, are however evident as is now discussed.

Fig. 4b shows low PtP values of  $\sim 3.5$  a.u for R1-S3440 and R2-S3441 from the WC North Saurashtra Basin, stations well sheltered from the influence of the more southerly discharges from the Gulf of Cambay. A weak  $\text{Mn}^{2+}$  hyperfine signature is seen in R2-S3441.

Fig. 4c: shows, strong PtP  $\sim 200$  a.u., broadline peaks with similar g-values from R4-S3444 S Saurashtra Bay, and proximal (*c.* 400km) R6-S3452 and R7-S3453 from north and south of the Gulf of Cambay, respectively. These strong, large, broadline spectra are potentially influenced by discharges from the WC Gulf of Cambay. Similar EPR spectral characteristics are displayed for coastal stations down to the northern extremities of the Western Ghats. They exhibit strong EPR absorption consistent with ferrimagnetic minerals being present in moderate concentrations (i.e. here between 9 to 10 ppm, Fig. 1). All broadline spectra (e.g. WC Fig. 4c and EC Fig. 4f) are typical of sediments associated with high para or ferrimagnetic content, that is from river catchments or coastal locations proximal to highly populated regions generating anthropogenic pollutants.

In Figs. 4d and 4e no single EPR spectral component dominates enabling the weaker impurities to be clearly resolved and characteristic  $\text{Mn}^{2+}$  and broadline  $\text{Fe}^{3+}$  (ferric) components to be seen. Fig. 4d displays weaker multicomponent spectra, R12-S3191, from the SW Ghats and R14-S3182 and R15-S3180 from Bhatkal and Mangalore stations, representing a site separation range of *c.* 150 km. They have low PtP values (*c.* 1.0 a.u.), characteristic of unimpacted continental shelf sites consistent with lower total impurity content, (i.e. here low Fe concentrations of between 1 and 2.7 ppm). The lower overall level of iron rich material means that the weaker narrow line components are more clearly resolved and contribute to a larger percentage of the overall spectral absorption. The  $\text{Mn}^{2+}$  hyperfine signature is particularly clear in R12-S3191 more weakly in R13-S3192, consistent with lower levels of anthropogenic pollution and riverine sediments. Both the of the latter two stations are situated in the west coast SW Ghats region remote from the outfall of major rivers or deltas.

Fig. 4e displays weak multicomponent spectra from either side of the Southern Indian peninsular, i.e. west coast R17-S3170 and R19-3165 from the N and Central Cochin respectively,

and east coast R21-S3025 and R22-S3026 from the N Cauvery Delta. For R22-S3025 a clear  $\text{Fe}^{3+}$  peak is seen at  $g = 4.6$ , (see also Table 1) at  $\sim 0.15T$ , comparable to  $g = 4.7$   $\text{Fe}^{3+}$  peaks observed by Engin et al. (2006) in powdered fossil gastropod shell at room temperature. The spectra display a strong fairly uniform, weakly field dependent behaviour below  $g \sim 2$ . Similar behaviour is exhibited by the Cauvery Delta stations R23-S3024 and R24-S3025, Cochin R20-S3164 and R19-S3165, and Mangalore R16-S3173 (spectra not shown for visual clarity). These sediments all display low to medium PtP, between 1 & 4 a.u., and characteristics similar in to those of Fig. 4f. The stations which are adjacent to the northern Cauvery delta are very low in para and ferrimagnetic components consistent with their low Fe concentrations of between 2.2 and 2.8 ppm.

Figs. 4f shows moderate strength spectra (amplitudes of 25 to 65 a.u.) from the east coast, R26-S3019 N Penner, R28-S3014 and R27-3017 Krishna estuary and R30-3244 from the S Visakhapatnam Delta region, representing a site range of *c.* 150 km. The spectra are visually similar to those of Fig. 4b but with strong  $g$ -shifts,  $\delta_g$ , of  $\sim 0.6$ , for R33-S3012, R32-S3013, R28-S3014, (not all spectra displayed) and Table 1. Spectra from Krishna (R28-S3014) and the South Visakhapatnam delta / North Krishna (R30-S3244 and R29-S3245, spectrum not displayed) with  $\delta_g \sim 1.7$  are consistent with lower  $\text{Fe}^{3+}$  concentrations, here between 6 and 8 ppm.

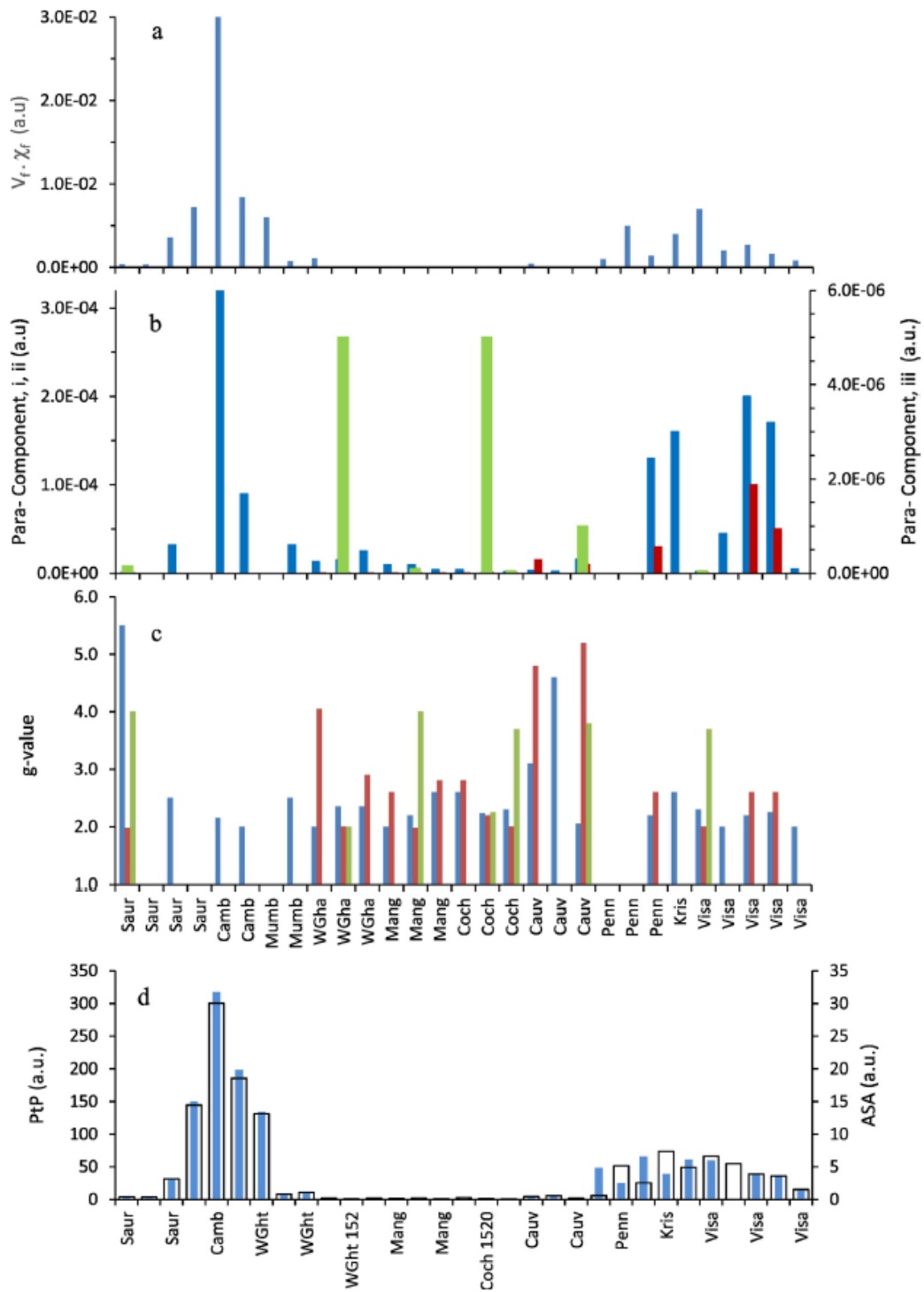
#### 4.3 EPR modelling parameters

Modelling EPR spectra enables the semi-qualitative classification of sediments discussed above to become quantitative. It also permits spatial association and variation to be studied in greater detail. Table 1 displays the principal modelling parameters that provide a good fit to the experimental spectra replicating peak positions with the overall area of fitted and experimental spectra differing by no more than a few percent (e.g. Fig. 2c, R7-S3453, Gulf of Cambay). It is seen from Table 1b that some spectra, such those of the Bhatkal/Mangalore stations (i.e. R14-S3182, R15-S3180, R16-S3173), require both a ferri- and at least one para- magnetic component, to accurately replicate the experimental spectra. In contrast, other stations, such as the two southern most EC Penner stations, (i.e. R26-S3019) can be modelled using a single ferrimagnetic component. The ferrimagnetic uniaxial anisotropy constant,  $K$  ( $\text{kJm}^{-3}$ ), is typically found to be similar in magnitude to that of magnetite. The ferrimagnetic damping constant,  $\alpha$ , increases for broader absorption lines. The paramagnetic spin-lattice relaxation times,  $\tau_{1n}$  ( $n = 1$  to 3), are longer for narrow intense lines consistent with a dilute or weaker magnetic environment, e.g.  $\tau_{13}$

= 4 mS for R1-S3440, R12-S3191, R20-S3164. The ferri- and para- magnetic volume and susceptibility products,  $V_f \cdot \chi_f$  and  $V_{p1} \cdot \chi_{p1}$  respectively of Table 1b, are proportional to the contribution that a component makes to the total EPR absorption. It is clear from Fig. 5a that the largest ferrimagnetic concentrations and susceptibilities are associated with the most intense EPR spectra corresponding to stations in the west coast NW Gulf of Cambay and east coast Visakhapatnam delta. This is consistent with the high values of Fe, determined by ICP. The g-factors, varying here from 2 to 5.5, are determined both by the paramagnetic impurity and its local environment, shifting to low fields (higher g) as the mean field from other magnetic components increases. Parameters n and  $H_f$  are the number and hyperfine splitting field (in mT), respectively, necessary to either reproduce a  $Mn^{2+}$  hyperfine absorption or simulate a broadened paramagnetic absorption component with shortened spin-lattice relaxation times. Examples of overlapping traces simulating a broad paramagnetic absorption are  $n_1 = 5$ ,  $n_3 = 7$ ,  $H_f = 30$  mT and 40 mT for R12-S3191 and  $n_1 = 11$   $H_f = 15$  mT for R15-S3180. Here Mn hyperfine absorption (flagged in Table 1 by  $n_2 = 6^*$ ) has been modelled using  $H_f = 10$  mT, e.g. R1-S3440, R12-S3191. A wide range of paramagnetic impurity g-values is observed. The largest, 5.5, occurring at the most northerly Saurashtra station, R1-S3440, is probably due to the presence of ferrimagnetic minerals. If both ferrimagnetic and paramagnetic minerals are present only when their EPR contribution is comparable or when the paramagnetic component is dominant, are paramagnetic species and likely to be readily resolvable.

Figs. 5b and 5c display the coastal geographical trends in principal paramagnetic components and the departure from  $g = 2$  determined by EPR modelling. The largest paramagnetic components (Fig. 5b) are associated primarily with the larger WC rivers and EC deltaic margins. The principal ferri- and para- magnetic components are displayed in in these two figures as the products of the component's susceptibility and volume fraction,  $V_f \cdot \chi_f$  and  $V_{p2} \cdot \chi_{p2}$ , as it is this product which determines their contribution to the EPR spectrum. Fig. 5c displays up to three g-values per spectrum. Consistent with the discussion above, no simple correlation between g-values and total EPR absorption is observed due to spectral g-values being dependent upon both the specific sediment composition and concentration.

**Fig 5**



**Fig. 5.** Geographical variation in a) ferrimagn.  $V_f \cdot \chi_f$ , b) dominant paramagn.  $V_p \cdot \chi_p$ : i (blue), ii (red), iii (green), c) paramagn. g-Values  $g_i$  (blue),  $g_{ii}$  (red),  $g_{iii}$  (green), d) PTP (solid) and ASA (open) bars.



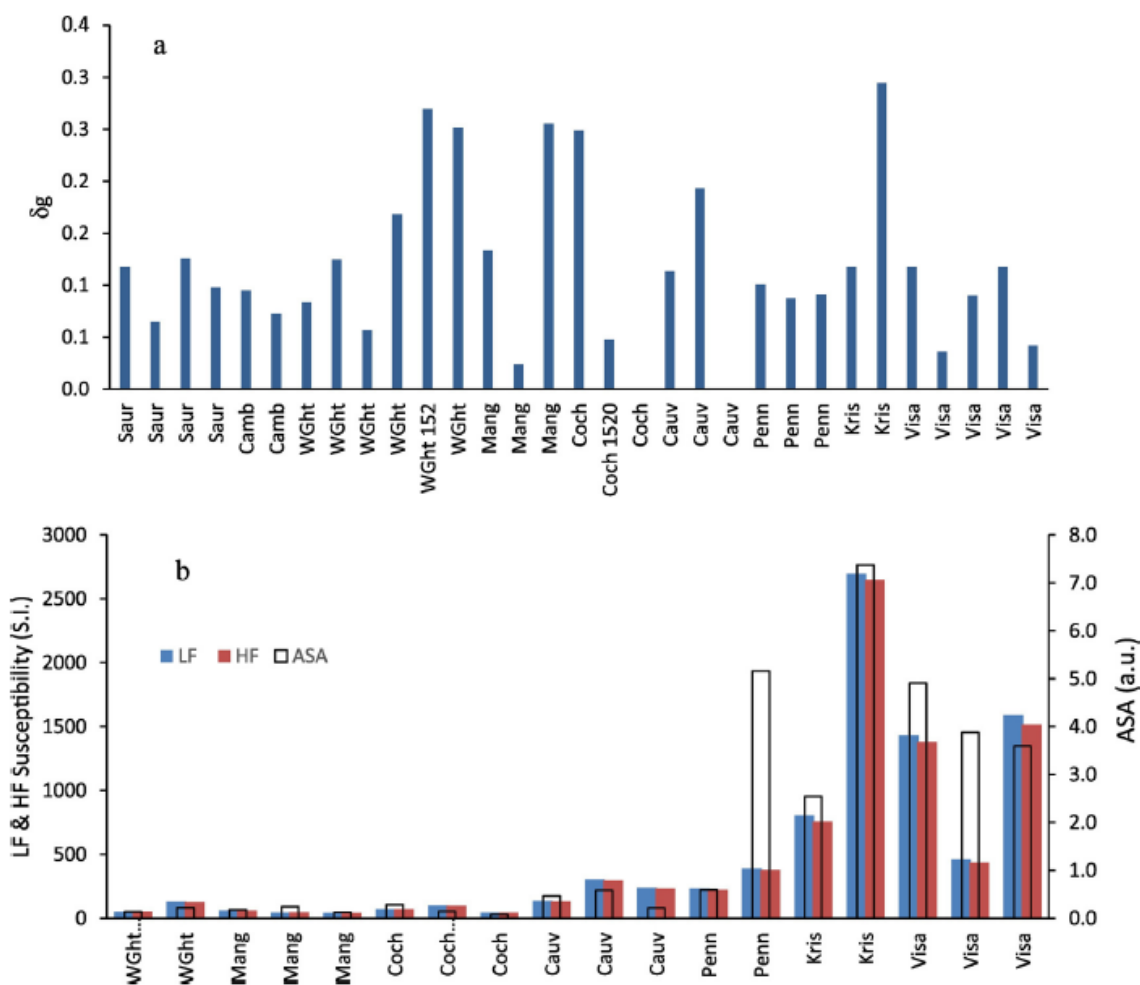
The geographical correspondence by station location of EPR absorption spectral area (ASA) and PtP (Fig. 5d) is similar, but not identical to, those of the impurity concentrations (Fig. 3). The correlation coefficients between ASA and PtP with total impurity concentration over all samples is similar, 0.707 and 0.673 respectively, thus some difference in the form of the geographical distribution of these parameters is to be expected. We find ASA and PtP to be highly correlated with  $r^2 = 0.980$  (Fig. S2). Below 100 ppm a weaker correlation is observed between PtP, ASA and impurities. ASA vs its proxy,  $\chi$ , also has a very high correlation coefficient of 0.97. For pure single component materials is expected to be negatively correlated with concentration due to strengthening of magnetostatic dipole-dipole interaction fields. Negative weak correlation between and impurity concentrations (i.e. Fe -0.577, Cu -0.492, Cr -0.528, Ni -0.546) are observed for these multi-component sediment samples. We find weaker (negative) correlation is shown between and both EPR area (-0.324) and PtP height (-0.315). Also, the correlation between ASA and total metal content is weak ( $r = 0.109$ ) at low impurity levels ( $< 4.5$  wt%), but greater ( $r = 0.67$ ) above 4 wt% (Fig. S3). The Pearson correlation coefficients between ASA and impurity concentration over all stations are ASA-Fe = 0.707, ASA-Cu = 0.652, ASA-Ni = 0.506 and ASA-Cr = 0.472. The low total metal content / low ASA stations all lie between the Southern Western Ghats through Cochin, around the southern Indian peninsular and northwards as far as the Penner River. That is, away from the Gulf of Cambay and the Eastern Krishna and Visakhapatnum. These low total metal concentration stations also display characteristically weaker multicomponent EPR spectral signatures. Slightly over half of these stations (R12-S3191 to R20-S3164) have sediment input associated with granites and gneiss, the remainder (R21-S3026 to R25-S328) with basaltic sediments (Table S1). This geological difference does not, however, appear to determine the EPR absorption (or the magnetic susceptibility, see section 4.4 below).

For lower impurity concentrations the peak width,  $\Delta H$  (T), clusters around two principal values when samples are classified by total impurity concentration (Fig. S4). This may suggest that a single species is predominantly responsible for these linewidths. This behaviour is consistent with the complementary case for four outlying points ( $\Delta H > 0.24$  T) for low total impurity multicomponent concentrations ( $< 50$   $\mu$ g/g). Low concentrations of impurities with differing g-values can result in spreading of the partially resolved weak spectral components over a relatively wide field range effectively broadening the composite spectrum of the sample. The values of  $\Delta H$  determined by the difference between the spectral cross-over field and  $g = 2$  possess

no simple geographical dependence, being largely determined by the dominant components found at any given station (Fig. 6a). The maximum and mean shifts observed, 0.294 and 0.125, respectively, are much smaller than those determined from modelling the g-values of individual components. That is, in these multicomponent environmental sediments the g-value determined from spectra cross-over is not primarily dependent upon one dominant impurity as the contribution of several broadline components may determine the composite sediment spectrum. This is consistent with no significant or analytically consistent correlation being observed between  $\delta_g$  and composition. Thus, overall we do not consider  $\delta_g$  to be a robust proxy parameter for impurity level due to superposition of multiple components within the spectra in complex environmental sediments.

#### 4.4 Comparative Environmental Magnetism Measurements

Fig. 6b demonstrates that between the Western Ghats and Visakhapatnum, the environmental magnetism LF and LF magnetic susceptibilities (Table S3) are greatest in the regions associated with the Krishna and Visakhapatnum, sources of anthropogenic pollution and watersheds in which Deccan Basalt occur such as those above the tributaries of the Godavari. We find very strong correlation coefficients between LF and HF susceptibilities and primary EPR spectral parameters (ASA in particular) and metal impurities, (Table 2). HF and LF are themselves highly correlated (0.999) by the function  $HF = 0.97LF$ , (see also Alagarsamy 2009). The small difference between LF and HF indicates that there are relatively few fine grained superparamagnetic particles in these coastal marine sediments. This is not perhaps surprising as such particles are more susceptible to bio-chemical uptake, oceanic dispersal and oxidation and so likely to have shorter chemically unaltered residence times either on the continental shelf or in the river catchment. Further, Fe, Cr, Cu and Ni are strongly correlated, (Table 2, Fig. S1). A strong correlation between high magnetic susceptibility and heavy metal concentration is consistent with the fact that magnetic iron and manganese oxides are commonly found in close association with clay minerals which have a strong absorptive capacity for metals (Alagarsamy and Zhang, 2010, Kersten and Smedes, 2002). The geographical distribution of ASA and the high correlation factors exhibited between ASA, LF and HF, give confidence that the extra fingerprinting capability of EPR is consistent with more conventional environmental magnetism methodologies and chemical assay.



**Fig. 6:** The geographical variation in a)  $\delta g$  determined by spectral crossover field, b) correlation between LF, HF and ASA (open bars).

**Table 2** EPR, metal and susceptibility Pearson correlation coefficient are for stations from the WC southerly Western Ghats stations to the EC N. Visakhapatnam deltaic stations.

	HF	ASA	PtP	dH(T)	Fe	Cr	Cu	Ni	Totl. Metals
LF	0.999	0.858	0.634	-0.279	0.792	0.821	0.821	0.738	0.792

## **5. Concluding remarks**

We have demonstrated that EPR can be employed to evaluate the concentration and chemical form of paramagnetic metals in sediments from marine (and by extension, terrestrial) environments to yield distinctive EPR spectral ‘fingerprints’; spectra that can be characterized quantitatively by employing an appropriate and detailed electromagnetic EPR model. Further, we have presented an EPR baseline study of metal ion concentrations in Indian continental shelf marine sediments impacted by anthropogenic pollution. The results indicate that there is considerable variation in the form and detail of the EPR spectra from along the continental shelf, the components of which reflect the coastal location and the origin of fluvial inputs. These in turn strongly contribute to the assemblage of paramagnetic species within the sediments. This bestows an EPR spectral ‘fingerprint’ upon the sediment, one that is sensitive to, and indicative of both location and inputs and, inversely, has the potential to assist in source apportionment in sediment un-mixing models and environmental impact assessment. As the EPR spectrum of many paramagnetic metal ions is unique and oxidation state dependent, constituent paramagnetically active metals can also be identified. In addition, g-values, g-shifts and hyperfine splittings, provide information on the (magnetic) micro-environment of metals within sediments. Chemical evidence has also been presented for bio-toxic concentrations of metals of anthropogenic origin impacting well beyond the shallow coastal margin. The progressive and distinctive largescale variation observed in the composition of the continental shelf sediments across the coastal sites is consistent with low lateral sediment transport as suggested by Borole (1988). The experimental methodology, results and analysis presented demonstrate that electromagnetic EPR spectroscopic modelling combined with AAS / ICP and environmental magnetism measurements are effective tools for the qualitative and quantitative analysis of marine environmental sediments.

## **Acknowledgements**

R.A. thanks the Director, of the NIO for kind permission and encouragement during the period of work. SRH and R.A. acknowledges the support and facilities provided by the School of Science and the Environment at MMU and the NIO, respectively. The research did not receive any specific grant funding from agencies in the public, commercial or not-for-profit sectors.

## Dedication

We dedicate this paper to the memory of Sambasiva Rao, Department of Chemistry, Pondicherry University, India, mentor and colleague and inspiration for this work.

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**Supporting Information (available online, for Supporting tables see next page)**



## Supporting Tables

Table S1: Sampling stations area, position, and dominant sediment. The four digit station ID shown geographically on Fig.1. Chronologically i) EC voyage 130, N to S, Jan, post Monsoon, ii) WC voyage 139, S to N, May/June., pre-Monsoon, iii) EC voyage 143, N to S, Nov., post Monsoon, iv) WC voyage 151, N to S, Mar, pre-Monsoon.

Voyage	N-S-E Rank	Station	Coastal Area	Dominant Natural Sediment.	Lat	Long	Depth (m)
130	34	3010	N Visa. delta.	Basaltic	16 <sup>0</sup> 26.0'	81 <sup>0</sup> 31.0'	40
130	33	3012	N Visa. delta.	Basaltic	16 <sup>0</sup> 26.0'	81 <sup>0</sup> 31.0'	40
130	32	3013	N Visa. delta	Basaltic	16 <sup>0</sup> 11.0'	81 <sup>0</sup> 47.5'	55
130	28	3014	Krishna	Basaltic	15 <sup>0</sup> 54.5'	81 <sup>0</sup> 14.6'	50
130	27	3017	Krishna	Basaltic	15 <sup>0</sup> 39.5'	81 <sup>0</sup> 00.0'	48
130	26	3019	N Penner	Basaltic	15 <sup>0</sup> 00.3'	80 <sup>0</sup> 16.7'	52
130	23	3024	N Penner	Basaltic	12 <sup>0</sup> 00.0'	80 <sup>0</sup> 05.6'	49
130	22	3025	N Cauvery delta	Basaltic	12 <sup>0</sup> 00.0'	80 <sup>0</sup> 04.2'	50
130	21	3026	N Cauvery delta	Basaltic	11 <sup>0</sup> 00.0'	80 <sup>0</sup> 02.5'	52
139	20	3164	N Cochin	Granite / Gneiss	10 <sup>0</sup> 02.5'	76 <sup>0</sup> 00.0'	35
139	19	3165	N Cochin	Granite / Gneiss	10 <sup>0</sup> 01.0'	75 <sup>0</sup> 40.1'	90
139	18	3171	N Cochin	Granite / Gneiss	10 <sup>0</sup> 58.2'	75 <sup>0</sup> 39.0'	33
139	17	3170	N Cochin	Granite / Gneiss	10 <sup>0</sup> 58.2'	75 <sup>0</sup> 18.7'	73
139	16	3173	Mangalore	Granite / Gneiss	12 <sup>0</sup> 00.0'	74 <sup>0</sup> 40.0'	75
139	15	3180	Mangalore	Granite / Gneiss	12 <sup>0</sup> 59.0'	74 <sup>0</sup> 20.9'	60
139	14	3182	Bhatkal	Granite / Gneiss	14 <sup>0</sup> 00.0'	74 <sup>0</sup> 19.0'	40

139	12	3191	SW Ghats	Granite / Gneiss	14 <sup>0</sup> 59.7'	73 <sup>0</sup> 20.0'	75
139	13	3192	SW Ghats	Granite / Gneiss	14 <sup>0</sup> 59.6'	73 <sup>0</sup> 40.0'	49
143	31	3242	Visa. delta	Basaltic	16 <sup>0</sup> 31.0'	82 <sup>0</sup> 30.7'	700
143	30	3244	S Visa. delta	Basaltic	15 <sup>0</sup> 39.1'	81 <sup>0</sup> 06.4'	660
143	29	3245	S Visa. delta	Basaltic	14 <sup>0</sup> 54.1'	80 <sup>0</sup> 20.5'	80
143	25	3248	Penner	Basaltic	13 <sup>0</sup> 30.5'	80 <sup>0</sup> 31.7'	120
143	24	3249	Penner	Basaltic	13 <sup>0</sup> 07.8'	80 <sup>0</sup> 32.6'	120
151	1	3440	N Saura. B	Basaltic	22 <sup>0</sup> 53.7'	68 <sup>0</sup> 22.0'	23
151	2	3441	N Saura. B	Basaltic	22 <sup>0</sup> 24.0'	68 <sup>0</sup> 38.0'	22
151	3	3443	S Saura. B	Basaltic	21 <sup>0</sup> 54.1'	68 <sup>0</sup> 56.0'	45
151	4	3444	S Saura. B	Basaltic	21 <sup>0</sup> 30.0'	69 <sup>0</sup> 10.0'	57
151	6	3452	N Gulf of Cambay	Basaltic	20 <sup>0</sup> 14.1'	72 <sup>0</sup> 11.9'	30
151	7	3453	S Gulf of Cambay	Basaltic	19 <sup>0</sup> 30.0'	72 <sup>0</sup> 16.0'	30
151	8	3462	Mumbai / NW Ghats	Basaltic	18 <sup>0</sup> 20.4'	72 <sup>0</sup> 41.6'	25
151	9	3463	Mumbai / NW Ghats	Basaltic	17 <sup>0</sup> 50.0'	72 <sup>0</sup> 46.0'	32
151	10	3464	W Ghats	Basaltic	17 <sup>0</sup> 19.0'	72 <sup>0</sup> 50.0'	60
151	11	3471	Mid W Ghats	Basaltic	16 <sup>0</sup> 06.0'	73 <sup>0</sup> 00.0'	70

Table S2: Sampling stations, depths and Fe, Cr, Cu and Ni concentrations.  
The four digit station numbers are cross referenced geographically on Fig.1, not available  
(n.a.), not detected (n.d.).

Part a

<b>Voyage</b>	<b>N-S-E Rank Index</b>	<b>Station ID</b>	<b>Depth (m)</b>	<b>Fe wt %</b>	<b>Cr ppm</b>	<b>Cu ppm</b>	<b>Ni ppm</b>
130	34	3010	40	n.a.	n.a.	n.a.	n.a.
130	33	3012	40	8.58	106.28	113.20	71.38
130	32	3013	55	6.68	106.40	113.32	77.92
130	28	3014	50	7.93	133.22	140.14	76.39
130	27	3017	48	6.97	96.20	103.12	78.36
130	26	3019	52	6.38	90.71	97.63	75.96
130	23	3024	49	2.25	7.39	14.31	18.12
130	22	3025	50	2.25	6.26	13.18	27.79
130	21	3026	52	2.76	3.71	10.63	20.37
139	20	3164	35	1.20	-3.10	3.82	0.32
139	19	3165	90	3.43	4.59	11.51	11.54
139	18	3171	33	1.99	-1.43	5.49	6.49
139	17	3170	73	1.97	1.26	8.18	9.02
139	16	3173	75	1.47	2.71	9.63	10.95
139	15	3180	60	3.02	6.52	13.44	16.07
139	14	3182	40	3.11	14.08	21.00	16.88
139	12	3191	75	1.13	5.17	12.09	10.69
139	13	3192	49	2.74	19.39	26.31	16.85

## Part b

<b>Voyage</b>	<b>N-S-E Rank Index</b>	<b>Station ID</b>	<b>Depth (m)</b>	<b>Fe wt %</b>	<b>Cr ppm</b>	<b>Cu ppm</b>	<b>Ni ppm</b>
143	31	3242	700	6.66	103.76	110.68	70.20
143	30	3244	660	6.62	111.60	118.52	81.18
143	29	3245	80	6.02	83.46	90.38	76.67
143	25	3248	120	1.98	13.50	20.42	25.61
143	24	3249	120	1.67	5.41	12.33	7.80
151	1	3440	23	4.49	28.67	35.59	52.60
151	2	3441	22	6.04	41.64	48.56	66.70
151	3	3443	45	5.17	44.42	51.34	39.43
151	4	3444	57	5.41	52.66	59.58	41.20
151	6	3452	30	9.27	121.80	128.72	67.87
151	7	3453	30	10.3	7.00	142.78	80.47
151	8	3462	25	8.89	98.17	105.09	75.17
151	9	3463	32	5.39	35.12	42.04	32.28
151	10	3464	60	6.29	96.43	103.35	71.35
151	11	3471	70	2.92	35.39	42.31	39.53

Table S3: High (HF) and Low Frequency (LF) magnetic volume susceptibility by coastal location along the more mid latitude sections of the western and eastern coast.

	Station in NW-S-NE order	Coastal Location	Mean LF (SI vol. susc.)	Mean HF (SI vol. susc.)
West Coast Pre- Monsoon Voyage 139	3191	W. Ghats	51.0	51.7
	3192	S.W. Ghats	127.0	126.3
	3184	Bhat.	33.3	35.0
	3182	Bhat./Mang.	59.3	61.7
	3180	Mangalore	44.2	46.8
	3173	Mangalore	40.8	43.5
	3171	Mangalore	20.8	21.0
	3170	N. Cochin	72.3	72.3
	3165	Cochin	103.5	99.7
	3164	N. Cochin	44.8	45.2
East Coast Post- Monsoon Voyage 130 & 143*	3026	N. Cauvery	134.8	129.3
	3025	N. Cauvery	305.3	297.1
	3024	N. Cauvery	239.8	234.6
	3249*	S. Penner	52.0	51.2
	3248*	Penner	233.8	223.6
	3019	N. Penner	388.5	376.0
	3018	Krishna	1722.0	1666.7
	3017	Krishna	806.7	757.6
	3014	Krishna	2699.2	2649.0
	3245	S. Visa.	1431.0	1379.5
3013	Visa.	463.5	436.5	
3012	N. Visa.	1590.0	1516.2	