

Metal Signature of Atmospheric Aerosol from Kochi, the Queen of Arabian Sea, Kerala, India

Gayathree Devi, P.K., Akhil, P.S. and Sujatha, C.H.*

Department of Chemical Oceanography, School of Marine Sciences, Cochin
University of Science and Technology, Cochin-16, Kerala, INDIA

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ABSTRACT: The present research article highlights the metal (Cd, Cu, Pb, Zn and Fe) distribution pattern in the RSPM generated in different hot spot sites located at Kochi, the Queen of Arabian Sea. These sampling sites are categorized under three different zones as estuarine, riverine, and coastal. Two sampling phases are selected in order to check the consistency in pollution trend after a two year gap and are described in Phase I and Phase II, respectively. Metals are noticed to be intensely concentrated in the post monsoon months in both phases. Among the metals, Fe is revealed as the prominent metal at the estuarine sites. Estuarine and riverine zone expresses the overall enrichment pattern with slight difference at coastal regime in phase I. In phase II, insignificant metal load with irregular pattern is observed. Source apportionment study reveals that major sources of metals are from automobile exhausts and the estuarine zone is entangled with 45.9%.

Keywords: aerosol, atmospheric pollution, Cochin, metals.

INTRODUCTION

Aerosol chemistry, the forerunner in the atmospheric chemistry discipline is a highly relevant subject in the current era with wide discussion on chemical toxicology. Atmospheric trace/ heavy metals have augmented exponentially due to human activities inclusive of crustal and anthropogenic source since the 19th century (Chen *et al.*, 2008). Nowadays, metal toxicity with respect to aerosol has become a severe threat for the comfortable existence of biota and sustainability in the ecosystem. The atmosphere has now been recognized as a prominent source of both metals and nutrients to the ocean (Spokes

et al., 1994) and terrestrial surfaces. Human intervention involving relic fuel (Nriagu, 1996; Wang, 2004; Fomba *et al.*, 2013) combustion and industrial processes prefaces into secondary aerosols sustaining in the fine particle fraction increasing the pollution scenario in the atmosphere. The incorporation to repositories such as ice nuclei and cloud condensation nuclei, in addition to RSPM, provide significant source of these metals in stored condition similar to the accumulation of metals in sediments.

The two major types of sources releasing particulates into the atmosphere include natural and anthropogenic emission mode. Natural sources result from a variety of processes acting on crustal minerals, including volcanism, erosion, and surface

* Corresponding Author Email: drchsujatha@yahoo.co.in,
Phone: +484 2382131, Fax: +91-484-2374164

winds, affiliated to forest fires and the oceans (Eleftheriadis and Colbeck, 2001; Al-Momani *et al.*, 2005; Kulkarni *et al.*, 2007; Rastogi and Sarin, 2009; Fomba *et al.*, 2013). Anthropogenic sources, especially high temperature, include tire and rubber abrasion (Pacyna *et al.*, 1986; Duce and Tindale, 1991), sea salt generation, automobile exhausts, and urban developmental activities including municipal waste incineration.

Variable quantities of toxic trace metals such as Pb, Fe, Cu, Zn, Ni, and Cd pollute the environment including the atmosphere. Prolonged excessive inputs of such elements incorporated to ultrafine particulates may impose acute and chronic adverse health effects (Van *et al.*, 1996; Fang *et al.*, 2000; Ye *et al.*, 2003; Berman and Snyder, 2010) and enhance burden on ecosystems through various biogeochemical cycles (Jickells, 1995; Van *et al.*, 1996; Fang *et al.*, 2000; Cong *et al.*, 2010) and deterioration effects on materials. Major organs such as heart, lung, liver, nervous system are severely affected by toxic metals produced via anthropogenic activities preventing them from normal functioning. The health effects of these acidic or lethal species (Berman and Snyder, 2010) mostly include respiratory diseases, lung cancer, heart diseases, and damage to other organs (Yasutake and Hirayama, 1997; Prieditis and Adamson, 2002; Magas *et al.*, 2007; Wild *et al.*, 2009) via accumulation in animal tissues (Gajghate *et al.*, 2012) termed as bio-magnifications. Mineral dust-derived trace elements, like Fe, may act as micro nutrients controlling the phytoplankton growth of the ocean (Morel and Price, 2003; Jickells *et al.*, 2005). Well-known essential trace metals such as Zn and Fe alter the biochemistry in human body if they exceed the permissible limit.

Injection of toxic trace element can cause regional and local effects which have potential and far reaching effects propagating through generation to

generation. Trace elements can undergo long-range transport through the atmosphere and deposit in remote regions far away from populated areas (Kyllonen *et al.*, 2009), near urban centers (Sabin *et al.*, 2006), and significantly modify seawater chemistry influencing oceanic ecosystems (Duce and Tindale, 1991; Jickells, 1995; Guerzoni *et al.*, 1999) and are spread over larger areas (Fomba *et al.*, 2013). It is known that elements such as Fe, Mn, Cu, Cd, and Zn are vital for marine productivity (Morel and Price, 2003). In addition to dry deposition, wet scavenging preface to augmentation in concentration in the terrestrial and aquatic surface (Scudlark *et al.*, 1994; Wu *et al.*, 1994; Shimamura *et al.*, 2006). The prominent mechanisms which control the dissolution of metals are the photochemical and organic complexation processes (Spokes *et al.*, 1994).

Researchers, such as Yaaqub *et al.* (1991), (enrichment factor calculation), Chester *et al.* (1994), (solid state speciation), Heimbürger *et al.* (2010), and Chowdhury *et al.* (2015a, 2015b, 2016), (Air- noise pollution, climatic and anthropogenic changes) assessed the ambient air quality status in India. Srinivas *et al.* (2011) reported a comparative study on marine aerosol (PM_{2.5}, PM₁₀) in the region of Bay of Bengal during the period 2006-2009 and observed that Al, Ca, Mg, Fe, and Mn exist in the coarse mode associated with mineral dust and high enrichment factors of trace metals recognized in the marine atmospheric boundary layer of South Bay of Bengal. A spatiotemporal analysis in aerosol trace metals in Eastern Mediterranean Basin was conducted by Koçak *et al.* (2004) and observed enhanced concentrations of Al, Fe, and Mn at southerly sampling stations. From the literature survey, an idea was generated to characterize these trace contaminants in the coastal scenario of Kochi situated on the bank of Arabian Sea, which would derive basic data set

providing preliminary information in the field of atmospheric metal contamination leading to environmental impact assessment in this region.

MATERIALS AND METHODS

Description of Study Area

Kochi is the important industrial and coastal capital city of Kerala State located in the southwest part of India, bounded between 9°56' and 10°10' N, and 76°10' and 76°25' E and this industrial agglomeration possessing about thousands of industrial units flanked by the Arabian sea on the west and crisscrossed by backwaters, of which the most prominent is Vembanad Lake. Many

portions of the region are water logged for most times of the year. The sampling sites are marked in the site map (Fig. 1).

The scan of city shows that there is significant increase in the anthropogenic input over the years due to recent ongoing developmental activities in order to make the city a versatile one. The sampling site specifications chosen are ample enough to provide a complete appropriation about the declining air quality. It can be proclaimed that this study is the first attempt to get the baseline data on aerosol particulate matter in Kochi city and its counterparts prioritizing the dual character such as marine and land influence.

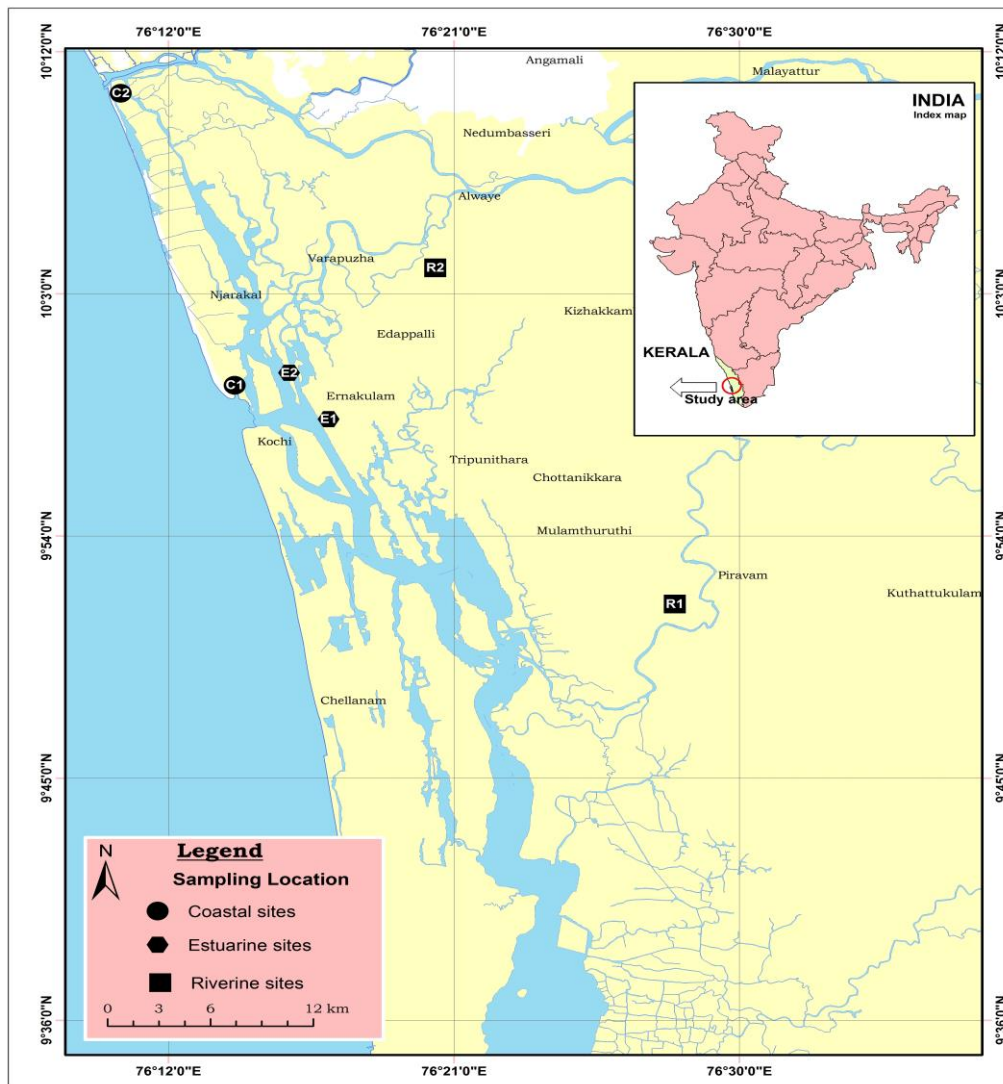


Fig. 1. Map showing the sampling locations

Description of Sampling Location

The selected sites are in the vicinity of estuarine, riverine, and coastal areas of Kochi City on account of their participation from these aquatic sources prone to spread over the troposphere which could also be counteract. Both E1 (9°95' N, 76°29' E) and E2 (9°98', 76°26' E) represent **estuarine sites**. It is in the curbside situated in the metropolitan city. Diesel fueled terrestrial and water traffic systems export and harbor related activities are intensified in these scenarios. R1 (9°33' N, 76°35' E) and R2 (10°05' N, 76°34' E) are two **riverine sites**. At R1, automobiles are the major source for both particulate and trace gases. Fossil fuel burning and construction work liberate pollutants and add to the already existing polluted atmosphere. The fresh water source may release reduced nitrogen species and sulphur compounds to the environment. R2 is an industrially cluttered region augmented with industrial emissions.

Insidious trace metals originated from industries elevated the pollution level to a great extent. Biomass burning and vehicular emissions concurrently engender to a slight extend and confound to the deterioration of the environment. The two **coastal sites** C1 (9°58' N, 76°14' E) and C2 (10°15' N, 76°17' E) make the difference in the sea salt contamination which is boomed in their pollutant discharge. These pollution sources are related to fisheries and retting of coconut husk.

Sampling Equipment

A manual air monitoring HVS APM-415 (Envirotech) was used for collecting ambient surface aerosols incorporated with PM₁₀. Ambient air is drawn into the sampler through a cyclonic separator to create a cyclonic flow and small dust particles less than 10 micron stokes diameter (PM₁₀ or RSPM) were assessed along with the air drawn through the filter and collected on it. PM₁₀ in the ambient air was collected on pre-calibrated (*i.e.*

equilibrated by placing it before and after for 24 hours in a desiccators) nuclepore filter paper and it is monitored at a flow rate of 1.1-1.4 m³/min by means of U-tube manometer and a pilot tube at the blower exhaust. A heavy duty blower with continuous rating 24 hrs maximum with proper carbon brush maintenance and operating on 230 V AC and 50 Hz was fitted with the hopper assembly.

The sampling duration was three hours from each site. An average of three sets designated as one sample from each site was performed for the estimation. In this investigation, two sampling phases are included in order to check the consistency in pollution trend after a two year gap. The first phase encompasses four months viz May 2010 (pre-monsoon), January 2011 (post-monsoon), May 2011 (pre-monsoon), and November 2011 (post-monsoon), whereas the second phase was selected to include three sampling months: October 2013, January 2014, and March 2014 comprising three sites which are screened out as one estuarine, coastal, and riverine site. Most of the sampling was done around noontime when the atmospheric boundary layer was well developed. The differences in filter mass is the concentration of RSPM and is expressed in µg/m³ and are tabulated in Table 1 and 2.

Metals incorporated on PM₁₀ particulates were characterized and metal quantified are cadmium, copper, lead, zinc, and iron by adopting the acid digestion method. One fourth of the filter paper 8"x10" diameter is digested with di acid mixture (5:1 HNO₃-HClO₄) (Loring and Rantala, 1992). The content was filtered through (pore size, 0.45 µm; diameter, 25 mm) and final volume was made up to 25 ml by double distilled water (Milli Q) and final trace metal concentration was determined by AAS (Perkin Elmer 3110).

Table 1. Distribution of respirable suspended particulate matter phase I ($\mu\text{g}/\text{m}^3$)

SITES	May-2010	Jan-2011	May-2011	Nov-2011
E1	33.3	4344	2794	283.3
E2	48.8	594.4	1233.4	166.6
R1	15	389.4	5050.5	66.6
R2	116.6	1555	2227	611
C1	1977	4283	5511	388.8
C2	140	122	1694	88.8

Table 2. Distribution of respirable suspended particulate matter phase II ($\mu\text{g}/\text{m}^3$)

SITES	Oct-2013	Jan-2014	Mar-2014
E1	0.047	0.03	0.02
R2	0.06	0.26	0.58
C1	1.12	0.23	0.36

RESULTS AND DISCUSSION

Spatiotemporal variability of toxic metals in Phase I and Phase II has been carried out and are included in subsequent portions. Analytical data of spatiotemporal analysis

of metals has been tabulated in Table 3 and Table 4 in Phase I and Phase II, respectively. The spatial and temporal orientation pattern of metals such as Cd, Cu, Pb, Zn, and Fe are illustrated below.

Table 3. Distribution pattern of metals in phase I ($\mu\text{g}/\text{m}^3$)

Sites	Trace Metal	May-10	Jan-11	May-11	Nov-11
E1	Cd	BDL	BDL	BDL	0.608
	Fe	1.92	62.12	16.492	8.216
	Pb	0.12	0.4	0.14	3.48
	Zn	0.24	17.44	3.3	1.64
	Cu	0.92	1.64	0.14	0.384
E2	Cd	BDL	BDL	BDL	0.14
	Fe	3.28	96.32	24.492	17.36
	Pb	0.024	BDL	0.688	4
	Zn	0.92	15.8	2	3.864
	Cu	0.23	0.2	0.688	0.708
R1	Cd	BDL	BDL	BDL	0.168
	Fe	2.36	14.68	11.4	13.272
	Pb	0.12	BDL	1.08	3.8
	Zn	1.52	10.32	0.8	2.312
	Cu	0.96	0.24	0.424	0.552
R2	Cd	BDL	BDL	BDL	0.108
	Fe	1.52	103.84	32.72	14.96
	Pb	0.12	BDL	0.4	3.44
	Zn	0.48	23.16	22.9	3.144
	Cu	1.52	0.2	0.416	0.544
C1	Cd	BDL	BDL	BDL	0.108
	Fe	3.36	11.16	6.72	22
	Pb	0.12	BDL	0.12	3.28
	Zn	0.36	23	7.00	1.47
	Cu	0.64	0.24	0.096	0.288
C2	Cd	BDL	BDL	BDL	0.108
	Fe	0.36	12.12	11.48	13.116
	Pb	0.12	BDL	0.8	3.4
	Zn	0.36	12.12	25.4	3.4
	Cu	0.72	0.36	0.228	0.484

Table 4. Distribution pattern of metals in phase II ($\mu\text{g}/\text{m}^3$)

Sites	Trace Metals	13-Oct	14-Jan	14-Mar
E1	Cd	0.23×10^{-3}	BDL	BDL
	Fe	0.39×10^{-3}	0.204×10^{-3}	0.8×10^{-3}
	Pb	0.03×10^{-3}	BDL	BDL
	Zn	0.4×10^{-3}	2.1×10^{-3}	0.03×10^{-3}
	Cu	0.3×10^{-3}	0.11×10^{-3}	0.01×10^{-3}
R2	Cd	0.07×10^{-3}	BDL	BDL
	Fe	0.42×10^{-3}	0.5×10^{-3}	0.1×10^{-3}
	Pb	0.38×10^{-3}	BDL	BDL
	Zn	0.034×10^{-3}	0.026×10^{-3}	0.03×10^{-3}
	Cu	0.06×10^{-3}	0.02×10^{-3}	0.03×10^{-3}
C1	Cd	0.05×10^{-3}	BDL	BDL
	Fe	0.45×10^{-3}	0.55×10^{-3}	0.4×10^{-3}
	Pb	0.45×10^{-3}	BDL	BDL
	Zn	0.04×10^{-3}	0.02×10^{-3}	0.11×10^{-3}
	Cu	0.07×10^{-3}	0.02×10^{-3}	0.5×10^{-3}

Distribution of Cadmium

The variability in seasonal and spatial distribution pattern of Cd follows the trend as shown below. The six sites of three different sets represent the following trend in Cd distribution path. The experimental data shows that only in the post-monsoon month, November 2011, Cd showed detectable concentration of ($0.608 \mu\text{g}/\text{m}^3$) at the estuarine point, E1. In spite of the extensive utilization of this metal in industries, in paint application, and battery, severely contributing to the pollution load, only rare samples inferred detectable load. It is understood from the analytical data that in all samples, slightly enriched concentration of Cd, in the same post-monsoon month, was detected. The increase in load observed is attributable to the resuspension of particulate Cd dispersed in the ambient atmosphere. It may also be due to primary emission from painting in harbor related works and automobile tires. The data obtained shows that the loading ranges from BDL- $0.608 \mu\text{g}/\text{m}^3$. The maximum concentrations in the post-monsoon period can be credited to the resuspension, coagulation, and potential input from battery related works. In this study, majority of samples show below detectable limit values indicative of absence of Cd pollution.

E2, the estuarine point, exhibits the same temporal trend as at E1 for Cd. Both these sites are situated on the bank of Cochin estuary. The sites E1 and E2 are collectively noted as estuarine zone. This zone has a common source comprising automobiles and other anthropogenic activities including small scale industries. Extensive biogenic emission from the Cochin estuary is a significant pollutant source in this estuarine zone and the release of this toxic element to a small extend likely exist. An industrial hub releasing enormous toxic emissions including this metal aggravates the metal pollution. Construction related work injecting this element via crustal remnants was progressing at that time in this zone. Besides, the refuse burning causes additive effect on pollution status.

The data in this research work reflects that majority of samples amount to below detectable limit (BDL) values similar to the estuarine site, E1, which is indicative of absence of Cd pollution. The significant rise in concentration to $0.14 \mu\text{g}/\text{m}^3$ observed in the post-monsoon period, November 2011, can likely be linked to the proximity to the harbor and launching of Cd containing particulates from sources viz batteries and electrochemical industries.

Besides, a catalyst factory dealing with this metal is situated in the nearby area. The value is observed to be varying from BDL in the months May 2010, January 2011, and May 2011 to $0.14 \mu\text{gm}^{-3}$ in the month November 2011. The two sites, E1 and E2, experience the same temporal pattern which reveals that their fate in the atmosphere is controlled by identical dispersion mechanism and may have the same origination. The spatial enhancement order with respect to Cd is $E1 > E2$.

R1 is a rural site showing similarity with estuarine zone (E1 and E2) in temporal alignment pattern. This site is weakly laden with anthropogenic emissions compared to other stations. The slightly highest value observed is $0.168 \mu\text{gm}^{-3}$ in late post-monsoon period, November 2011, and is more affected than the estuarine zone with respect to Cd pollution. Elevation in concentration of this highly toxic and anthropogenic trace metal (Cd) in the month November 2011 can be endorsed to the change in the prevailing air flow rate, mostly easterlies.

Reloading by the air currents and the high stability as a result of inversion endorse to the significant values so obtained and indicates that rain fall has less effect in the concentration in the present analysis. It is due to the incorporation of this element in the ultrafine particulate matter in the atmosphere with considerably high relative humidity. Though the pollutant dispersion depends on the atmospheric conditions such as wind pattern, temperature, rainfall, etc., in the present investigation, it is inferred that the temporal enhancement is independent of rain fall. The concentration varies from BDL- $0.168 \mu\text{gm}^{-3}$. The enhanced value ($0.168 \mu\text{gm}^{-3}$) is likely attributable to the advection of windborne air masses loaded with Cd particulates from the industrial hub (R2), which accumulates the trace metal content and aggravate the pollution load.

R2, the industrial spot, depicts the

elevated mass in the month November 2011 ($0.108 \mu\text{gm}^{-3}$) similar to the earlier stated riverine site, R1. This can be credited to the recharging of the point by specific industrial pollutants by wind. The industry (Minerals and Metals Limited) in this industrial sector is likely provided with nonferrous smelters and the emission from flue gases generated by household waste incineration plant and is possibly the attribute for enhancement in Cd concentration. Point sources such as rare earth and manure unit inject metal species and acidic gases such as SO_2 into the ambient environment. These aggravate the pollutant level in the comparatively blank atmosphere and adversely affect the biotic species. The other three samples depict below detectable mass similar to other sites as discussed earlier. The predominant reactions such as photochemical changes and complexation with organic ligands (Spokes *et al.*, 1994) result in a quantum variation in these trace species. The frequent washing of the pollutant by high momentum precipitation sweeps away the coarse particulates formed as a result of physiochemical transformation entrapping this metal in cloud condensation nuclei and brings the concentration to the undetectable level.

The values range from BDL- $0.108 \mu\text{gm}^{-3}$. In this sector, refuse burning may elevate the concentration level of the metals, especially Cd. The spatial enhancement order with respect to Cd in the riverine zone follows the order $R1 > R2$ and indicates extensive removal of the metal from this industrial site which is a prominent pollutant charger in the study area.

Both the coastal zones, C1 and C2, show similarity in concentration as that recorded earlier at R2. In these sites, the prevailing source is coastal aerosols which is highly affected by continental aerosol as observed from the data. The data obtained in the present study showed that the

improved pollutant level at these coastal sites, C1 and C2, similar to R2, the riverine site, is $0.108 \mu\text{gm}^{-3}$ in the month November 2011. Majority of the samples at C1 show below detectable limit as observed at other sites. The enhanced concentration can be ascribed to the introduction of pollutant from secondary pollutant formation reactions (long term process) such as condensation of volatile species and also as a result of coagulation and neutralization at acidic pH. The pyrogenic release of metal, from water transport systems, in the ultrafine mode can intensify the pollution load. The concentration observed ranges from BDL- $0.108 \mu\text{gm}^{-3}$. The data obtained for Cd metal shows that the interring rainfall has no significant effect in the distribution pattern. The industrial site (R2) is polluted to a lower extend than the rural riverine site (R1) which gives an insight on transport of Cd containing particulate to distant locations.

The coastal site C2, impacted with reduced weight of traffic exhausts, is experienced with enhanced load of Cd owing to the combustion of fossil fuels, nonferrous metal smelters (installed in industries in a nearby industrial hub) and also from waste incineration unit.

Earlier reports pointed out that pronounced transformation mechanisms associated to trace metals are photochemical and complexation with organic ligands (Spokes *et al.*, 1994). Chakraborty and Gupta (2009) reported that the seasonal variability of Cd from monsoon to post-monsoon concentrations exists, in a study conducted at Kanpur, which reveals that rain has no effect (as also noted in the present study). From the current data it is also recognized that the two sites in the coastal zone are equally enhanced in Cd level. Cd exhibits the same seasonal trend at all sites in the sampling period, November 2011, the post-monsoon month.

Distribution of Copper

The estuarine spot, E1, shows the post-monsoon (January 2011) increasing value ($1.64 \mu\text{gm}^{-3}$) for Cu. The values vary from minimum ($0.14 \mu\text{gm}^{-3}$) to a maximum ($1.64 \mu\text{gm}^{-3}$). Least mass at this estuarine point is $0.14 \mu\text{gm}^{-3}$ in the month May 2011. Haritash and Kaushik (2007) reported a mass range in a rural area Hisar City (BDL - 18.86 mg/g) of Cu in respirable dust particle. The Cu profile exhibited in the month January 2011 the maximum concentration of $1.64 \mu\text{gm}^{-3}$ and in the month May 2011 the low concentration ($0.92 \mu\text{gm}^{-3}$) is noticed at this estuarine region, E1. The irregularity in temporal distribution can be associated to the unevenness in pollution sources and input-output temporal change in mechanisms as a result of variability in atmospheric conditions such as inversion. A similarity with Cd (November 2011) enhancement pattern at this site is noticed for Cu which falls in the post-monsoon month, January 2011.

Estuarine site, E2, reveals the maximum concentration of $0.708 \mu\text{gm}^{-3}$ in the post-monsoon month, November 2011. The low concentration at this point is $0.2 \mu\text{gm}^{-3}$ in the post-monsoon month, January 2011. E1 and E2 are reversely related in concentration pattern where post-monsoon enhancement is noted at E2. The unlikeness in distribution pattern at the two sites in the estuarine zone could possibly be linked to the difference in wind pattern and is supported by the earlier study of Chakraborty and Gupta (2009). The maximum concentration is due to import by air parcel in the post-monsoon month, November 2011, and the wet removal in the month January 2011. The intersite spatial order is $E1 > E2$ and can be associated to the nearest to the urban area for Cu emissions solely from break wear of road vehicles and the wear of trolley wires from railways in the estuarine zone and transference of particulate matter

containing Cu from industrial sources situated nearby.

The site with both rural and riverine characters, R1, shows similar behavior to E2 which enlists the maximum concentration of Cu as $0.96 \mu\text{gm}^{-3}$ in the month May 2010 and the decline in load to $0.24 \mu\text{gm}^{-3}$ in the month January 2011. The elevation may be associated to the transference of the particulate matter from industrial plant to this point. Further, inhibited dispersion due to prevailing inversion can also be added to the above fact. The depression in the month January 2011 can be attributed to the dissolution of pyrogenically originated metal by complexation with organic ligands and transformation to the coarse mode. Photochemical changes are seemingly relevant in this context since there are very few close sources and most significant contribution is probably due to long range transport and contributes to the enhancement in this site which lacks a distinguishable source. Moreover, pyrogenic emission in this rural area cannot be neglected similar to all the sampling points in the study area. Decrease from pre- to post-monsoon month and the subsequent increase sharply till post-monsoon month except E1 is observed in the present study. The concentration range noticed from the data indicates the concentration configuration as $0.24 \mu\text{gm}^{-3}$ (January 2011) to $0.96 \mu\text{gm}^{-3}$ (May 2010) at the rural station, R1.

Temporal heterogeneity in Cu at the industrial point R2 is depicted below. The industrial site R2, with prominent industrial source (Minerals and Metals limited) for Cu, can be positioned thirdly with respect to Cu enrichment. The disposal of particulates, via long range transportation, is one of the attributes for the reduction in load at this site. The loading ranges from $0.2 \mu\text{gm}^{-3}$ in the month January 2011 to $1.52 \mu\text{gm}^{-3}$ in the month May 2010. The same temporal mode is observed for Cu at R1 and R2 which can be linked to the occurrence of

the same type of sources and atmospheric dispersion mechanisms. The spatial enhancement order with respect to Cu is $R2 > R1$. This trend is the reversal of spatial trend with respect to Cd.

The allotment of Cu, at the coastal site C1 can be described as follows. May 2011 ($0.096 \mu\text{gm}^{-3}$) depicts the lowest flux in the current study. The highest influx noticed is in the month May 2010 i.e. $0.64 \mu\text{gm}^{-3}$. This site, which lacks a close source, shows similarity as that of sites E1, R1, and R2.

The coastal site C2 behaves in the same pattern as C1 but shows heterogeneity in concentration. A minimum of $0.228 \mu\text{gm}^{-3}$ in the month May 2011 and utmost loading of $0.72 \mu\text{gm}^{-3}$ in the month May 2010 is observed in this coastal regime. Long-range transport and coastal activities and release of this metal from water bodies due to the remineralization by microorganisms contribute to the endorsement. The coastal site is abundantly polluted with sea salt and complexing with organic particulate in alkaline condition can also intensify the pollution status. The spatial enhancement order with respect to Cu is $C2 > C1$. C1 and C2 show identity in temporal enhancement and decline.

Except for E1 and E2, all the sites show the same temporal enrichment in Cu distribution. At E1, in the month January 2011 and E2 in the month November 2011 a maximum is noticed. It is clear from the data that coastal zone (C1 and C2) demonstrate same sequential trend with elevated loading in the month May 2010 and decline in loading in the month May 2011 (E1). Similar seasonal enhancement was observed by Haritash and Kaushik (2007) in a study on RSPM and endorsed the same to the low effect of precipitation and identified more concentration in residential area than commercial.

In the present study, the spatial allocation trend for Cu is estuarine zone, ($E1 > E2$) > riverine zone, ($R2 > R1$) >

coastal zone ($C2 > C1$) and the temporal trend can be expressed as R1, R2, C1, and C2 exhibits enrichment in the month May 2010, pre-monsoon period. In the present study, it is identified that E1 differs from all the other sites (January 2011). Despite industrial sources, lead fueled vehicles can confound to the yield. The analysis implies that estuarine zone is highly affected by metallic pollution (Cd and Cu) and is due to the spreading of this metal via wind to these areas from industrial source. The spatial enhancement order with respect to Cu follows: $E2 > E1 > R2 > R1 > C2 > C1$ with the inference that estuarine zone is the hot spot with respect to Cu giving signature in the month May 2010.

Distribution of Lead

The station on the bank of Cochin Estuary, E1, with immense automobile and marine activity in addition to extensive urban developmental activities, indicates the variation in monthly concentration from $0.12 \mu\text{gm}^{-3}$ in the month May 2010 to $3.48 \mu\text{gm}^{-3}$ in the month November 2011. From the results, it is clear that these pyrogenically derived metals may be more associated to ultra-fine particles (PM_{10}). The slightly elevated load $0.4 \mu\text{gm}^{-3}$ of January 2011 and $0.14 \mu\text{gm}^{-3}$ of May 2011 are observed in the present study. Apart from this, the variability in sources and conversion mechanisms such as gas to particle conversion can influence much to the pollution event. The use of leaded petrol in this point may be one of the reasons for Pb pollution. Complexation with organic ligands and other photochemical process endorses to the variation in pollution level in the pre-monsoon month May 2010.

E1 and E2 are stations in close proximity experiencing pollution from sources. The range reflected at this estuarine point is $0.024 \mu\text{gm}^{-3}$ in the month May 2010 and the highest ($4.00 \mu\text{gm}^{-3}$) in the month November 2011. Generally, the automobiles use unleaded petrol but rare occasions may be there of mixing kerosene

with petrol. Besides, the use of vehicles, with damaged functionalities and emanation of particulates incorporating Pb to the surroundings due to wear and tear can exaggerate the pollution intensity. The spatial enhancement order with respect to Pb recognized from the current study is $E2 > E1$.

R1, the rural spot, denotes the heterogeneity in spatial and seasonal trend in Pb as illustrated below. The major source for this metal is automobile releases. This site, lacking any industrial sources, is experiencing industrial emissions from the distant industrial hub. Similarity with other sites in pyrogenic release is also possible. E2 and R1 exhibits identical temporal and concentration enhancement with respect to Pb. The concentration goes below detectable limit in the month January 2011 and reaches a maximum of $3.8 \mu\text{gm}^{-3}$ in the month November 2011. The reflected trend is the resultant of road, air, and water transportation, import from distant places, reloading of particulates, and variations in atmospheric condition which result in cumulative enhancement. Slight contributions from automobiles also add to the elevated concentration. In the month November 2011, maximum concentration noted is $3.8 \mu\text{gm}^{-3}$. As already mentioned, the unloading of particulate laden with Pb from the industrial spot via air circulation and fossil fuel burning possibly endorse to the enrichment.

R2, the industrial hub, releasing abundant toxic chemicals in the form of particulates, effluents, and vapors, indicates the temporal configuration with the lower limit in concentration (BDL) in the month January 2011 and an upper limit of $3.44 \mu\text{gm}^{-3}$ in the month November 2011. The temporal trend shown by the estuarine zone and the riverine zone including R2 is similar. The spatial enhancement order with respect to Pb is $R1 > R2$ which is identical to Cd trend

whereas Cu enhancement order is reversely related at this site.

From the results, the time series concentration enhancement in the coastal zone follows the pattern as: C1, the coastal site, lacking prominent source of Pb depicts the profile as BDL- $3.28 \mu\text{g m}^{-3}$. Insufficiency in mass is reflected in the post-monsoon month January 2011 and enhanced concentration is noticed in the month November 2011 experiencing moderate rain (3 cm). The data shows that coastal influence can cause a slight contribution in this site in addition to sparse vehicular exhausts. The elevated load in the month November 2011 is possibly due to inhibited dispersion and points to lack of influence on wet removal mechanism in pollution load aroused as a result of incorporation into ultrafine particulates.

At the second coastal site, C2, the values configure a variance in concentration from BDL- $3.4 \mu\text{g m}^{-3}$. Similarity in magnitude of Pb concentration at the two coastal sites is noticed and can be linked to the influence of same source and meteorology on pollutant dispersion. In the month January 2011, the value is below detectable limit and shows similarity in concentration with estuarine zone and riverine zone including industrial site R1, R2, and C1 in this respect. In the month November 2011, it rises to the concentration maximum of $3.4 \mu\text{g m}^{-3}$ and exhibits almost the same degree of temporal variation. The spatial heterogeneity in Pb can be expressed as estuarine zone, E2 > riverine zone, R1 > estuarine zone, E1 > riverine zone, R2 > coastal zone, (C2 > C1). A clear trend in seasonal discrepancy is engendered with respect to the Pb concentration.

Haritash and Kaushik (2007), in a study on aerosols in Haryana, noticed higher concentration of Pb in commercial area and ascribed it to continuous use of leaded petrol. A maximum in the concentration, in the month May 2010 and a considerably

high concentration in the post-monsoon month November 2011 are exhibited by most of the metals. The seasonal decline in the month May 2010 may be associated to diminished emissions from vehicular transport and is discarded to distant places via hot air current.

As mentioned earlier, Koçak *et al.* (2004) identifies a decadal decline in Pb concentration which amounts to 40% and ascribes it to reduction in automobile exhaust. Their study in coastal area showed that no change in concentration was observed for Pb and Cd as these are associated to fine aerosol particulates directly injected into the atmosphere via high temperature process and are less efficiently scavenged compared to crustal originated elements and are less likely to exhibit winter-summer seasonal trend. Nair *et al.* (2006), in a study in Arabian Sea Coast and inland location, recorded a range in concentration of Pb, BDL- $0.06 \mu\text{g m}^{-3}$ in the Biosphere-Geosphere expedition and ascribed the source as fossil fuel and identified enhanced concentration of Pb at inland locations. Except for E1, the minimum value at all sites is in the post-monsoon month January 2011 with respect to Pb.

Estuarine zone exhibits sequential enhancement in the month November 2011. But in the present study, post-monsoon enhancement is likely endorsed to the association of the metals to ultrafine particulates. Chester *et al.* (2000) noticed a similar enhancement in Zn and Pb in a coastal area in United Kingdom mainland in the year 1998, whereas, in this study, enhancement is noticed in estuarine zone with respect to Pb and coastal area with respect to Zn. Chester *et al.* (2000) reported a concentration of Pb of 50 ng/m^3 in a study conducted in coastal area in UK mainland in the year 1998 and found that Ni, Cr, Cu, Zn, and Pb have been enriched at all the sites. In this study, the estuarine zone is emerged as the most polluted center. The average concentration range of

Pb follows the order: R1 > E2 > E1 > R2 > C2 > C1.

Distribution of Zinc

E1, the estuarine site, experiences vehicular emissions and also refuse burning emissions and shows the following profile for Zn. It is loaded with Zn particulates in the range 0.24-17.44 μgm^{-3} (Table 3). A bare minimum is noticed in the month May 2010 and slightly high in the month January 2011. There is a possibility of Zn particle emission from catalyst manufacturing unit which is transported to this region in the post-monsoon period. An additional stability acquired owing to low degree of inversion, preventing the pollutant from dispersion. In the pre-monsoon month May 2010, effective transportation to secluded places can occur generating a stability condition. The elevation in mass at 17.44 μgm^{-3} in the month January 2011 gives clarity in the fact that the less effective dispersion pattern is aroused as a result of inversion condition and also showing the absence for the wet removal of Zn thinning out. The enhancement observed in the post-monsoon month January 2011 reflects that most of the load may be associated to fine particulates rather than coarse ones.

The second estuarine site, E2, shows the following distribution prototype with respect to Zn. At E2, the loading ranged from 0.92 μgm^{-3} in the month May 2010 to 15.8 μgm^{-3} in the month January 2011. E1 and E2 are close to each other and exhibit the same temporal enhancement. Here, the same climatic and source factors may be prevailing and hence exhibit the same distribution mode. This study reveals that rainfall has negligible effect on Zn concentration as cited by Chakraborty and Gupta (2009).

Fresh water zone, R1, similar to estuarine zone, exhibits the least mass of 0.80 μgm^{-3} in the month May 2011 and the highest concentration noticed is 10.32

μgm^{-3} in the month January 2011. In the summer month, May 2010, the value was 1.52 μgm^{-3} and 2.312 μgm^{-3} in the month January 2011. The import through wind from distant locations can be in large quantity and the impending emissions from batteries, welding, and painting can endorse to the concentration so obtained. Apart from that, the entrainment and condensation of vapors of Zn salts in addition to the contribution from road dust (Chakraborty and Gupta, 2009). As a cumulative effect of all these include for Zn loading in the month January 2011 (10.32 μgm^{-3}) is found as the maximum level. The least mass in the month May 2011 can be ascribed to the high momentum air circulation, which carries away the Zn containing particulates to outlying regions. The data in the present study give an insight that same temporal configuration is exhibited for Zn at the estuarine zone including E1 and E2.

At the industrial spot R2, same as for the all sites as known, this metal lacking natural source of Zn is fully contributed by anthropogenic source. R2 also shows similarity to R1 in temporal distribution indicating transference of Zn containing particulates to far-off places. The maximum concentration of 23.16 μgm^{-3} in the post-monsoon month January 2011 and the lowest mass of 0.48 μgm^{-3} in the month May 2010 is noticed. The enhanced mass obtained can be attributed to the cumulative effect of transportation from distant places, enhanced resuspension, coagulation and addition from budding sources. The effective accumulation as a consequence of inversion in the atmosphere can be operated in the month January 2011. Apart from the above fact, a catalyst unit, producing Zn, is in the vicinity of the sampling point. Hence, all the inferred results show to be above the detectable limit. Extensive and unplanned waste management practices viz refuse burning, land reclamation, and construction

related work can add up to the above mentioned cause. A study conducted by Gajghate *et al.* (2012) in Mumbai reported a range in concentration of Zn as 2.59-5.45 $\mu\text{g m}^{-3}$. They added that the major source of Pb and Zn are wood combustion, vehicular traffic, metal alloy industry, and dry deposition.

One of the concentrations at C1 shows the same magnitude in concentration of 23.0 $\mu\text{g m}^{-3}$ in the month January 2011 as that at R2. The industrial zone R2 is suffered from industrial emissions and the same source profile in addition to coastal emissions from the coastal site. This is the maximum loading at this site. The minimum concentration 0.36 $\mu\text{g m}^{-3}$ is in the month May 2010. The attribution for the above enhancement could be as follows. In the former case, accumulation of pollutant due to airborne transportation may be prominent and, in the latter case, dispersal mechanism may exceed the accumulative effect. As per the data, concentration of Zn is 0.36 $\mu\text{g m}^{-3}$ in the month May 2010 and 23 $\mu\text{g m}^{-3}$ in the month January 2011. The enhancement noticed can also be endorsed to the Zn released from a catalyst unit situated in close proximity brought to this point by wind. The same seasonal pattern as for E2, E1, R1, R2 is observed at this site, C1, which is situated in the Arabian Sea coast.

Data obtained from the present study indicates the following points with regard to heterogeneity in Zn distribution in the coastal zone. C2, the site with enhanced coastal activity, shows the following configuration pattern. The nominal concentration noticed is 0.36 $\mu\text{g m}^{-3}$ in the month May 2010 with the highest load of 25.4 $\mu\text{g m}^{-3}$ in the month May 2011. These highest masses noticed among all the sites may be associated to industrial influx as reported by Gajghate and Pipalatkhar (2012). The spatial enhancement order with respect to Zn is C2 > C1.

At all sites, except C2 (pre-monsoon May

2011 maximum), there is a post-monsoon (January 2011) maximum and a pre-monsoon minimum (May 2010). Estuarine zone R2 and coastal zones (C1 and C2) exhibits May 2010 minimum. R1, where January 2011 maximum and May 2011 minimum is observed, is the least polluted site with respect to Zn pollution and C2 (May 2011 maximum) is extensively polluted. Chester *et al.* (2000) reported a loading of 41 ng m^{-3} in a coastal area in UK Main land. Nair *et al.* (2006) observed an increase in mass fraction of Pb and Zn over inland and at close to forest regions whereas in the present study coastal zone exhibits higher concentration with respect to Zn. The spatial allocation trend of Zn is coastal zone, C2 > riverine zone, R2 > coastal zone, C1 > estuarine zone, (E2 > E1) > riverine zone, R1. A post-monsoon maximum for Cd and Zn at all sites is noted. Chester *et al.* (2000) noticed a similar enhancement in Zn and Pb in a coastal area in UK mainland in the year 1998.

Distribution of Iron

The distribution of Fe at the curbside and estuarine spot E1 exhibits the depiction as shown below. Data showed that the concentration of 1.92 $\mu\text{g m}^{-3}$ in the month May 2010 is the lowest concentration noticed and the highest value is 62.12 $\mu\text{g m}^{-3}$ in the month January 2011 at this estuary bound region, E1, in Phase I. Chakraborty and Gupta (2009) reported a seasonal variability at Kanpur as 378.04 ng/m^3 (monsoon) and 763.469 ng/m^3 (post monsoon) and revealed that wet deposition has no effect on Fe stratification and observed post-monsoon enhancement for Ca, Mg, and Fe, associated to coarse particulates especially for Fe as in the present study. Rusting of damaged water vessels can release Fe aerosols to the atmosphere in addition to refuse burning. The lowest mass observed is 1.92 $\mu\text{g m}^{-3}$ in the month May 2010 and can be associated to the effective dispersion and the unstable

condition aroused due to horizontal transport of pollutants from this point.

More than that, the industries (Minerals and Metals Limited) incorporating with metallic products release zinc particles and are situated nearby. Ye *et al.* (2003) reported a mass of Fe at Hainan Road and Tongji as 2.08 and 2.0 μgm^{-3} , respectively, as the mean percentage and observed seasonality in $\text{PM}_{2.5}$ particulate in a study conducted in the year 1999 and observed enhanced concentration during the period from March to May of 1999. From the current data, it is noticed in the present analysis that the temporal enhancement with respect to Fe falls in the post-monsoon month January 2011.

E2, the estuarine site, is still farther to the shipyard than E1. Ample sources such as rusting of damaged vessels and instruments and construction related works occur in the study area. As per the results, it is seen that the concentration varied from 3.28 μgm^{-3} in the month May 2010 to 96.32 μgm^{-3} in the month January 2011, the highest value at this site and can be ascribed to the cumulative addition from May 2010 to January 2011 which shows post-monsoon enhancement is independent of wet removal on Fe distribution. In addition to the industrial emanations, the increase in mass can be endorsed to the lithogenic materials and reclamation of debris which are in the ultrafine status which sustains in the atmosphere and unplanned waste management practices existing. The spatial enhancement order with respect to Fe is $\text{E2} > \text{E1}$.

R1, the rural site, is less loaded than the estuarine zone E1 and E2. The minimum load of 2.36 μgm^{-3} in the month May 2010 indicates a less polluted environmental matrix and enhanced mass of 14.68 μgm^{-3} in the month January 2011 implies environmental deterioration. No point source such as stationary sources other than biogenic and transportation systems exist in this riverine spot. As a whole, it

can be concluded that this spot is the least affected area with respect to metallic pollution and the enhancement in Fe concentration may be due to transference from the industrial area via air circulation. But the enhancement in the post-monsoon month January 2011 could be recognized to the seldom solubility of Fe in wet deposition and rarely prospective introduction owed to Fe particulates.

An enhancement in Fe is reflected in this industrial site, R2, where ample sources exist in addition to industries. The pollution trend in this riverine site entangled with industrial emissions is illustrated below. The concentration varied from 1.52 μgm^{-3} in the month May 2010 to 103.84 μgm^{-3} in the month January 2011, which is the highest value, noticed for this element in the present case. The conversion to water soluble Fe salt by acidic gases such as SO_2 may be prominent and can be accounted for the low intensity in the concentration of Fe. In the month May 2011, the elevation is evidenced and can be ascribed to the release of Fe salts from fertilizer unit (FACT). Construction related work also aggravates the condition by releasing crustal particles. The enhanced level, especially at this industrial site, can be associated to the release of Fe containing particulates from the industrial unit. The spatial enhancement order with respect to Fe is $\text{R2} > \text{R1}$. Temporal trend is more constant with respect to Fe similar to other sites (January 2011 maximum).

The site with extreme coastal activities is embedded with damaged water vessels in addition to refuse burning contribute much to the pollution load with respect to Fe at the coastal site C1. This coastal site is more heavily loaded with respect to Fe than other metals. The major pollution sources are the distant industrial units with a slight percentage of oceanic origin. The most tainted time at this seaboard is in the month November 2011 and shows the highest concentration of 22 μgm^{-3} and the

less loading is $3.36 \mu\text{gm}^{-3}$ in the month May 2010. Entire sites are more heavily loaded with Fe than other metals.

At coastal site C2, the maximum loading noticed was $13.11 \mu\text{gm}^{-3}$ in the month November 2011 and the minimum in the month May 2010 as $0.36 \mu\text{gm}^{-3}$. A common source (building construction) releasing Fe particles mostly in the fine particulate form are evidenced from the above observation. The finite concentration of Fe at all sites can be ascribed to the permanent stationary source viz catalyst producing unit and the utilizing plant situated in the neighborhood. Extensive and unplanned waste management practices viz refuse burning and land reclamation, harbor and construction related work can add up to the pollution effected already. C1, C2, and R1 sites are equally polluted with respect to magnitude in the range ($10 \mu\text{gm}^{-3}$) in January 2011. Crustal species, Fe shows spatial enhancement order as $C2 > C1$. But in the present study the coastal zone behaves in unique manner in temporal enhancement (November 2011) and other sites show January 2011 maximum, though both are post-monsoon months.

Coastal zone is heavily polluted in the order $C2 > C1$ in terms of monthly maximum. In this instant, coastal zone is severely polluted in the month November 2011 whereas E1, E2, R1, and R2 show enhancement in the month January 2011. Among the coastal sites, C2 surpasses C1 in concentration, with respect to most of the metals studied. The spatial enhancement pattern with respect to Fe in this study follows: $R2 > E2 > E1 > C1 > R1 > C2$. Gillies *et al.* (2008) reported a loading of $0.133\text{-}0.132 \mu\text{gm}^{-3}$ of Fe in a source apportionment study at USA during the summer, 1998. Nair *et al.* (2006) showed that the mean mass concentration of Fe at inland locations is in the range $0.9\text{-}3.1 \mu\text{gm}^{-3}$ and at coastal region as $0.3\text{-}0.9 \mu\text{gm}^{-3}$ and mass concentration of Fe is positively correlated with that of acid

soluble fraction of Ca^{2+} with a correlation coefficient of 0.86.

It can be emphasized that the pollution load of Fe similar to Zn and Cu never goes below detectable limit and R2 is the spot of enhanced Fe pollution among all sites.

SPATIOTEMPORAL VARIABILITY OF METALS IN PHASE II

It is revealed that most of the metals are highly concentrated at the estuarine zone and an analogous temporal maximum at January 2011 is realized in the spatiotemporal variability of metals in Phase I. Table 4 is the tabulation of metal data in Phase II. In Phase II, one each from coastal, estuarine, and riverine sites was sorted out on the basis of intensity in pollution. The following portion is focused on the spatial and temporal changeability analysis of metals by and large anthropogenic in origin. The sampling period includes October 2013, January 2014, and March 2014.

Distribution of Cadmium

Most of the sources of Cd are anthropogenic in origin. The metal Cd, with almost 100% anthropogenic origination, exhibits spatial and temporal variation in concentration as formulated below. The experimental data showed the following inferences. The estuarine station E1 depicts the range BDL in the month January 2014 and March 2014 to $0.23 \times 10^{-3} \mu\text{gm}^{-3}$, the site in the industrial belt shows the range BDL in the month January 2014 and March 2014 to $0.07 \times 10^{-3} \mu\text{gm}^{-3}$, and Coastal site C1 shows the variation in the concentration as BDL in the month January 2014 and March 2014 to $0.05 \times 10^{-3} \mu\text{gm}^{-3}$. The spatial enhancement order is $E1 > R2 > C1$.

Distribution of Copper

The three representative sites which are characterized as estuarine, riverine, and coastal (E1, R2 and C1) depict the concentration variability in the following scheme. The range observed at E1, is $0.01 \times 10^{-3} \mu\text{gm}^{-3}$ in the month, March 2014 to

$0.3 \times 10^{-3} \mu\text{gm}^{-3}$ in the month, October 2013. The least amount in concentration may be ascribed to the effective transportation and extensive wet removal of this metal incorporated to coarse particles formed as a consequence of physio-chemical transformation.

Industrial scenario R2 shows the lower limit in Cu concentration as $0.02 \times 10^{-3} \mu\text{gm}^{-3}$ in the month January 2014 and an upper limit of $0.06 \times 10^{-3} \mu\text{gm}^{-3}$ in the month October 2013. The highest value is in the month October 2013. Possibility of air mass transference cannot be ruled out for the low range noticed at this point with enormous industrial sources. The concentration range is in the order $E1 > R2$.

At C1, three samples as similar to E1 and R2 were collected in the months October 2013, January 2014, and March 2014. The range followed in Cu distribution pattern is: $0.02 - 0.5 \times 10^{-3} \mu\text{gm}^{-3}$. Data shows that the upper limit is noticed in the month March 2014, whereas lower limit was shown in the month January 2014. Oceanic input is relevant in this context in addition to the transported material from the industrial unit via wind. This is the site exhibiting highest range in Phase II in Cu samples. The effective wet scavenging in the month January 2014 cannot be ruled out in this case.

The spatial enhancement profile noticed in the case of Cu is coastal zone, $C1 > E1 > R2$, Koçak *et al.* (2004) reported enhancement in Cu concentration at Erdemli (Turkey) and identified the major source of Cu as fungicides, herbicides and mining of ore in the Black Sea region. In the present study, the major source which accounts for the enhancement can be identified as application of insecticides (Koçak *et al.*, 2004) used for pest control in distant localities, agricultural purposes, and transport of particulates from the industrial area in close proximity to study area, especially in coastal zone.

Particulate incorporated with Cu

emanating from the nearby industrial location and sea salt contribution collectively can endorse to the pollution enhancement. The estuarine site is least polluted with respect to Cu. The loading is less than the range reported by Nair *et al.* (2006) at Trivandrum in the Biosphere-Geosphere program. A decrease in trend from the month October 2013 to January 2014 and further increase to March 2014 is noticed in Phase II. Trace metal analysis by Chakraborty and Gupta. (2009) proves that wash out has no effect on trace metal concentration and Venkata Raman *et al.* (2002) analyzes and establishes that no periodic trend exist in concentration of Cu temporally showing support to the observation in this study. Gillies *et al.* (2008) reported a range ($0.012 - 0.024 \times 10^{-3} \mu\text{gm}^{-3}$) Cu in a source apportionment study at Reno and Sparks during the summer 1998.

In this work, March 2014 is the most polluted month and January 2014 is the feebly enhanced month. It indicates rain fall has no effect in the concentration and Cu emanated may be from anthropogenic source. Least concentration is noticed at E1 ($0.01 \times 10^{-3} \mu\text{gm}^{-3}$) in the month March 2014 and largest mass of $0.5 \times 10^{-3} \mu\text{gm}^{-3}$ (March 2014) at C1 in the current investigation. Cu allocation pattern exhibits extensive similarity in spatial configuration order in the whole study area. The overall trend for Cu revealed that Cu is enhanced at the coastal zone, C1 indicating strong anthropogenic influence in the month March 2014.

Distribution of Lead

The range at the spot in the estuary site E1 is BDL during the months January 2014 and March 2014 and a maximum load of $0.03 \times 10^{-3} \mu\text{gm}^{-3}$ during the month October 2013. Industrial site depicts the following variability profile. The range at the industrial spot R2, evidenced from the data, is BDL in the months March 2014 and January 2014 and the highest

maximum of $0.38 \times 10^{-3} \mu\text{gm}^{-3}$ in the month October 2013.

The coastal spot C1 denotes the range as BDL in the months January 2014 and March 2014 and an upper limit of $0.45 \times 10^{-3} \mu\text{gm}^{-3}$ in the month October 2013. The temporal trend in Cu is more consistent in this phase than the previous phase. The spatial enhancement profile is $C1 > R2 > E1$.

Distribution of Zinc

The concentration of Zn, at estuarine location with immense traffic density, E1, ranges from show values $0.03 \times 10^{-3} \mu\text{gm}^{-3}$ in the month March 2014 to $2.1 \times 10^{-3} \mu\text{gm}^{-3}$ in the month January 2014. The lowest value in the month March 2014 can be ascribed to the extensive export of pollutants to the nearby localities. Enhanced concentration in the month January 2014 is owed to the high rate of transportation of pollutants through wind, diminished wash out, and absence of inversion. Launching of Zn laden particulates from the industrial site can endorse to the situation at this estuarine site.

R2 is the industrial site immensely loaded with anthropogenic pollutants. The mass profile is illustrated below. The estimated mass ranged from $0.026 \times 10^{-3} \mu\text{gm}^{-3}$ (January 2014) to $0.034 \times 10^{-3} \mu\text{gm}^{-3}$ in the month October 2013. As cited already, atmospheric conditions and source characteristics are vitally important in assessing the concentration in the atmosphere.

The range is $0.02 \times 10^{-3} \mu\text{gm}^{-3}$ in the month January 2014 to $0.11 \times 10^{-3} \mu\text{gm}^{-3}$ in the month March 2014. The maximum in the load can be associated to the high rate of transported matter from distant places. Emission from biomass burning and release from damaged water transport vessels can also add up to the reasons. The spatial allocation trend is estuarine zone, $E1 > \text{coastal zone, } C1 > \text{riverine zone, } R2$. C1 exhibits the post-monsoon maximum in the month March 2014 and R2 shows the maximum in the month October 2013,

whereas both exhibit minimum in the month January 2014. The spatial distribution pattern is estuarine zone, (E1) $>$ coastal zone, (C1) $>$ riverine zone, (R2).

Distribution of Iron

Fe at E1 shows the lower limit of $0.204 \times 10^{-3} \mu\text{gm}^{-3}$ in the month January 2014 and an upper limit of $0.8 \times 10^{-3} \mu\text{gm}^{-3}$ in the month March 2014. The industrial hub R2 indicates the range as $0.1 \times 10^{-3} \mu\text{gm}^{-3}$ in the month March 2014 and $0.5 \times 10^{-3} \mu\text{gm}^{-3}$ in the month January 2014. The coastal spot C1 indicates the range as $0.4 \times 10^{-3} \mu\text{gm}^{-3}$ in the month March 2014 and the maximum ($0.55 \times 10^{-3} \mu\text{gm}^{-3}$) in the month January 2014 and is different from the trend at E1 and R2. At coastal station, in Phase II, the Fe profile reflects that in the month January 2014. The spatial allocation order is riverine zone, $R2 >$ estuarine zone, $E1 >$ coastal zone, C1 similar to the spatial configuration in Phase I. At E1 and R2, March 2014 is the intensively polluted month, whereas at C1, January 2014 is the polluted month.

The present analysis implies a January 2014 maximum and March 2014 minimum for Fe content. The hot air current circulates causing enhanced photochemical changes and extensive material transference. The composite factors result in suppressed mass loading. In the month January 2014, the maximum enrichment is revealed which means that rainfall has null effects on pollutant dispersion evidencing their anthropogenic origination. Enhanced diminished dispersion is also attributable to the above mentioned factors. Finally, the results can be concluded that Industrial zone is in compromisely contaminated with crustal component, Fe in January 2014 is the extremely polluted month except in the coastal zone and therefore it gives an insight into strong pollution source in the study area. In the industrial zone, January 2014 is the heavily polluted period. It is inferred that January 2014 is the highlighted period with respect to Fe concentration at industrial site

and coastal site, estuarine spot is the hot spot with respect to metals in Phase I, and metal enhancement is more prominent in Phase II. The spatial and temporal enhancement with respect to metals is well defined in Phase II.

The overall evaluation of metal concentration showed that in both phases, Fe is enriched at industrial site R2 in Phase I and at the estuarine site E1 in Phase II during the post-monsoon months (January 2011 and January 2014). The Hot spot with respect to most of the metals quantified happens to be in the estuarine site (E1) with similar temporal variability.

SOURCE APPORTIONMENT STUDIES OF METALS

A statistical analysis, Principal component analysis (PCA) using Varimax rotation with software (SPSS) was operated on the metal data and emerged out the following ideas. Principal component analysis gives evidences for the metal enhancement from various sources in most of the sites (Fig. 2). The source apportionments have been done on the quantified metals and are included in the Table 5.

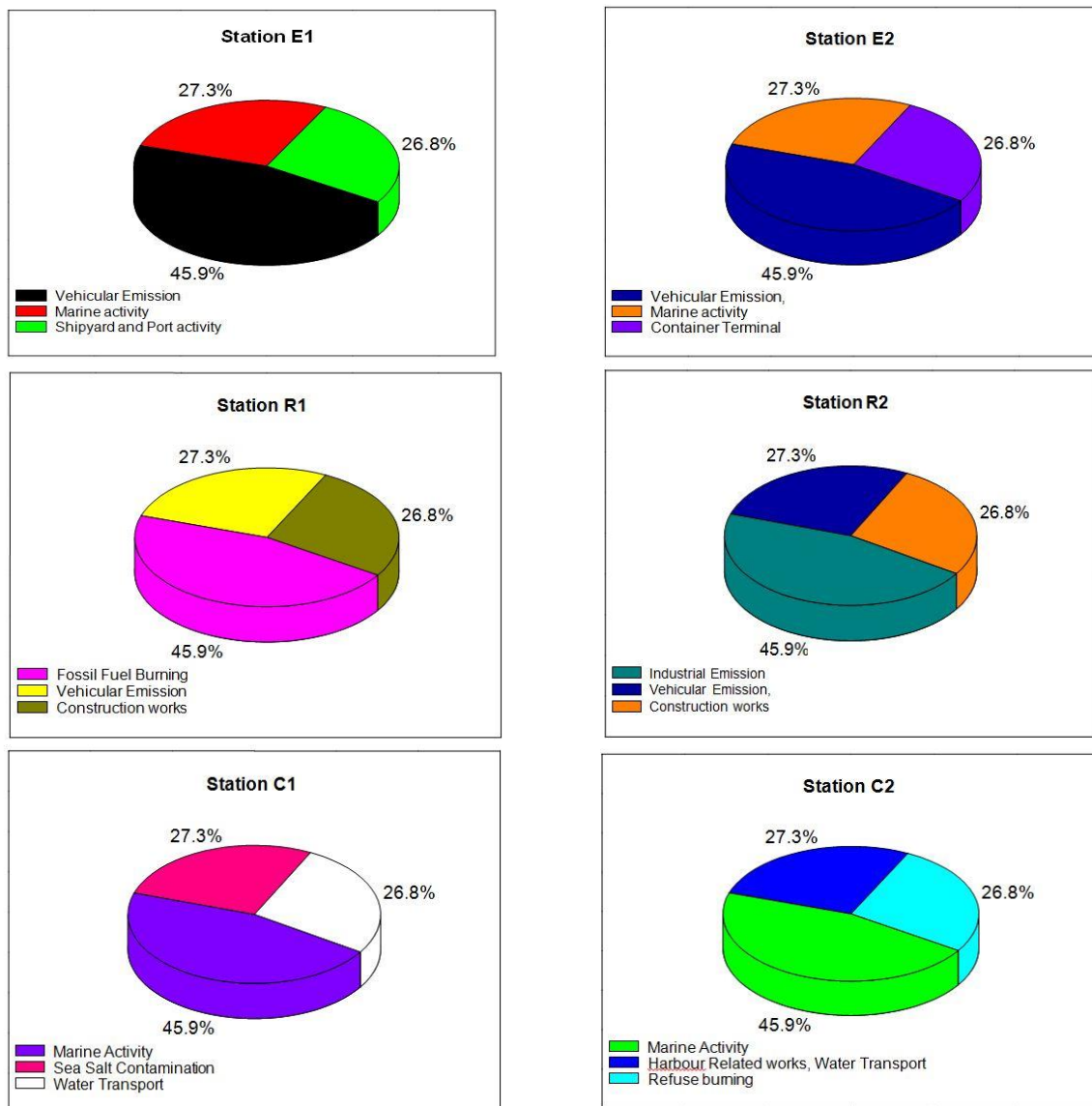


Fig. 2. Source apportionment study for PM₁₀ using factor analysis of all stations

Table 5. Enrichment pattern of metals in phase I and phase II

Trace metals	Phase1	Phase2
Cd	E1,November 2011	E1,October2013
Cu	E1,May 2010	E1, October2013
Pb	E2,November 2011	C1, October2013
Zn	R2,January 2011	E1, January 2014
Fe	R2,January 2011	E1, January 2014

The source identification for Pb and Cd was examined and is detailed as follows: At E1, 45.9% of the elements are originated from vehicular emission sources, the remaining portion 26.8% were contributed by shipyard related activities and 27.3% was contributed by marine activities. At the second estuarine site, E2, similar to E1, 45.9% are originated from vehicular sources. 26.85 were contributed by container terminal related activities and 27.3% contributed by marine activities similar to estuarine zone E1.

The statistical methods utilized for identification of sources revealed that at the riverine sites R1 and R2, these metals find variability in sources. It reveals that 45.9% at R1 is contributed by fossil fuel burning. In the fresh water zone R1, 27.3% was contributed by vehicular emissions and another 26.8% was contributed by construction works. The industrial site R2 highlights that 45.9% source contribution is effected by industrial emission; 27.3% contributes to the metal pollution via vehicular emission. 26.8% is contributed by construction works which is almost the same extend as that of vehicular emissions.

Coastal sites depict the following pattern of source categorization. At C1, marine activity contributes 45.9% to metal pollution. 27.3% source contribution was effected by sea salt contamination. The remaining 26.8% was injected into the ambient environment by water transportation. C2, the second coastal destination, highlights the following source configurations. Marine activity exhibits more contribution (45.9%) towards the quantified metals; 27.3% was contributed

by water transport and harbor related activities. 26.8% of the metal pollution was contributed by refuse burning.

CONCLUSION

Fe is identified as the prominent metal in the two phases. In Phase I and II, estuarine site exhibited as the hot spot for metals in the post-monsoon period. Levels of Cd concentration were below detectable level in most of the stations throughout the study campaign. In Phase I, the estuarine, riverine, and coastal sites exhibited a similar trend for metal concentration (Fe > Zn > Cu > Pb > Cd) except in the coastal site C2. In Phase II, there is no regular trend pattern recorded in the concentration of metals analyzed and are cluttered in post-monsoon period. Source apportionment study reveals that the major sources which contribute towards metal pollution are automobile emission (E1 & E2), fossil fuel burning (R1), industrial activity (R2), and marine activity (C1 & C2). The present investigation is a start and could provide a baseline data for pioneers dealing with unraveling the environment of Cochin Metropolis, Kerala, India.

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