

Assessment of crustal element and trace metal concentrations in atmospheric particulate matter over a coastal city in the Eastern Arabian Sea

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Abstract

Major/crustal elements (Al, Ca, Mg, K and Fe) and trace metals (Mn, Cr, Cu, Pb, Zn, and Ni) in atmospheric particulate matter at three sites in Goa (a coastal city in the Eastern Arabian Sea) were assessed during winter (December) and summer (March-May) months of 2015. A significant spatial and temporal variability was observed in PM₁₀ mass concentration, crustal element and trace metal composition at the sampling area (viz. pristine, urban and industrial location). Using diagnostic crustal element ratio (viz. Fe/Al, Ca/Al and Mg/Al), mineral dust component were characterized and found to show large spatial and temporal variability. The concentration levels of trace metals were further assessed for enrichment factor (EF) analyses wherein reported elements were classified as two major groups. First group consist of Cr, Cu and Pb with $10 < EF < 100$ compared to continental crustal values (w.r.t. Al) suggesting dominant contribution from anthropogenic with minor contribution from natural sources and the second one consist of Zn and Ni showing very high EF (>100) which are solely derived from anthropogenic sources. Source identification for trace metals were further assessed based on Principle component analysis (PCA). PCA highlights major contribution of trace metals are from anthropogenic emissions at all three locations. However, contribution from mineral dust were observed at pristine and urban locations during winter month. The reported data of trace metal concentrations in aerosols gives a baseline information on atmospheric supply of micro nutrients to the Arabian Sea which have implication to the various surface ocean biogeochemical processes.

Key words: Aerosols Trace metal PCA Enrichment factor Arabian Sea

Introduction

Since the nineteenth century, ambient metal concentrations have increased in the atmosphere which can be attributed to the increased emission from anthropogenic and natural sources (Kowalczyk et al., 1982; Gertler et al., 2000; Wrobel et al., 2000 and Pakkanen et al., 2001). Trace metals from natural sources are mainly from dust emissions, volcanic eruptions, and biomass burning (Nriagu, 1989). However, major anthropogenic sources are pyro-metallurgical processes, combustion processes including emissions from vehicles, burning of fossil fuels for power generation, and large industrial process such as ore and metal smelting (Pacyna, 1984; Blagojevic et al., 2009). Additionally, incineration of urban waste water treatment sludge, urban waste and metal smelting are also identified as important sources of trace metals to the atmosphere (Sweet and Vermette 1993; Sullivan and Woods 2000). Al, K, Ca, Fe, Mn, Cr and Mg are the metal species usually associated with mineral dust and crustal species (Eleftheriadis et al., 2001; Kulkarni et al., 2007; Rastogi and Sarin, 2009; Kumar and Sarin, 2009) and those atmospheric metal species usually associate with anthropogenic activities includes Cd, Cu, Ni, Zn and Pb (Pacyna et al., 2001; Kumar and Sarin 2009; 2010). On global scale, wind-blown mineral dust are major emitter of metals (account for 60-80%) with moderate to minor contribution from volcanic eruption (15-25%) and forest fires as well as sea spray (< 10 %) constituting the natural sources (Nriagu 1979). However, in recent decades, anthropogenic emissions of metals have exceeded natural emissions significantly (Pacyna and Pacyna, 2001). In general, emission and concentration of metals into the atmosphere have large spatial variability depending on climate, wind velocity and surface topology.

In the recent years, owing to rapid urbanisation and industrialisation air quality has deteriorated from emission of toxic metals in the atmosphere, which has emerged as serious environmental issue (Wahid 2006; Borbely-kiss et al., 1999). Subsequent to emission, they undergo long range transport via aeolian pathway and get deposited to ocean and land surfaces (Arimoto et al., 2004). This lead to contamination of agricultural lands, terrestrial and aquatic ecosystems. They may, nevertheless, in some cases serve as a source of nutrients to these systems (Jickells et al., 2005). They may also produce adverse effects on human health due to their inevitable accumulation in the food chain (Van Malderen et al., 1996; Fang et al., 2000). Metal accumulation in human tissues, through food chain and inhalation, can cause injuries in the human nervous systems and internal organs. Considering their vulnerable nature to mankind (Golomb et al., 1997) the study of these metals leading to air pollution is of extreme importance. Apart from the health impact at local to regional scale, trace metals also act as limiting/co-limiting nutrients for surface ocean primary productivity (Moore et al., 2013). In contrast, some of the trace metals, for example Cu, can act as

toxicant and reduce primary productivity (Pytan et al., 2009). The atmospheric outflow (movement of air parcel from continent to ocean), which is enriched in trace metal composition (Srinivas and Sarin, 2013), can significantly modulate surface ocean biogeochemical processes. It is thus, essential to quantify their concentration levels at different ecosystem and assess their sources and distribution on spatial as well as temporal scale.

Here we report on trace metal and crustal element composition in aerosols collected from three different representative sites (pristine, urban and industrial) in a coastal city (Goa) located in the Eastern Arabian Sea. The site witness reversal of wind patterns (Agnihotri et al., 2015) and thus allows us to assess seasonal variability of aerosol trace metal composition over North East Arabian Sea. One of the main goals are to assess the trace metal levels, identify their sources and quantify the contribution of these sources to the observed trace metal concentrations. So far, there are no study existing on trace metal concentration in aerosols from this region. The reported data will be complementing the efforts undergoing International GEOTRACES programme (Anderson, 2019).

Material and Methods

Observation sites and prevailing meteorology

Goa is a small state along the west coast of India surrounded by Arabian Sea in the West and Western Ghats in the East. Because of its scenic beauty, it attracts many tourists and hence, tourism is considered as the major industry in Goa. Apart from this, export of iron ore extracted from midland of Goa is a major economic activity. Mining contributes about 20.4% of the gross domestic product to the state's economy. Mining in Goa is now highly mechanised employing in open caste mining adding to the deterioration of air quality in this region. Major sources of atmospheric emission from open caste mining includes clearing of land, transportation and loading and unloading of ores. Along with this, the dust emanating from the haul roads contributes considerably to the particulate matter content in the atmosphere. In general, the air quality of Goa was found to be most depreciated along the ore transportation routes which are also evidenced by a considerable load of particulate matter observed by Singh and Parverz (2015).

For this study, aerosol samples were collected at three sampling sites representing different segments of the region and activities, which include Goa University close to the coast; Port station at Vasco and Industrial station at Cuncolim (Fig. 1). Goa University is close to the coast and Panaji city and there are no industries located in the proximity but have moderate population and vehicular movement with less commercial activities. Mining is a routine activity of Goa at Marmugoa port which is a premier hub for maritime trade of India. Our second sampling site (Vasco) is in close

proximity of Mormugoa port. Third sampling site is located near industrial areas which undergoing rapid industrialization in last two decades. Metallurgical, Cobalt and metal industries, alloy and steel melting and rolling industries are located near this sampling site.

In general annual average mean temperature however stands at 21°C but the mean annual maximum and minimum temperature are 32°C and 22°C respectively. Goa does not experience a normal winter due to Western Ghats which prevents the entering of cold dry winds. Hence the maximum temperature does not dips lower than 12°C. Goa gets 90% of its rain from the south west monsoon as it lies along the coast and windward side of the Sahyadri hills. The strong westerly winds which sweep across the Goa during wet season and decreases in their intensity in October and remain moderate in strength throughout the dry season. However these winds blow in an easterly to north-easterly directions in the morning and westerly in the afternoon. We collected samples during March, April and May, 2015 (henceforth referred as summer month (SM) samples) and in December, 2015 (referred as winter month (WM) samples) at all three locations. Due to logistic reasons, we could not continue sampling for January and February, 2016, which could have constituted WM samples. Nevertheless, seasonal variability in the crustal and trace metal composition have been discussed (in section 3) based on these samples.

Meteorological parameters such as atmospheric temperature, relative humidity, wind speed and wind directions at the three sampling sites were obtained from AWS datasets of Space Applications Centre, Ahmedabad. Average atmospheric temperature is 28°C, 29°C and 30°C during summer months and 28°C, 27.4°C and 27°C in winter months and average relative humidity is 75%, 51% and 80% in summer months and 69%, 66% and 69% in winter months at Goa University, Vasco and Cuncolim respectively (refer to Supplementary material 1). Maximum atmospheric temperature is high in summer months than the winter months at all the three sampling sites. Similarly maximum relative humidity is in summer months except at Vasco site where maximum relative humidity is in winter months. Cuncolim site has experienced maximum atmospheric temperature and relative humidity compared to Goa University and Vasco sites (Supplementary material 1). The prevailing wind directions are South West at Goa University and North East at Vasco and Cuncolim during summer months (Supplementary material 1). During winter months winds are predominantly North East at Goa University, South West at Vasco and North East at Cuncolim respectively.

Aerosol collection

Ambient atmospheric aerosols (PM₁₀- particulate matter less than 10 micron aerodynamic diameter) were collected from all locations in campaign mode during different phases in summer and

winter months of year 2015 (date of sampling for each sample are detailed in supplementary material 2). Samples were collected on Whatman glass microfiber filter papers (GF/A; size 8 X 10 inches) by using respirable dust sampler 460 NL (Envirotech, India; with flow rate 1.1 m³/min). The dust sampler was installed on identified building terrace (at all three sites) which are typically at significant height (~10-12 m a.g.l) to avoid contamination from local soil. Twenty four hour average sampling was done for 8 days (23 March to 12 April) at Goa University, 10 days (13 April to 06 May) at Vasco and 12 days (19 May to 02 June) at Cuncolim during summer months (SM; March-May). A total of 7 samples were collected at Goa University (01-08 December); 4 samples (17 to 24 December) at Vasco and 4 samples (09-14 December) at Cuncolim site during winter months (WM; December). Total number of samples collected along with their collection dates are mentioned in Supplementary material 2. Subsequent to sampling, all samples were preserved in a zip-lock and brought to our laboratory and stored at -19 °C till the analyses.

Mass concentration

Mass concentration of all PM10 samples were measured using a Mettler Toledo microbalance (model no. ML204). The filter papers were weighed under controlled conditions of temperature and humidity before and after collection of particulate matter. Prior to weighing, all filters were conditioned at a relative humidity of 40±5% and temperature of 22 ± 1 °C for 5-6 hrs. The difference between initial and final weight of filters were normalized by volume of air pumped to calculate mass concentration in µg m⁻³.

Sample analysis

A piece of filter (area ~120 cm²) containing particulate matter was cut and digested with a mixture of supra-pure concentrated hydrofluoric acid, nitric acid, per-chloric acid and deionised water (2:1:1:3). The protocol for digestion of samples has been adapted from Kessarkar et al.,(2013), wherein they have digested suspended sediment samples from estuaries and rivers. The substrate used for sample collection were made of silica and easily get digested with the use of HF. Post digestion, samples were evaporated almost to dryness on the hot plate. The residue after cooling was dissolved and diluted to 50 ml with 2% HNO₃. The samples were stored in high density PVC bottles and subsequently analysed for crustal elements (Al, Fe, Ca, K and Mg) and trace metals (Cu, Mn, Zn, Pb, Cr, and Ni) on ICP-OES (Model: Agilent 710 series) at CSIR-National Institute of Oceanography, Goa.

The instrument sensitivity was frequently monitored with respect to mixed standard solutions (Merck, Germany, 23 elements). In addition, multi element calibration standards were run after every 10 samples to check on the short term fluctuations in the ionization efficiency of plasma source on

ICP-OES. For all instrumental analyses, filter blanks were analysed together with sample filters and suitable corrections were made for crustal elements and trace metals. The coefficient of variation (%) for repeat extracts for different elements are Al (10); Ca (8); Mg (7.); K (9); Fe (7); Mn (5); Cr (7); Cu (6); Pb(5); Zn (5); and Ni (5). The concentration of individual elements in the samples was determined from the calibration curve generated based on standards run in different concentrations.

Data analysis techniques

The important sources of trace metals to aerosols are: (a) crustal source; (b) anthropogenic source and (c) sea salt generation (oceanic source). The degree to which a trace metals in an aerosol is enriched or depleted, relative to a specific source can be assessed to a first approximation using an enrichment factor (EF). EF relative to Earth crust composition gives an idea about the increase in concentration of metals due to human activities. Enrichment factor for each metal is calculated by dividing its ratio to the normalizing element (here we are using Al; which is considered as a conservative trace element for crustal matter) by the same ratio found in the upper continental crust (McLennan, 2001; Saad et al., 2018). Al is one of the most abundant elements on the earth which usually has no contamination concern and had been widely use to study the sources and contamination of trace metals in riverine, estuarine and coastal environment (Zhang and Liu 2002; Feng et al., 2004). The enrichment factors is defined as:

$$EF_{=Al} = \frac{\frac{M}{Al} (Sample)}{\frac{M}{Al} (UCC)}$$

Where $(M/Al)_{sample}$ is the ratio of metal and Al concentrations in the sample and $(M/Al)_{UCC}$ is the ratio of metal and Al concentrations of the upper continental crust. This calculation assumes that contribution of anthropogenic Al is insignificant at the sampling region. An EF close to one indicates that an element has few sources other than windblown crustal material. Values much higher than unity imply sources other than crustal dust. These sources may include anthropogenic activities and natural processes, e.g. biogenic processes, forest wild fires, volcanic eruptions, sea salts etc.

Another important statistical tool, principal component analyses (PCA) was performed on elemental data to identify possible sources of the metals. In the present study PCA Varimax Kaiser normalized rotation was performed (computational detail of PCA is discussed in supplementary material S3) on the data set of metals from three sampling sites i.e. Goa University, Vasco and Cuncolim in two different seasons using Statisitca 7.0 (StatSoft).

Results and Discussion

Spatio-temporal variations of crustal and trace elements have been studied over three sampling sites during SM and WM. The average PM10 (particulate matter less than 10 μm aerodynamic diameter) mass and crustal as well as trace metal composition for all three station in two different season is detailed in Table-1.

Variability in PM10 mass concentration

PM10 mass concentration is an important contributor to the ambient air quality and found to be significantly high in several Indian cities (Guttikunda et al., 2014). Daily variation of PM10 mass observed over three distinct site at Goa in two seasons is shown in Fig. 2. The average mass load for Goa University (GU) is the lowest ($48.8 \pm 21.1 \mu\text{g m}^{-3}$) among three sites with almost similar load found for Vasco and Cuncolim locations during summer months (Table-1). A similar trend is observed for winter months for three sites with lowest loading at GU ($98.7 \pm 35.8 \mu\text{g m}^{-3}$). The lowest mass load at GU can be attributed to its geographical location which is relatively pristine site, with negligible vehicular/industrial emissions. However, the other two sites are near to port and industrial area. The mass load observed at GU in winter is comparable with the value reported by Agnihotri et al., (2015) from nearby location at National institute of Oceanography (NIO) during winter months. Agnihotri et al., (2015) had reported total suspended mass load of $80.78 \pm 29.46 \text{ mg m}^{-3}$, slightly less than our value. This may be mainly due to sampling collection site and height at which aerosol collection were done. At NIO, samples were collected at $\sim 30 \text{ m}$ above ground level whereas, at GU it was collected at 10 m a.g.l . In addition, NIO site is 500 m away from Arabian Sea and more pristine compared to GU. An overall increase in mass load is observed at all three locations during winter as compared to summer season. The variation in mass loading largely depends on meteorological parameter, for example, wind speed. High wind speed can disperse particulate matter more effectively and can dilute mass concentration. In our present study, we observed high wind speed during summer compared to winter (Supplementary material 1). High winds can help in dispersal of particulate matter and thus, we observe an overall lower values during summer. Furthermore, the weak winds were observed at Cuncolim stations during both season, and we find highest mass load at this site in both season. This clearly highlights, role of meteorological factors as well as emission sources in deciding the abundance of particulate matter.

An average mass load for Goa can be considered ~ 60 and $131 \mu\text{g m}^{-3}$ (by taking average of mass load at three sites) during winter and summer. This average value is compared with other coastal locations viz. Vishakhapatnam, Trivandrum and Chennai (Guttikunda et al., 2014) in India. The summer load is comparable with Trivendrum ($62.9 \pm 17.8 \mu\text{g m}^{-3}$) and are lower than

Vishakhapatnam ($91.2 \pm 34.8 \mu\text{g m}^{-3}$) and Chennai ($121.5 \pm 45.5 \mu\text{g m}^{-3}$). However, winter value at Goa exceed from annual average of these cities. The high values of mass loading also depend on urban population and the expansion of cities. The increase in population increases the demand of motorized vehicle (both personal and public transport) which further leads to deterioration of the ambient air quality. Chennai, being highly populated among all coastal cities have very high annual average mass load. Thus, the mass load shows large variability at local scale and depend on various factors as stated above.

Composition and characterization of PM10 using crustal elements

The concentration of crustal elements (Al, Ca, Mg, K and Fe) in PM10 samples collected from three different stations during March-April (SM) and in December (WM) 2015 is shown in Fig. 3. Significant differences were observed in concentration of crustal elements at three different locations. At Goa University, Al and Ca showed an increase in concentration from March to April while no clear increasing or decreasing trend was observed for Mg, K and Fe. These metals (Mg, K and Fe) display an increase in concentration during first few days and thereafter a decreasing trend is observed. Calcium at Vasco showed a decreasing trend from April 13 to May 06, whereas Al and Mg showed almost a constant variation except on April 29 where highest peak was reported. Similarly, at Cuncolim Fe showed an increase in concentration from 19 May to 02 June whereas, Al and Mg showed a similar pattern of distribution with a maximum peak on 23 May. These observation suggest, no significant pattern or trend in the variability of crustal element at all three station in Goa. However, we find large spatial variability with Cuncolim showing highest value of crustal element (except Ca and Mg) followed by Vasco and GU. Although, Cuncolim shows highest for Ca and Mg, but they were high at GU compared to Vasco. This might be due to increased influence of Sea-salt at GU than Vasco. On the other hand during WM at Goa University, most of the crustal elements did not show any clear pattern except K showed a decreasing trend from 01 Dec to 08 Dec (Fig. 4). Though the distribution is not clear, Ca and K however showed a similar distribution pattern with maximum concentration on 19 Dec to 21 Dec and Al and Mg with maximum peak on 24 Dec respectively, at Vasco. The spatial variability of crustal element during winter is different than summer wherein GU is showing highest value for Al, Ca and Mg while Vasco have highest Fe. This suggest the impact of mineral dust derived from local emission sources during winter and this impact is observed prominently over pristine site. The contribution from mining activity is also observed at Vasco showing high Fe values. This further indicate dominant role of emission sources than meteorological parameter.

Major source of these elements (Al, Fe, Ca, Mg, K) are mineral dust which is derived from crust (Usher et al. 2003), however, recent studies have indicated contribution of some of these metals from sources other than mineral dust. For example, Andreae, (1983), have reported significant contribution K from biomass burning aerosols. Ca and Mg can also be derived from Sea-salt aerosols (Kumar and Sarin, 2009), especially over coastal locations. Fe can be emitted from various combustion sources including biomass and fossil fuel burning sources (Schroth et al., 2009; Kumar and Sarin, 2010). In this study, we are limited by water-soluble composition of PM10 samples, thus, it is difficult to decouple contribution from various sources. Here, presuming all crustal elements are derived from mineral dust, we attempt to characterize dust using diagnostic elemental ratios viz. Fe/Al, Ca/Al and Mg/Al. These ratios have been used as a proxies to identify source of mineral dust in Africa (Chiapello et al., 1997), Asia (Zhang et al., 1996) and over western India (Kumar and Sarin, 2009). Average Fe/Al, Ca/Al and Mg/Al ratio for all three sites in SM and WM are detailed in Table-1. A very high Fe/Al ratio (0.94 ± 0.74 and 1.12 ± 1.01) is found in aerosols collected from Goa University and Cuncolim site respectively. In contrast, relatively low Fe/Al ratio (0.42 ± 0.43) is observed for Vasco site which is comparable to UCC ratio of 0.44 (McLennan, 2001). A significant decrease in Fe/Al ratio is observed for winter month for all three sites. This indicate influence of distinct sources to the dust collected in Goa at two distinct season. A large spatial variation is observed for this ratio at our study site and can be attributed to different emission source associated with the three location. Previous work by Kumar et al. (2008), have reported 0.51 ± 0.05 and 0.72 ± 0.37 over Arabian Sea and Bay of Bengal respectively. The influence of combustion sources has been attributed to high Fe/Al ration for Bay of Bengal as compared to Arabian Sea which received mostly pristine dust during sampling period. In our study, we observe, higher ratio in summer compared to winter, which is an anomalous observation. This is because, enrichment in Fe indicate contribution from anthropogenic sources, however, we did not observe high Fe/Al ration for Cuncolim site which is near to industrial emission source and more prone to receive anthropogenic Fe. In order to conclusively interpret Fe/Al ration, comprehensive long term measurement is required. Similar to Fe/Al ratio, we also analysed Ca/Al and Mg/Al ratios for both summer and winter months at three sites in Goa (Table-1). High Ca/Al ratio (w.r.t UCC value of 0.37) is observed for Goa University (0.76 ± 1.74) and Cuncolim site (0.53 ± 0.83) and a comparable value of 0.15 ± 0.35 is found for Vasco site. This is similar to what has been observed for Fe/Al ratio during summer season. However, a very low value were found for all three sites during winter (Table-1). In contrast to Fe/Al and Ca/Al ratios, we observed higher Mg/Al ratios for winter compared to summer (Table-1). These ratios indicate the influence of local sources rather remote sources or dust from long-range transport. This is mainly due to the difference we found in ratio compared to those reported over

Arabian Sea (Kumar et al. 2008) located in the western side of Goa. The Arabian Sea receive dust from nearby arid/sem-arid region (e.g. Arabian Peninsula, Southwest Asia and Thar Desert) and ratios reported here are significantly different and highly variable as compared to our sampling site. The relative contribution of crustal element from local vis-à-vis remote source is beyond the scope of this study. However, a long term study at this site may reveal characteristics and sources of dust and their contribution to ambient particulate matter more comprehensively.

Trace metal composition and their variability

The average concentration of trace metals during two different seasons (SM and WM) at Goa University, Vasco and Cuncolim are shown in Table-1. Their daily concentration on collection date during summer and winter season is displayed in Fig. 4. Zn is found to be most abundant among all trace metal analysed (Table-1) followed by Mn and Cu at Goa University site and Pb and Mn at Cuncolim site during summer months. Other than Zn, all trace metals are on lower side at Vasco site as compared to other two locations. This indicate, Vasco is possibly cleanest among three location in terms of trace metals other than Zn. This observation suggest no significant pollution source is impacting to ambient air during collection period at Vasco, although Zn levels are highest for this site during summer. The highest concentration of trace metals (which are anthropogenically derived) are observed at Cuncolim site mainly because it is being an industrial location. Several industries, viz; metallurgical, steel melting, rolling, tyre re-treading and thread rubber, crown caps, construction additives & allied products etc. influence concentration of anthropogenic elements in Cuncolim region. An overall significant increase is observed in the all trace metal average concentration during winter months. More than 5 times increase is observed for Zn, being most abundant among all as observed during summer, at Cuncolim site. Around 1.5 times increase is found for Goa University and Vasco location. Pb being second abundant metal shows a contrast increasing trend as shown by Zn. More than 5 times increase in Pb is found for Goa University and Vasco, but no significant increase is observed at Cuncolim site. Also, more than 10 times increase is observed in Ni concentration for all sites. These marked difference in seasonal to daily distribution pattern arises possibly due to strength of emission sources of aerosols and ambient meteorological parameters. Meteorological factors such as wind speed, wind direction, mixing height, temperature and relative humidity play important roles in determining the pollutant levels in ambient atmosphere (Tayanc 2000; Singal and Prasad 2005). Temperature and relative humidity in the present study did not show much variation during SM and WM, however the marked distinctions were observed in wind pattern during two seasons at three sampling sites (see Supplementary material S1). During SM wind direction is mainly from SW to NW direction at Goa university, whereas at Vasco and Cuncolim

wind flow mainly in W to N directions(Fig.S1). Hence, the aerosol prevailing during this period is a mixture of both continental air mass and maritime. This is also supported by marine contribution of K and Ca as these elements are abundant in seawater. Further, dryness of the soil during summer causes the soil particles to be easily transported in the air by wind and dilutes the pollutant (Pekey et al. 2010).High K at sampling site thus may be from oceanic sources which are associated with the formation of sea salt. Similarly during WM, winds are prevailing mostly from NE to SE direction at Goa University, ESE to SW at Vasco and N to SSW at Cuncolim (Fig.S1). In general during winter months, wind blows from North east to South west direction and carries anthropogenically derived trace metal rich continental air mass. In addition, we did not observe any significant correlation between strength of wind speed and daily trace metal concentration in a particular season. However, we observe a high trace metal content in ambient air during winter months compared to summer months. These seasonal variations can be explained based on calm wind condition during winter compared to summer. Due to calm wind condition, the dispersal is not as efficient as during strong wind condition. Moreover, the tourism is on its peak in December and number of motor vehicle rises exponentially on road adding significant amount of fossil fuel burning emissions. These are possibly major cause for an increase in trace metal concentration during winter month. Thus, these observation suggest the role of emission sources being more prominent than meteorological parameter to explain daily as well as seasonal trace metal variations over Goa.

Enrichment factor analysis

The enrichment factor (EF) of metals which are mainly sourced from anthropogenic activities (Cr, Cu, Pb, Zn and Ni) in aerosol samples is shown in Fig. 5. Based on varying EF, the trace metals can be divided into 2 sub-groups. First Group includes elements such as Cr, Cu and Pb having enrichment factors around 10 and above but less than 100 which are moderately enriched in metals. These trace metals are mainly contributed by anthropogenic sources such as vehicle emissions/oil combustion and re-suspended road dust with high traffic densities (Triphatee et al. 2014; Samara and Voutsas 2005; Shah et al. 2006; Viana et al., 2008) with possibly partial contribution from crustal sources. The second group of metal includes Zn and Ni with enrichment factors >100 indicating that they are severely contaminated from anthropogenic activities (Al-Momani, 2003; Tripathy et al. 2014) with no contribution from geogenic source. All three sites shows significant enrichment of Cr (EF > 100) for few days during summer months. In comparison, surprisingly, no significant enrichment of Cr is found during winter at all three sites. This indicate sources contributing Cr (steel industry) are not active during sampling period. Similar to Cr, Cu and Pb also shows similar trend of high enrichment for few days during summer month compared to winter months. However, on

average, Cu and Pb display high enrichment during winter months at Vasco and Cuncolim site. No significant differences in EF of Cu and Pb, were observed for Goa University site suggesting no seasonal impact on trace metal concentration at pristine location which is least affected by industrial or anthropogenic emission sources. Cu and Pb are mainly derived from fossil fuel combustion, traffic and industrial activities (Cong et al., 2010). Thus, relatively high enrichment of Cu and Pb is observed at Vasco (port site) and Cuncolim (industrial site) during winter month.

Zn and Ni are primarily derived from fuel burning and traffic sources (Cong et al. 2010). We observed very high enrichment for these two metals at all three sites. However, a large variability is observed for samples collected during summer months. This is similar to what is found in other metals as discussed above. This clearly hints to the trace metal concentration have day to day variability and largely attributed to activation of source emission. The seasonal high of EF for Zn and Ni during winter months is similar to those observed for other metals. This suggests seasonal variability in metal concentration may be attributed to meteorological changes, however, daily variation in metal concentration depends on the activity of emission source region

Source apportionment

The principal component analysis (PCA) is a statistical tool which is used to explain most of the variance in the data set. The aim of this tool is to find direction of multivariate space with maximum variability (Reimann et al. 2008; Tripathee et al. 2016). Subsequently, principle components (PC) will be identified which are orthogonal to each other. The number of principal components will depend on the variability of the data available and on the number of examined elements (Tripathee et al. 2016). Fig. 6 shows 3D plots which describe the PC loadings for metal data of the study period during both seasons. For interpreting of the metal data the method of Kaiser Criterion (Kaiser 1960) is followed which will retain only those factors having eigen value >1 . Factor loading >0.71 are typically regarded as strong loading and <0.32 as very weak loading (Nowak 1998).

During SM, PCA results of metal in PM₁₀ at Goa University showed three PCs (Fig. 6a). PC1 accounted for 56.55% of total variance and it is associated with strong positive loading on Ni and Zn and strong negative loadings on Mn, Cr, Ca, Al and Pb. This may be associated with vehicular emissions. Zn and Ni are mainly emitted from lubricating oil, break lining and tires (Cong et al., 2010). PC2 accounted for 17.94% of total variance and it is associated with strong positive loadings on Mg and strong negative loadings on K. This can be attributed from sea salt (Tripathee et al. 2017). Similar studies conducted on source identification at various places of Mumbai region which also indicated crustal matter and sea salt as main sources contributing to particulate pollution along with

other anthropogenic source (Sadasivan et al. 1984; Kumar et al. 2001; Tripathi et al. 2004). PC3 which accounted for 12.4% of the total variance has high loadings on Fe. This factor may be associated with road dust source. Similar to SM, three PCs were obtained at this site for WM, which accounted for 90.01% of total variance (Fig 6b). PC1 which accounted for 53.50% of the total variance showed a strong positive loading on Pb and Cu and a strong negative loading on Ni and Zn, almost reverse of what is found in SM. PC2 which accounted for 20.91% of the total variance showed strong positive loadings on Al and Mg which may be attributed to crustal source. PC3 which accounted for 16.59% of the total variance showed a strong positive loading on Mn, Fe and a good loading on Ca, K and Cr. This may be associated with mixed source i.e. crustal and anthropogenic source. PC2 and PC3 hints for enrichment in crustal sources during winter months at Goa University site. This is in line with the observation found for EF analyses, wherein, a decrease in EFs were found for all metals at Goa University site. In addition, an increase in average Al concentration (Table-1) at GU attest to the fact of increased dust contribution during winter.

At Vasco PCs obtained from PCA accounted for 87.06% of the total variance (Figure 6c). PC1 accounted for 39.44% of the total variance and showed strong positive loadings on Mn and Fe and strong negative loadings on Cu. This factor probably represent a mixture of re-suspended dust (Quiterio et al. 2004; Shah et al. 2006; Chakraborty and Gupta 2009) and iron ore mining activities which are considered to be the most important sources of these elements. Iron ore mining is the major economic activity in Goa where Marmagao Port is occupying a prominent position in India's premier iron ore exporting port. Apart from this Mn is mainly originated from airborne soil dust which exists in the form of MnO_2 (Von Schneidemesser et al. 2010). PC2 which accounted for 19.60% of the total variance showed strong positive loadings on Cr and Ni and a strong negative loading on Zn and is attributed to anthropogenic source. This is conspicuous, as no significant enrichment is found for Cr ($EF < 10$) at Vasco site during SM and WM. However, significant enrichment is observed for Ni, especially in WM, at this site. PC3 which accounted for 15.59% of the total variance showed strong positive loadings on Mg and Al and strong negative loadings on K. This factor indicates the contribution from crustal sources viz. mineral dust which possibly comes from mining activity and /or transportation of Fe ores. PC4 which accounted for 12.43% of the total variance and showed strong positive loadings on Ca and Pb. This factor may be attributed to road dust source. Ca is widely used as $CaCl_2$ in construction of roads and Pb has become part of the road dust due to the usage of leaded fuel over the years. It is evident from above, that mining activity contribute significantly to metal concentration at Vasco site. During WM, three PCs were obtained which accounted for 99.98% of the total variance (Fig. 6d). PC1 which accounted for 65.25% of the

total variance showed a strong positive loading on Zn and strong negative loadings on Pb, Cu, Mg and Mn. This indicates significant contribution from anthropogenic sources, however, it is difficult to decouple contribution from long-range transported aerosols or local sources. PC2 and PC3 accounted for 23.84% and 10.89 %, respectively, of the total variance. They mostly showed a strong positive loading on Cr and Al and strong negative loadings on K, Ni and Fe. This is interesting, as contribution from mineral dust is also observed during winter months. Cr can be contributed by dust derived from Oman region (Chinai et al., 2006). We also observed dust contributing to Goa University samples during winter. The increased dust contribution during winter is evidenced from increase in Al concentration during WM at Vasco similar to that found at GU.

At Cuncolim four PCs were obtained which accounted for 84.4 % of the total variance (Figure 6e). PC1 accounted for 31.03 % of the total variance which showed a strong positive loadings on Cu, Fe and Cr and strong negative loadings on Ni. This factor can be attributed to industrial emission of these elements during study period (Ahumada et al. 2007; Cetin et al. 2007; Dubey et al. 2012). PC2 which accounted for 20.53% of the total variance showed a strong positive loading on Al and Mg. This is possibly due to contribution from local dust as Al and Mg were not found to be significantly loaded in other two locations during SM. PC3 and PC4 accounted for 18.68% and 14.16 % of the total variance with a strong positive loading on Pb, Ca, Zn and K, indicating strong anthropogenic contribution which is expected being an industrial site. During WM, all three PCs accounted for 99% of total variance with strong contribution from anthropogenic sources.

Overall, we observe strong anthropogenic influence at Cuncolim site in both season. However, we observe contribution from mineral dust at Goa University and Vasco location during winter. In order to get a more representative variations in trace metal distribution, it is imperative to increase sampling frequency in different season.

Conclusions

The atmosphere is generally recognised as a major route for the transport of trace metals to the marine environment. In this study, we have assessed the metal concentration levels at a coastal location in the Eastern Arabian Sea. Major crustal (Al, Fe, Ca, Mg, K and Mn) and trace metals (Cr, Cu, Pb, Zn and Ni) were analysed in the ambient aerosol (PM10) samples collected from three different locations in Goa, during summer and winter month of 2015. This analysis is corroborated by statistical analyses wherein major element and trace metal source identification was done. This is a first maiden report on monitoring of concentration of crustal and trace metals in atmospheric aerosols over a coastal station in Eastern Arabian Sea (Goa), India. This study highlights high PM10

concentration during winter compared to summer at all three location. This is attributed to low wind speed and neutral stability during winter which is unable to disperse particulate matter more effectively. In addition, contribution of mineral dust (Al) during winter at two sites (GU and Vasco), further adds to high particulate mass concentration. A significant spatio-temporal variation is observed for both crustal and trace metal concentration during our study period at Goa. Higher abundances were observed at industrial (Cuncolim) and port (Vasco) sites compared to pristine (Goa University) location. Also, winter samples have higher concentrations for all crustal as well as trace metals compared to summer month samples. Based on diagnostic elemental ratios i.e. Fe/Al, Ca/Al and Mg/Al, mineral dust at Goa is characterized. A significant difference were observed in dust characteristics indicating distinct dust sources impacting at our study site. In order to assess crustal versus anthropogenic sources, enrichment factor analyses have been done. Cr, Cu and Pb were found to moderately enriched ($10 < EF < 100$), however, Zn and Ni displays very high enrichment ($EF > 100$) w.r.t crustal sources. An enhanced enrichment is observed for Cr, Pb and Ni in winter samples at Vasco and Cuncolim site. However, no such trend is found in samples collected from GU. Higher enrichment is observed for Zn and Ni during winter for all three station as compared to summer season. The PCA were also attempted to identify sources of metal at all three station in both season. Most of the trace metal are found to derive from anthropogenic sources with partial contribution from mineral dust during winter month at GU and Vasco station. These findings are partially in agreement with EF analyses and concentration data. A more comprehensive sampling with high sampling frequencies is required to understand seasonal differences of crustal and trace metal distribution at this site. However, present data provides a very important information of crustal and trace metal distribution on spatio-temporal scale over Eastern Arabian Sea.

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Table-1: Average mass concentration (in ng m⁻³) with standard deviation of PM10, crustal and trace element measured during this study at three location in Goa during summer and winter months. Average elemental ratio (diagnostic tracers) are also given in last three rows for all location during summer and winter.

	Summer									Winter									
	Goa University			Vasco			Cuncolim			Goa University					Vasco			Cuncolim	
*PM10	48.8	±	21.1	62.4	±	25.6	69.8	±	24.5	98.7	±	35.8	134.3	±	22.1	160.8	±	27.4	
Al	861.3	±	815.4	1800.0	±	1646.2	4272.1	±	2101.3	6535.6	±	3574.7	4411.0	±	1930.0	4758.5	±	1387.8	
Ca	191.8	±	106.2	55.3	±	39.7	125.6	±	56.1	105.4	±	74.7	48.9	±	34.4	36.4	±	7.1	
Mg	369.4	±	107.2	389.3	±	278.0	684.9	±	246.8	850.1	±	208.0	799.3	±	247.6	747.5	±	120.3	
K	1690.3	±	754.9	1974.9	±	1290.5	1347.3	±	1227.9	1026.9	±	407.4	882.5	±	619.1	1285.3	±	544.1	
Fe	418.5	±	228.7	312.4	±	178.2	466.1	±	372.1	871.3	±	437.1	1070.5	±	276.2	671.0	±	139.5	
Mn	18.6	±	19.1	3.4	±	4.0	47.0	±	50.2	32.8	±	13.2	32.6	±	8.8	131.4	±	36.4	
Cr	2.8	±	2.6	2.4	±	2.1	1.5	±	0.8	2.6	±	1.9	1.5	±	0.6	2.9	±	1.6	
Cu	10.5	±	16.0	5.2	±	0.8	5.7	±	4.0	20.4	±	19.4	23.2	±	3.8	10.1	±	2.7	
Pb	5.8	±	9.2	6.5	±	4.8	47.6	±	43.4	32.1	±	19.7	36.0	±	11.0	57.8	±	18.5	
Zn	356.6	±	233.3	438.7	±	311.3	260.2	±	125.6	573.3	±	105.5	644.0	±	207.4	1427.5	±	275.6	
Ni	5.2	±	2.3	7.1	±	0.8	7.8	±	2.0	54.8	±	21.3	52.4	±	40.1	58.1	±	7.1	
Fe/Al	0.94	±	0.74	0.42	±	0.43	1.12	±	1.01	0.31	±	0.51	0.29	±	0.15	0.15	±	0.06	
Ca/Al	0.76	±	1.74	0.15	±	0.35	0.53	±	0.83	0.04	±	0.07	0.01	±	0.01	0.01	±	0.00	
Mg/Al	0.13	±	0.10	0.03	±	0.02	0.17	±	0.05	0.29	±	0.43	0.19	±	0.05	0.17	±	0.05	

*PM10 is expressed in µg m⁻³

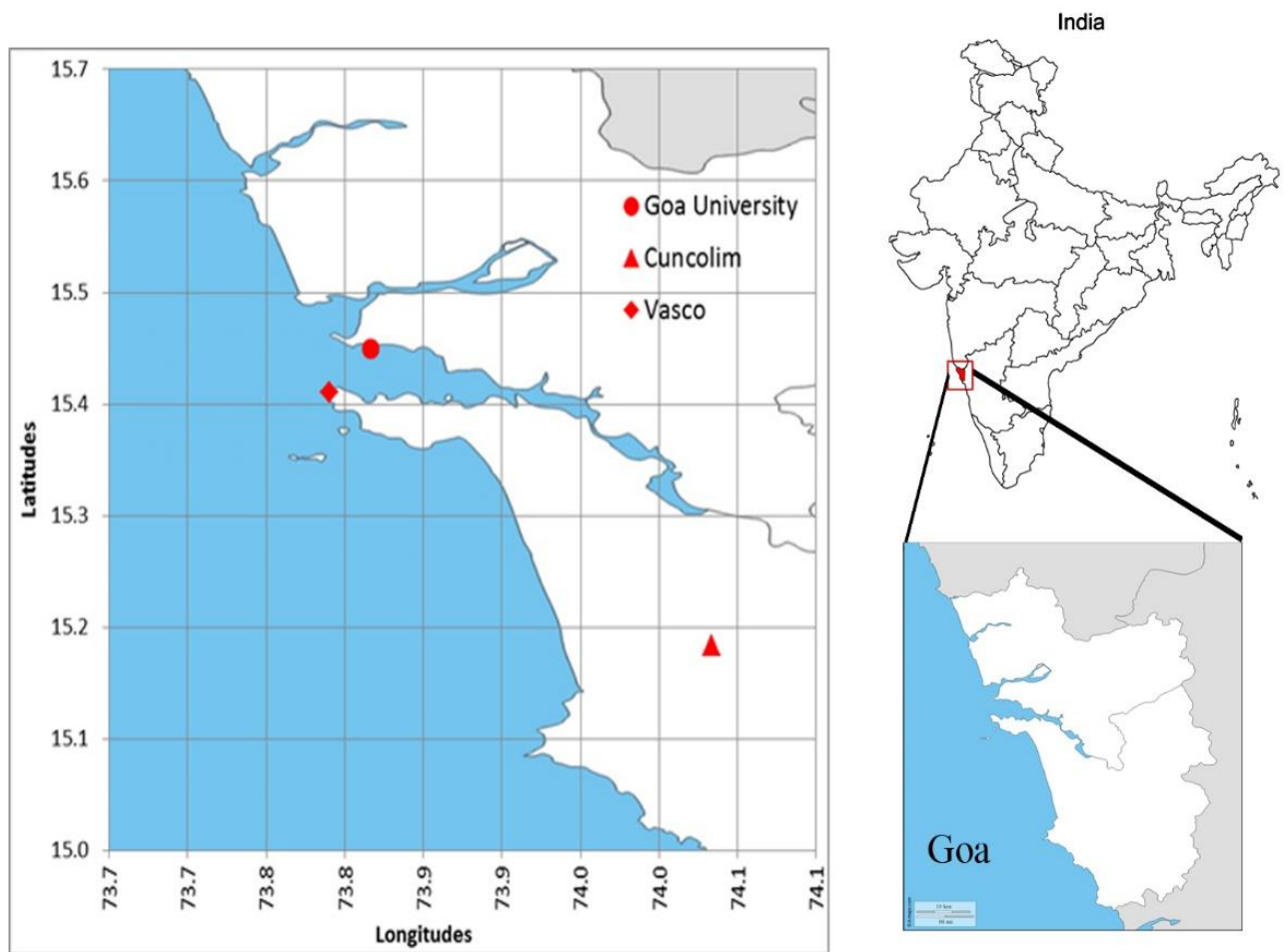


Fig.1: Aerosol sampling done at a coastal location in Eastern Arbian Sea. Location of three different sampling sites (in red dots) are shown in this map.

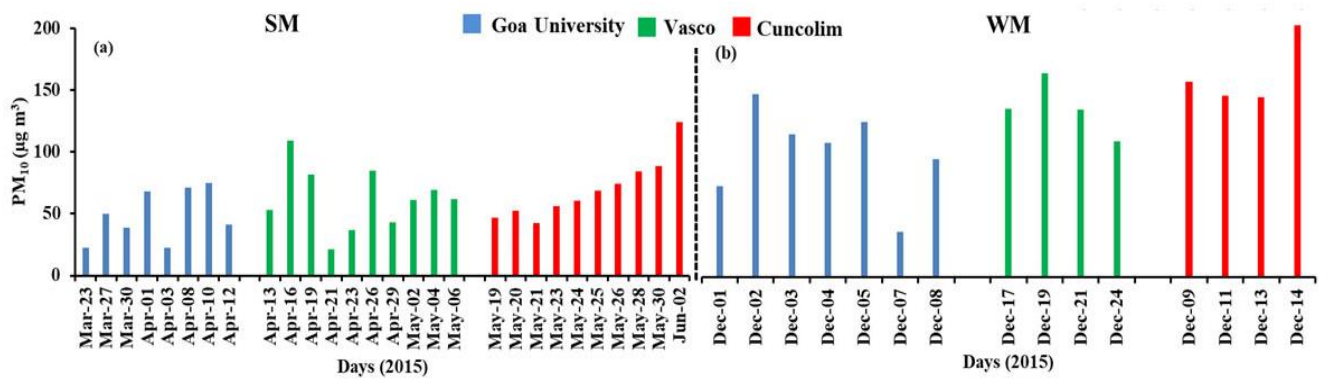


Fig. 2: Spatio-temporal variation of PM₁₀ mass concentration collected at three sampling sites during (a) Summer month and (b) winter month.

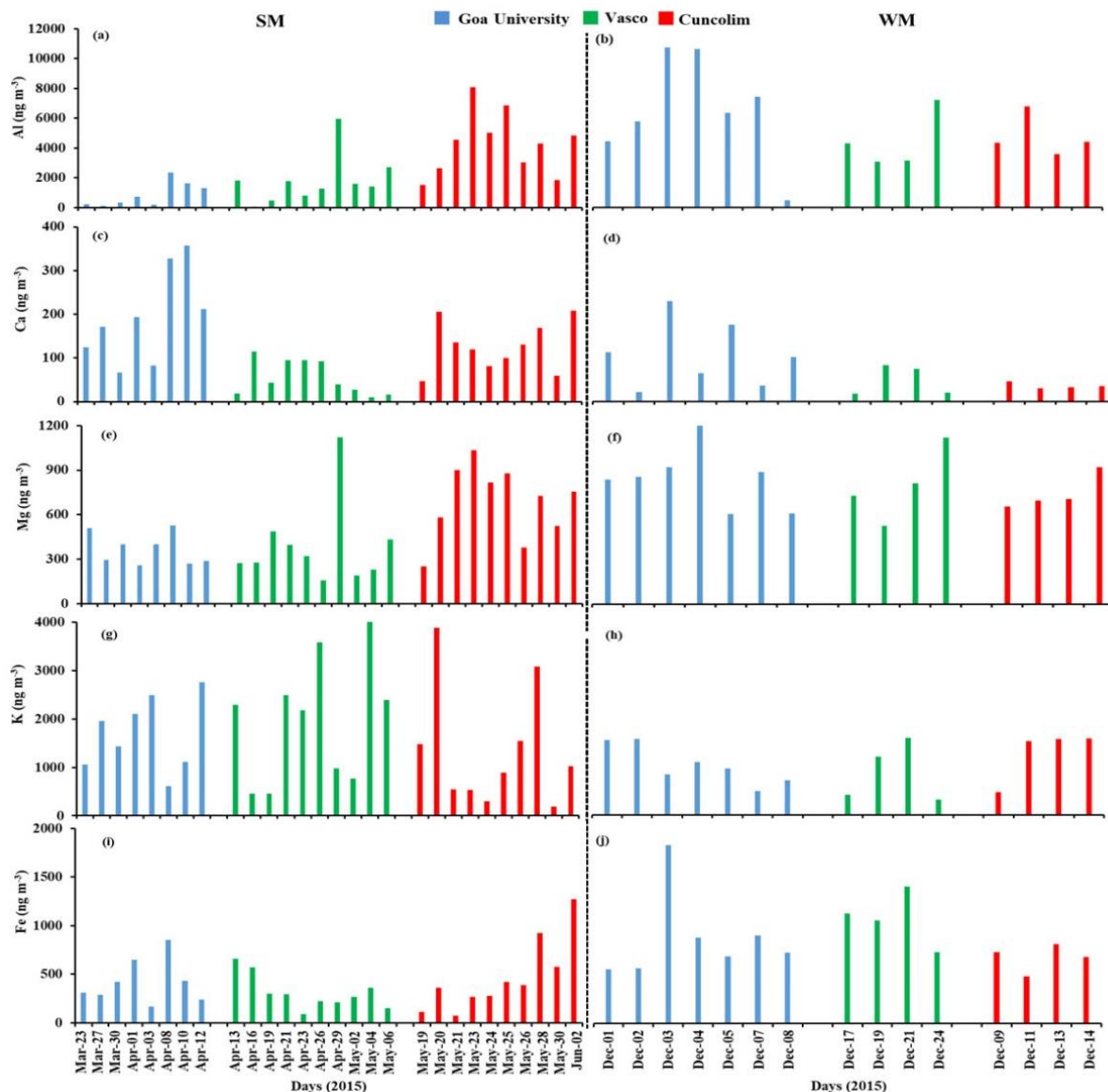


Fig. 3: Spatio-temporal variation of crustal elements (Al, Ca, Mg, K and Fe) in aerosols collected at three sampling sites during summer and winter month.

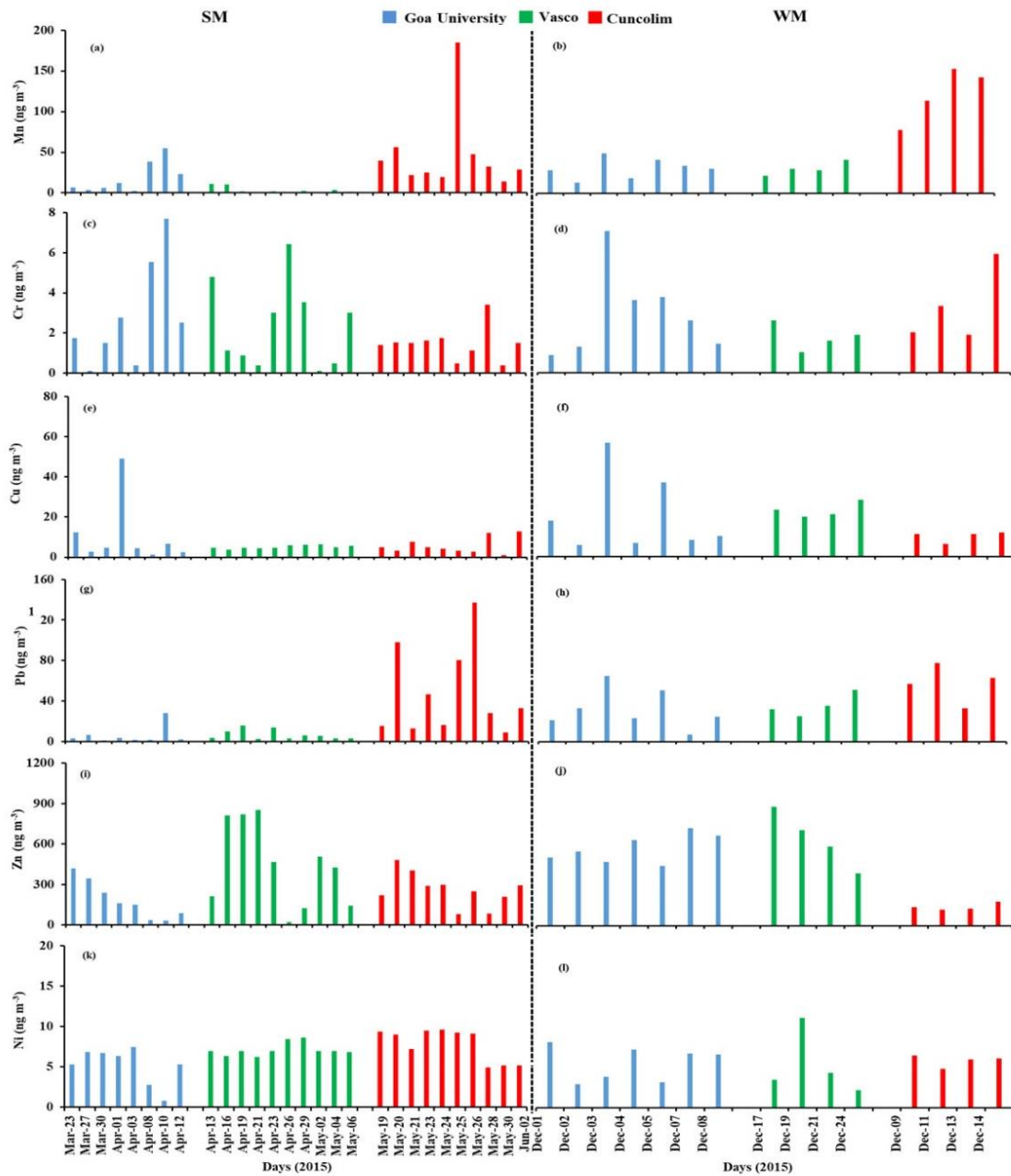


Fig.4: Spatio-temporal variation of trace elements (Mn, Cr, Cu, Pb, Zn and Ni) in aerosols collected at three sampling sites during summer and winter month.

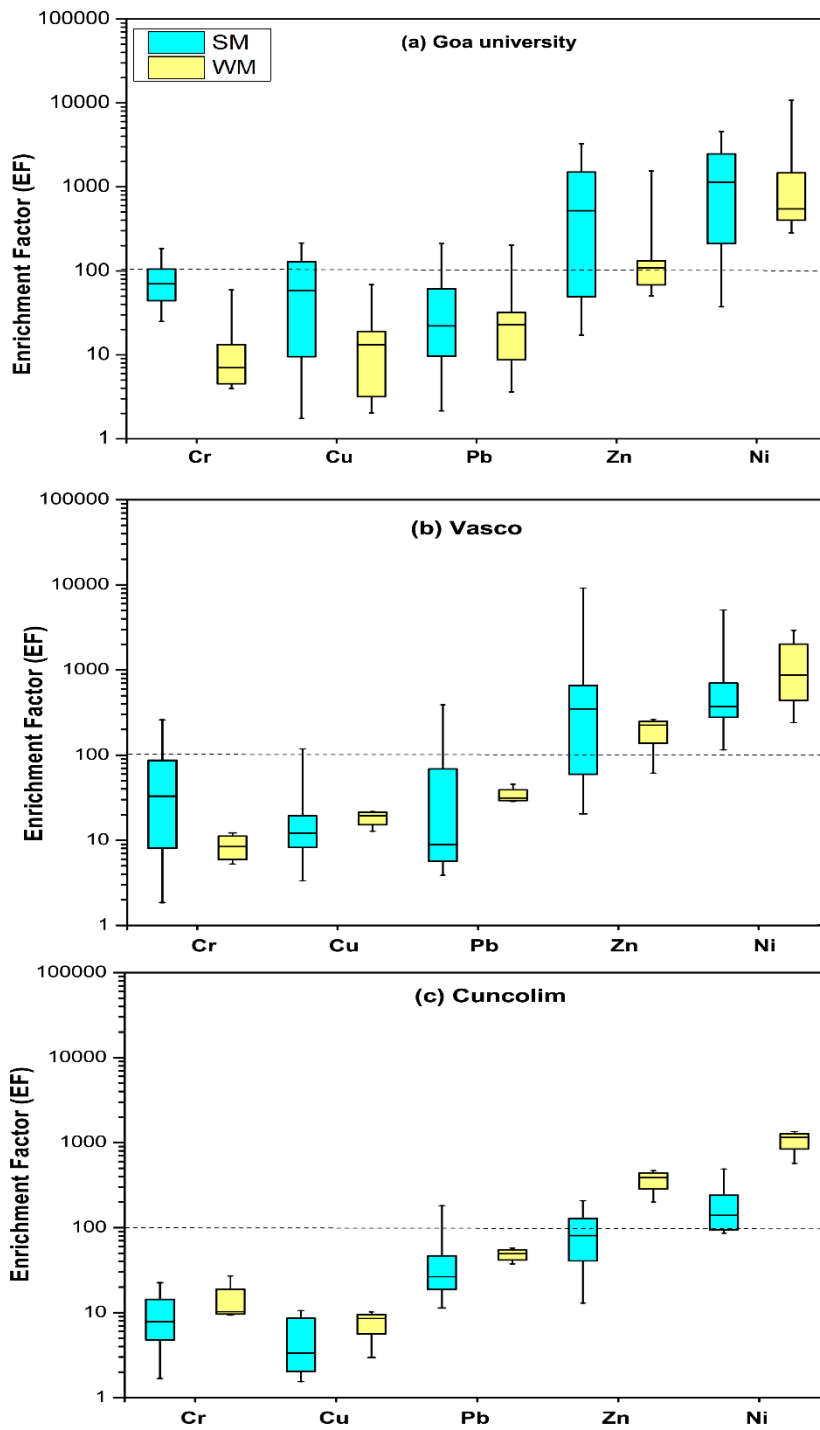


Fig. 5: Box-plot representation of the enrichment factors (EF) of trace metals (Cr, Cu,Pb, Zn and Ni) at three sampling site during summer and winter months.

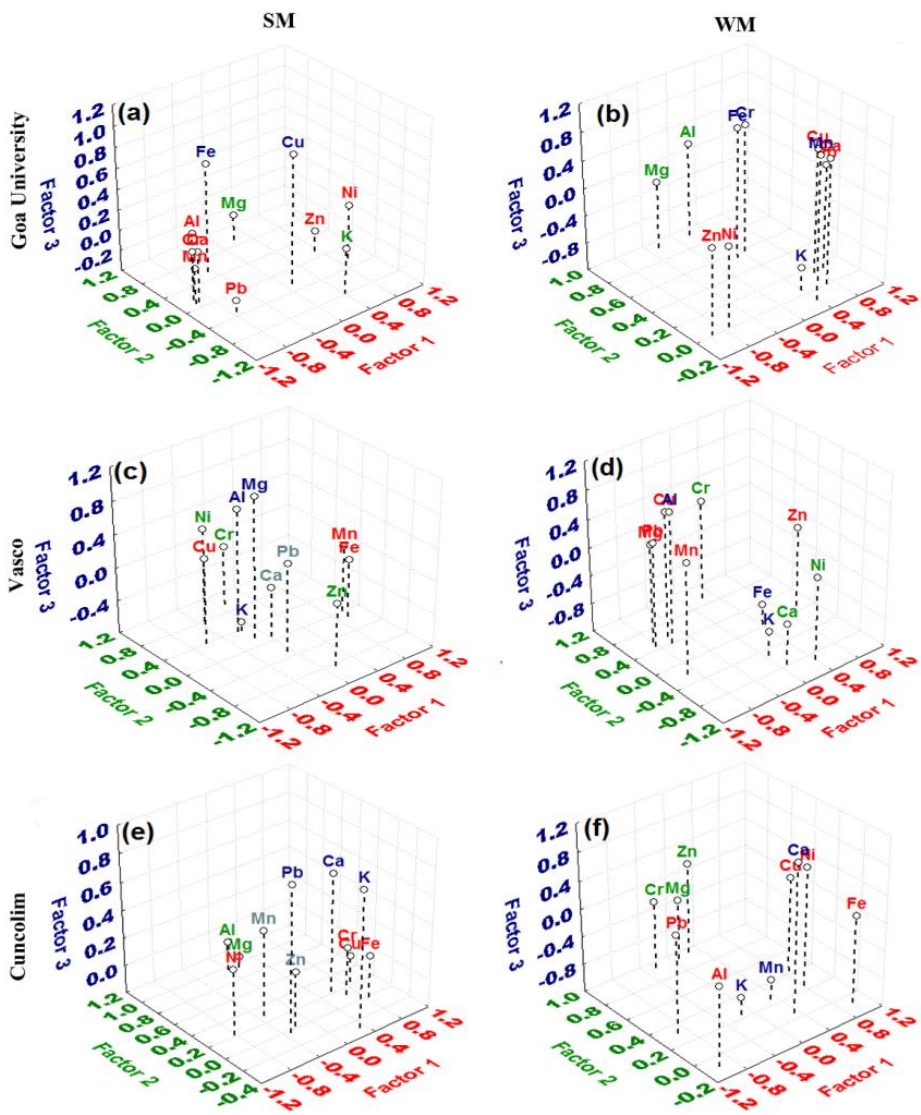


Fig. 6: Three dimension plot of the factor loadings for eleven components at three sampling sites.

Implication Statement:

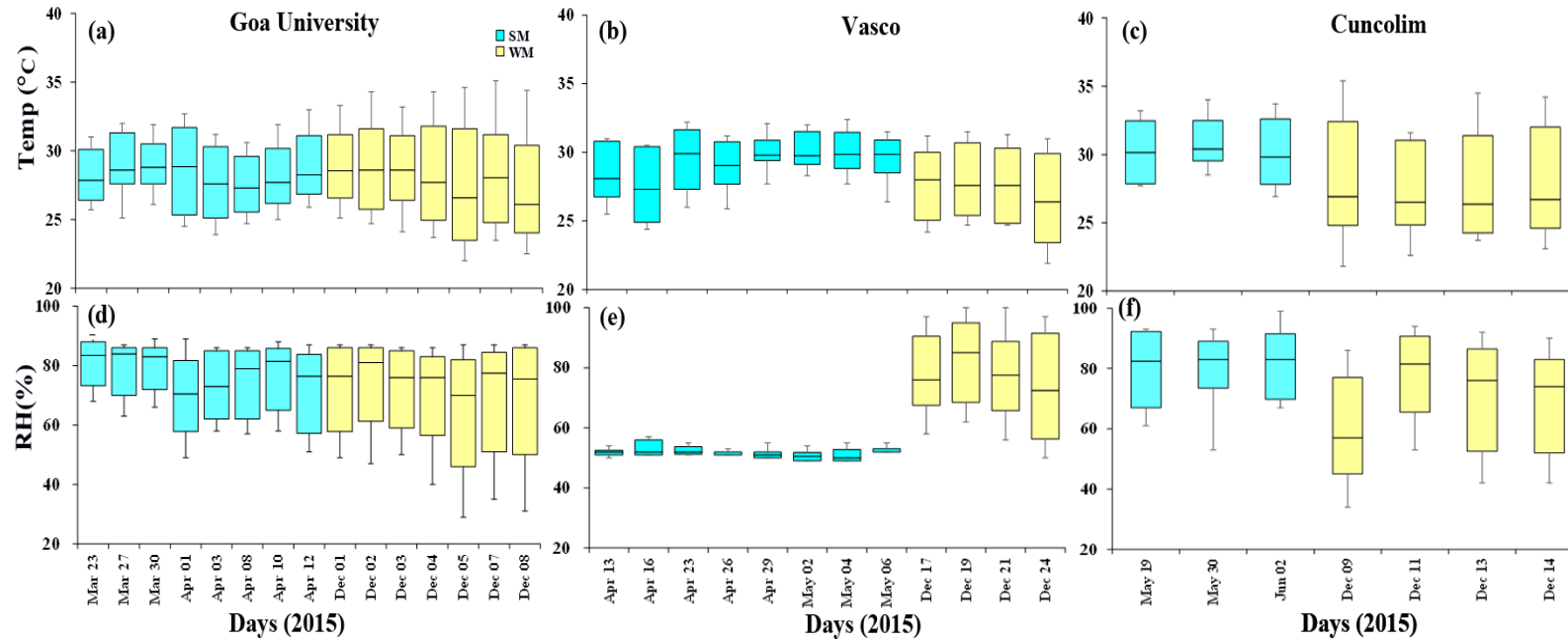
The manuscript entitled “**Assessment of crustal element and trace metal concentrations in atmospheric particulate matter over a coastal city in the Eastern Arabian Sea**” reports on crustal and trace metal composition and concentration level in atmospheric aerosols over a coastal city located on Eastern Arabian Sea. This study highlights role of various factor (meteorology and emission sources) controlling the abundances of metals over a costal site in Eastern Arabian Sea. The contribution from various sources (anthropogenic vis-à-vis natural) has been also identified using enrichment factor analyses as well as Principle Component Analyses. This study have implications to the supply of micronutrients to coastal Arabian Sea which can significantly impact various surface ocean biogeochemical processes.

Assessment of crustal element and trace metal concentrations in atmospheric particulate matter over a coastal city in the Eastern Arabian Sea

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Supplementary material 1:

Meteorological parameters ambient temperature, relative humidity, wind speed and wind directions at the three sampling sites were obtained from AWS datasets from of Space Applications Centre, Ahmedabad.



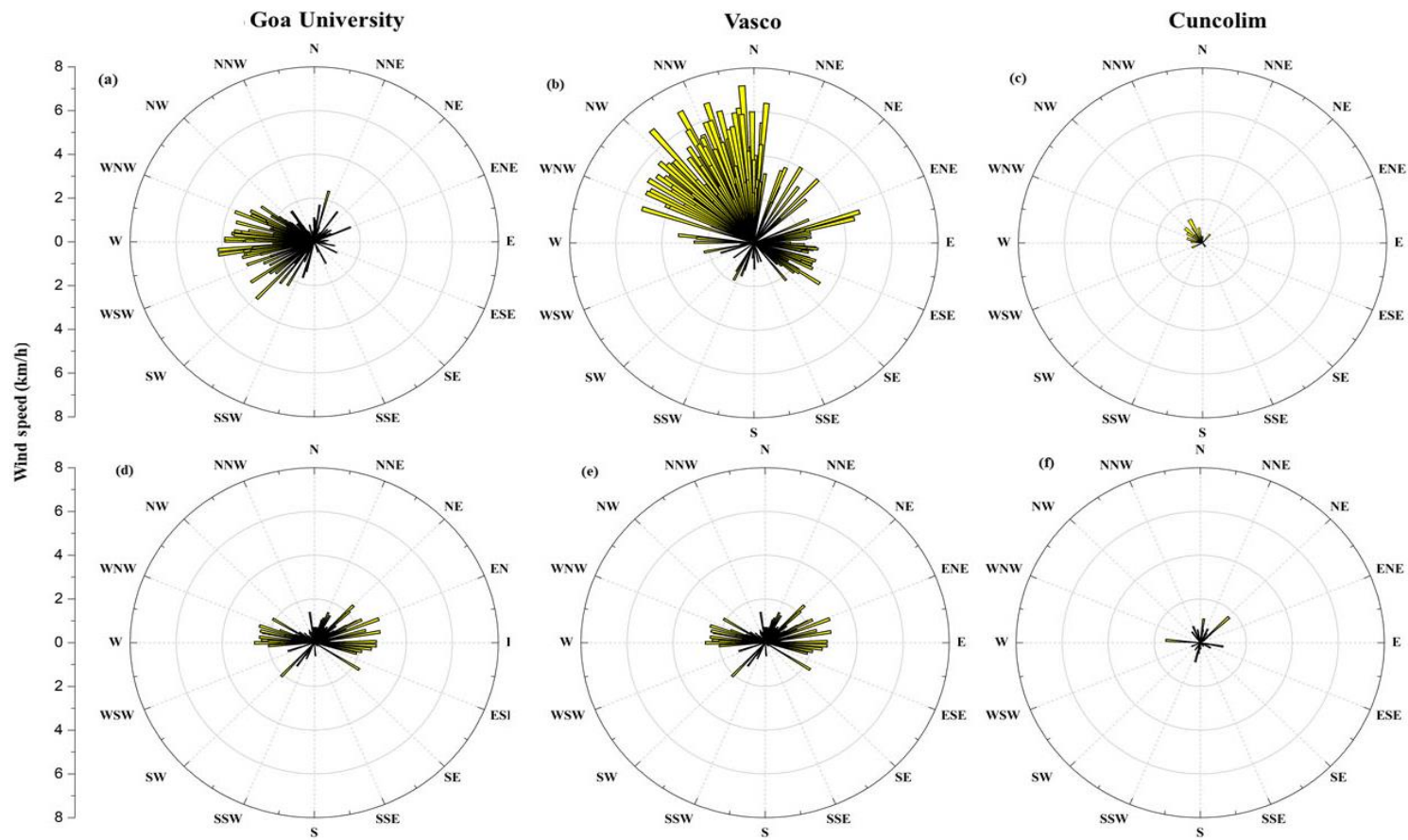


Fig. S1: Meteorological parameter (temperature, relative humidity, wind speed and wind direction) for sampling days are shown in below

Supplementary Material 2:

PM10 mass concentration (in $\mu\text{g m}^{-3}$) as well as concentration (in ng m^{-3}) of crustal elements (Al, Ca, Mg, K and Fe) and trace metals (Mn, Cr, Cu, Pb, Zn and Ni) in aerosols collected at three sites along with collection date are given below:

Goa University	PM₁₀($\mu\text{g m}^{-3}$)	Al	Ca	Mg	K	Fe	Mn	Cr	Cu	Pb	Zn	Ni
Sampling Day	ng m^{-3}											
Summer												
23-03-2015	22.3	220	124	509	1055	308	7.0	1.8	12.4	2.9	419	5.3
27-03-2015	50.1	120	171	297	1963	287	3.9	0.1	2.8	6.3	346	6.8
30-03-2015	38.9	340	67	402	1432	420	6.2	1.5	4.8	1.1	239	6.7
01-04-2015	68.3	740	193	260	2102	646	12.5	2.8	49.1	3.5	160	6.3
03-04-2015	22.7	200	82	401	2488	166	2.4	0.4	4.4	1.3	148	7.5
08-04-2015	71.4	2340	328	528	611	852	38.7	5.5	1.3	1.3	35	2.8
10-04-2015	75.0	1630	357	271	1113	432	54.9	7.7	6.6	28.2	30	0.8
12-04-2015	41.3	1300	212	287	2758	237	23.0	2.5	2.4	1.9	88	5.3
Winter												
01-12-2015	72.5	4412	112	841	1546	550	30.2	0.8	17.9	21.3	510	80.8
02-12-2015	145.2	5766	21	858	1567	562	14.2	1.1	5.7	33.1	552	29.0
03-12-2015	113.4	10730	228	923	831	1814	52.5	6.2	56.8	65.0	475	37.9
04-12-2015	106.5	10608	64	1220	1087	875	19.8	3.2	6.7	23.1	637	72.0
05-12-2015	123.3	6323	175	609	956	682	44.0	3.3	37.1	50.5	445	31.6
07-12-2015	36.0	7421	37	890	491	895	36.5	2.3	8.2	6.7	725	66.9
08-12-2015	93.9	489	101	610	710	721	32.7	1.3	10.4	24.8	669	65.7

Vasco	PM₁₀($\mu\text{g m}^{-3}$)	Al	Ca	Mg	K	Fe	Mn	Cr	Cu	Pb	Zn	Ni
Sampling Day	ng m^{-3}											
<i>Summer</i>												
13-04-2015	53.3	1810	19	273	2292	659	11.2	4.8	4.8	3.5	212	7.0
16-04-2015	109.0	100	115	278	453	570	10.2	1.1	3.7	9.7	811	6.3
19-04-2015	81.8	500	43	488	455	301	1.8	0.9	4.8	15.5	820	7.0
21-04-2015	21.3	1790	95	397	2488	294	1.5	0.4	4.6	2.5	854	6.2
23-04-2015	36.9	800	95	322	2182	91	1.6	3.0	4.8	13.8	466	7.0
26-04-2015	85.1	1260	92	159	3588	220	0.3	6.4	5.9	3.0	23	8.5
29-04-2015	43.1	5980	40	1121	975	209	2.3	3.5	6.2	5.8	124	8.6
02-04-2015	61.3	1610	27	190	773	267	0.4	0.1	6.3	5.3	506	7.0
04-05-2015	69.6	1420	10	231	4151	362	3.4	0.5	5.1	2.9	427	7.0
06-05-2015	62.1	2730	16	434	2392	151	1.6	3.0	5.7	2.8	144	6.8
<i>Winter</i>												
17-12-2015	134.0	4270	18.52	731	419	1118	23.2	2.3	23.5	32.0	883	34.1
19-12-2015	162.0	3064	82.53	528	1206	1046	32.3	0.9	19.8	25.3	712	111.1
21-12-2015	133.0	3126	74.47	814	1593	1395	30.3	1.4	21.1	35.5	591	42.9
24-12-2015	108.0	7184	20.03	1124	312	723	44.3	1.6	28.4	51.3	390	21.5

Cuncolim	PM₁₀($\mu\text{g m}^{-3}$)	Al	Ca	Mg	K	Fe	Mn	Cr	Cu	Pb	Zn	Ni
Sampling Day	ng m ⁻³											
Summer												
19-05-2015	47.0	1540	47	252	1479	112	39.4	1.4	5.1	15.4	218	9.4
20-05-2015	52.6	2641	205	581	3884	359	56.1	1.5	3.2	98.0	481	9.0
21-05-2015	42.2	4558	136	900	544	70	22.0	1.5	7.6	12.9	405	7.2
23-05-2015	56.0	8077	119	1034	536	265	24.8	1.6	5.1	46.6	290	9.5
24-05-2015	60.5	5022	82	818	302	275	19.8	1.8	4.2	16.2	296	9.6
25-05-2015	68.7	6862	100	880	885	423	185.0	0.5	3.3	80.2	78	9.2
26-05-2015	74.6	3031	130	379	1547	390	47.5	1.1	2.7	137.0	248	9.1
28-05-2015	84.0	4304	169	726	3084	921	32.1	3.4	12.1	28.0	83	4.9
30-05-2015	88.6	1840	60	524	186	574	14.3	0.4	1.0	8.6	208	5.2
02-06-2015	124.2	4846	208	755	1026	1272	28.9	1.5	12.9	32.7	294	5.2
Winter												
09-12-2015	155.0	4330	46	658	470	723	83.7	1.8	11.1	57.1	1410	64.4
11-12-2015	144.0	6760	30	698	1522	479	123.0	2.9	6.2	77.8	1200	48.0
13-12-2015	143.0	3553	33	709	1566	808	165.0	1.6	11.2	33.2	1280	59.4
14-12-2015	201.0	4391	36	925	1583	674	154.0	5.2	12.0	62.9	1820	60.6

Supplementary Material 3:

Computation of PCA was done by the following steps:

a. Data acquisition

Seasonal data for crustal and trace metals were organised for three different sampling sites for the PCA analysis.

b. Normalisation of data

However, because of the different scale among individual metal concentrations, all the data were normalized by subtracting their mean and then dividing by their standard deviation.

c. Calculation of covariance matrix

The covariance matrix is used to measure how much the dimensions vary from the mean with respect to each other. The covariance of two random variables is their tendency to vary together as:

$\text{cov}(X,Y) = E [E[X] - X] \cdot E [E [Y] - Y]$ where $E [X]$ & $[Y]$ denotes the expected value of X & Y respectively.

In the covariance matrix, the exact value is not as important as its sign (i.e. positive or negative). If the value is positive, it indicates that both dimensions i.e .X & Y increase. If the value is negative, then as one dimension increases, the other decreases. In the case, where the covariance is zero, the two dimensions are independent of each other.

d. Calculation of the eigenvectors and Eigen values of the covariance Matrix

From the covariance matrix, the eigenvectors and eigen values are calculated thereafter the eigenvalues are sorted in descending order which gives us the components in order of significance. The eigenvector associated with the largest eigen values has the same direction as the first principal components. The eigenvector associated with the 2nd largest eigen values determines the direction of the 2nd principal components. The eigenvector with the highest eigenvalue is the most dominant principle component of the dataset (PC1). Further for the interpreting of the data the method of Kaiser Criterion (Kaiser,1960) is followed which will retain only those factors having a eigen value >1 has been used for further interpretation. Factor loadings >0.71 are typically regard as strong and <0.32 weak loadings (Nowak,1998).