

Spatio - Temporal Trace Gas and Trace Metal Foot Prints in an Industrial and Marine Scenario

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Abstract A framework budget of ambient atmospheric gases and Particulate Matter are pooled over six stations in the metropolis of Kochi, Kerala, India, during the summer and winter seasons of 2010 and 2011. In order to assess the air quality in the coastal and industrial location, six topographically prominent and distinct areas are selected. The gases like sulphur dioxide, nitrogen dioxide and ammonia are selected owing to its importance on human health. Besides, particulate matter is monitored in order to quantify the trace metal present, which causes serious respiratory and cardiac problems. Elevated concentrations are observed in winter for all the parameters monitored compared to summer, which provides an insight in to the circulation of gases and particulate matter along the unlike seasons. The winter season with more stable atmospheric pattern tend to cumulate the pollutants rather than dispersing it due to temperature gradient. Industrial sites show prominent levels of sulphur dioxide and ammonia. Considerable increase in nitrogen dioxide unravels the folded increase in vehicular motors. The particulate matter study for selected trace metals untie the concentration of iron, lead, copper and zinc to be augmented in winter. Statistical methodologies are applied to assess the relationship between the seasons.

Keywords: Kochi, sulphur dioxide, nitrogen dioxide, ammonia, particulate matter, summer and winter

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1. Introduction

Pollution in any form is grave since the tranquility of the environment is embittered which causes serious squalor to flora, fauna and mankind. The major components of environment: atmosphere, hydrosphere and lithosphere exhibit triangular relationships among each other and any change in these components of the environmental segments cited above threaten the existence of biosphere as a whole, and affect adversely to the climate and basic amenities. The atmosphere with life surviving gases is an important drive area to cram. Atmospheric gases play vibrant role in regulating complex activities and aerosols are fetching hot spots due to their simultaneous interaction with human being and also lead to distortion in climate. Although the quantification of these species is not completely achievable, qualitative analysis of certain parameters can provide remarkable tips in predicting the prevailing air quality status of the study area. The area under consideration may exhibit different discrepancy due to topography, meteorological parameters, natural and anthropogenic input of pollutants to the surroundings. Further, rapid urbanization and industrialization has lead to lofting and large scale advection of these omnipresent species in the atmosphere. Studies are conducted on a global scale to assess the importance and potential impact caused due to these

ubiquitous species. The major gaseous pollutants include gases like sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone, ammonia and particulate matter (PM). The mounting civilization has caused abrupt changes in air quality. India, the land of diversity is no more an exception to this solemn issue. The country with 23 major cities of over 1 million people and ambient air pollution levels exceed in many of them [10]. The major metropolitan cities like Delhi, Calcutta, and Mumbai are in the clutches of this distress. Previous studies reveals that about 70%, 30%, 52% of total pollution in Delhi, Calcutta and Mumbai respectively are due to vehicular pollution [8] and these pollution has lead to moderate and serious health problems [13] The concentrations of toxic metals in Mumbai are scrutinized and conclude the major pollutants to be respirable suspended particulate matter (RSPM) and lead [5]. The observance of trace metal concentration follows the order industrial > heavy traffic > commercial > residential based on spatial variation [1,21]. Positive correlations among metal concentration and meteorological parameters are also established [21]. Anthropogenic activities are the source for increasing their abundance to atmosphere [17]. Kochi (also known as Ernakulam) is one of most populated city and is under the grip of pollution hazard. The district lies in coastal area and extend between 9° 45 and 10°15 N and 76°15 and 76°50 E. The scan of city shows that there is significant increase in the anthropogenic input over the years due to recent developmental activities on going in order to make

the city a versatile one. Hence the study becomes noteworthy in this sector. It is spread over an area 20408 square km and is amplified in pollution from sources like heavy traffic, land reclamation; industrial units, local and international untreated effluent plants, solid waste, fabrication works, incomplete burning and inevitable household sources. Few studies have been under taken regarding dispersion of atmospheric pollutants [7,9].

These sources are highly heterogeneous in nature and monitoring is necessary to provide a complete sequestration.

2. Materials and Methods

2.1. Sampling Site

Table 1. Site Characteristics with Sources of Pollution

Sampling Site	Type	Sources of Pollution
Marine Science	Estuary (E1)	Automobiles, solid waste, Cochin port trust
Bolgatty	Estuary (E2)	Vallarpadam Container terminal, automobiles.
Murinjapuzha	River (R1)	Automobiles, Rural area
Eloor	River (R2)	Automobiles, Industrial Belt Area
Vypeen	Coastal (C1)	Fish preserving unit, Harbour
Munambam	Coastal (C2)	Fish preserving unit

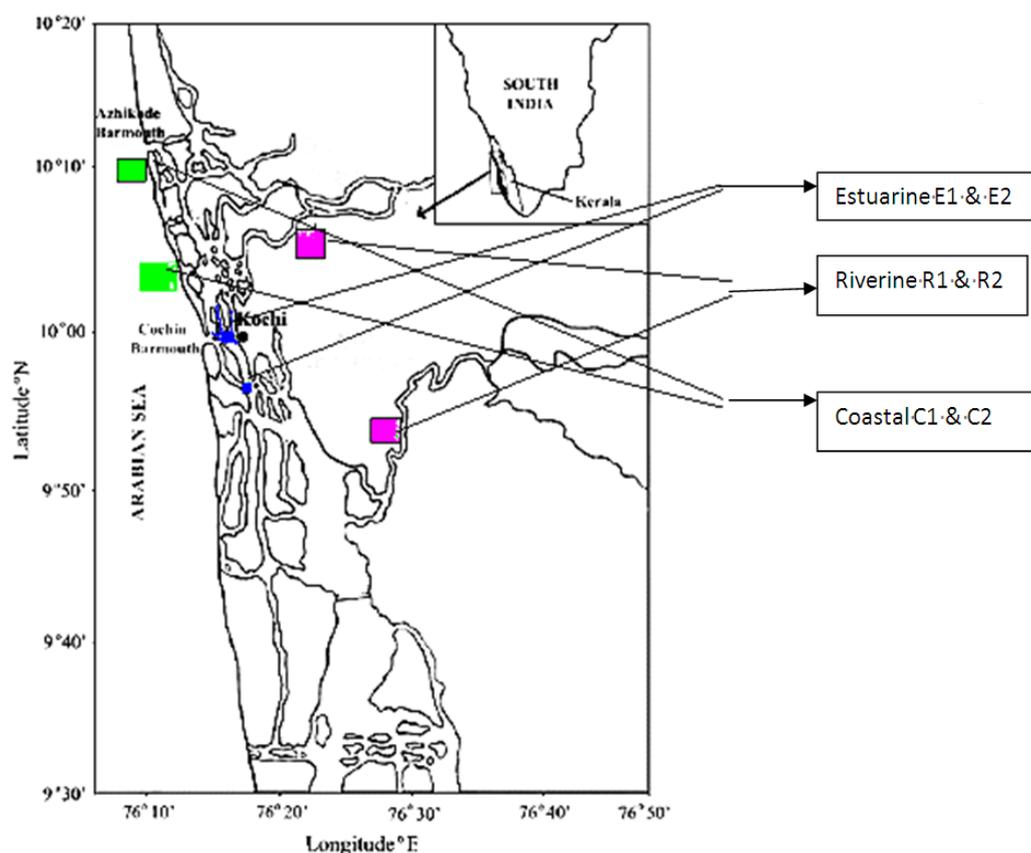


Figure 1. Location Sketch of sampling sites

The sampling site specifications chosen are ample enough to provide a complete appropriation about the declining air quality. Six sampling sites are selected in Kochi metropolis which represents different segments of the region. Both E1 and E2 represent estuarine sites. Marine aerosols and anthropogenic aerosol due to human activities deteriorate the environment severely. Industries and automobiles release toxic chemicals to the atmosphere. Biogenic emissions still worsen the situation. Oil refineries are a major source of tarry organic particulate matter in all these sites. Agricultural activities in some areas produce sugar like material which makes the pollutant an adhesive character and sticky nature. R1 and R2 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 populated region and augmented with industrial emissions. Though fossil fuel burning and automobile release are present to a slight extend, it contribute to the deterioration of the environment. The coastal site C1 and C2 makes difference that sea salt contamination is maximum in their pollutant discharge. A detailed description of the pollution sources in the study area is given in the Table 1. The map of the study area is given in Figure 1. The pollution sources are related to fisheries and retting of coconut husk. The selected sites are in the vicinity of estuarine, riverine and coastal areas so that the input from these aquatic sources into the troposphere could also be encountered. The categorization

of sites into these three different sets is on the firm understanding that each specific site has its own characteristic emanation. This study is the first attempt of this sort in this area.

2.2. Sampling Procedure

The sampling is done using high volume sampler of model APM 415 (Envirotech) maintaining the flow rate at 1 m^3 per minute. The inlet is placed 3 meters above the ground level. For sites without surrounding obstructive vegetation, topography or buildings, a minimum height of 2 meters above ground level is recommended. For continuously measured aerosol parameters, one-hour time resolution is appropriate with measure of the central value (arithmetic mean) and variability (standard deviation) reported for each parameter for each hour. Continuous monitoring is performed in the month of May (2010) and January (2011) for three hours. The gaseous pollutants like sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ammonia (NH_3) are monitored by collecting them in impingers with suitable absorbing media attached to the sampler. Nuclepore glass fibre filter paper of size $20 \times 25 \text{ cm}$ is used as collection substrate for particulate matter (PM_{10}). The impactor collects the particulate matter (PM_{10}) the atmosphere with an upper break up of 10 micrometer according to the specification. The collection substrate is pre-conditioned, desiccated and accurately weighed in an electronic balance before and after sampling. The blank filters are also kept at the same condition. After sampling the substrates and gases are brought back and kept in refrigerator for further analysis.

2.3. Analytical Procedure

Gaseous pollutants are analyzed by wet chemical methods and quantified by spectrophotometer. The samples in the absorbed medium are estimated colorimetrically. Sulphur dioxide is estimated using modified West and Geake method [24]. In brief, the gas is collected in an impinger containing 20 ml absorbing medium, sodium tetra chloro mercurate. It is treated with sulphamic acid, acid bleached p-rosaniline hydrochloride and the absorbance is measured at 560 nm. Nitrogen dioxide is determined using modified Jacob and Hochheiser method [12] in which the gas is collected in alkaline sodium arsenite and colour development is done by adding sulphanilamide and N [1-Naphthyl ethylene diamine dihydrochloride] with the absorbance at 540 nm. Ammonia is estimated by Indophenol-blue method [16]. The exposed filter paper is acid digested using a mixture of nitric and perchloric acids in the ratio 5:1 for trace metal quantification. The analysis is performed using ICP-AES (Inductively Coupled Plasma –Atomic Emission Spectroscopy) and the concentration of elements like Fe, Al, Cu, Cd, Zn and Pb are estimated.

3. Results and Discussions

3.1. Variation in Particulate Matter

The meteorological parameters under consideration include wind speed, wind direction, temperature and humidity. From the wind rose plot (Figure 2 and Figure 3),

it is observed that the prevailing wind at Kochi is south west in winter while in summer it is from North - Northwest. The average temperature in summer is 29°C and winter 27°C . Throughout the sampling period there exists moderate precipitation. The relative humidity is more in winter than summer and continuous rainfall is observed in almost all the months from May (2010) to January (2011). All these factors influence the nature of particulate matter composition and dispersion of gases. The PM_{10} concentration in the samples varies notably from summer to winter and is enhanced in winter season. Higher value at the sites C1 and C2 can be attributed to sea salt loading in both the seasons. The lofty value of PM_{10} in winter seasons at E1 and E2 is due to the anthropogenic activities, low wind velocity, low temperature and relatively stable atmospheric conditions with low dispersion rate and earlier reports also supports [21]. Gas-to-particle conversion may be effective due to photochemical reaction, increase in coagulation and resuspension may add onto the above cited fact. The trend is represented in Figure 4.

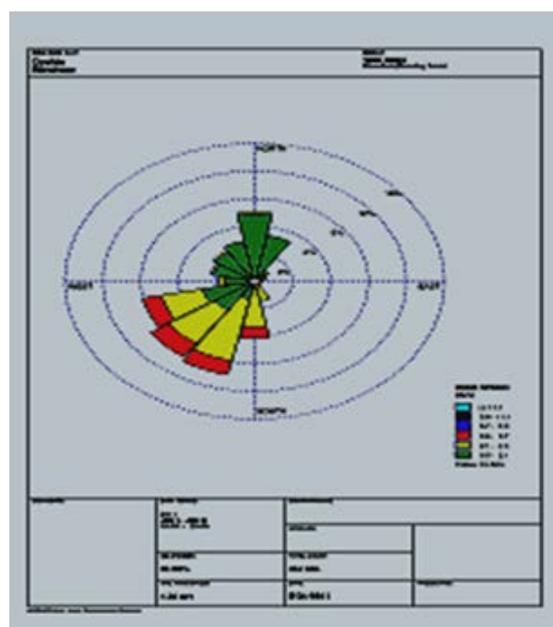


Figure 2. Prevailing SW wind in January

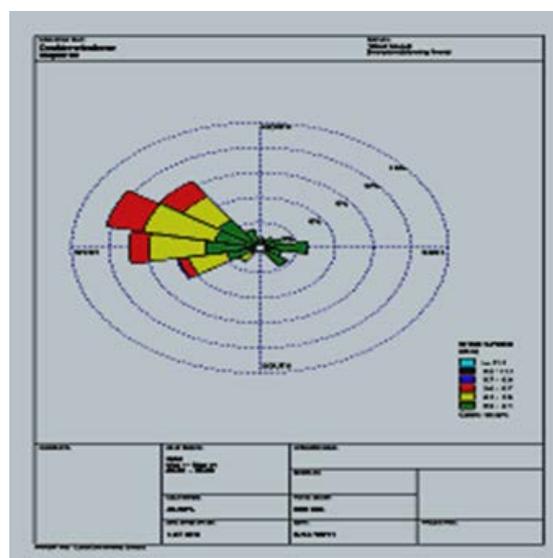


Figure 3. Prevailing W-NW wind in May

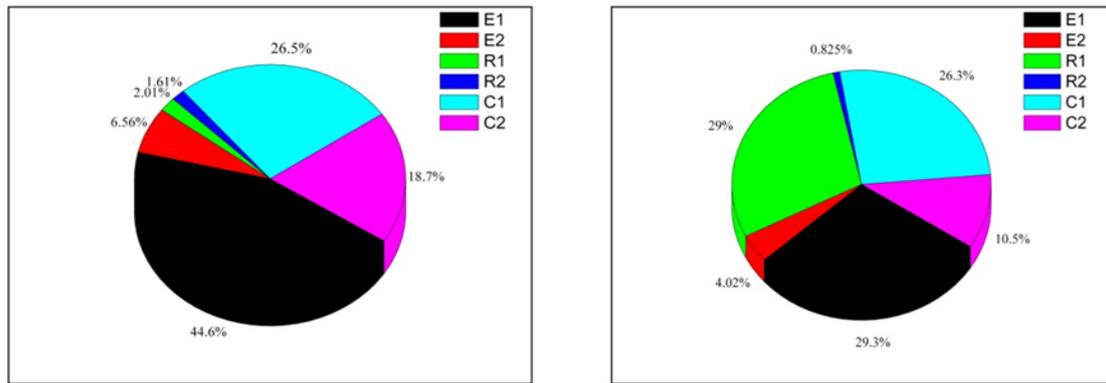


Figure 4. Variation of Particulate Matter in Summer and Winter

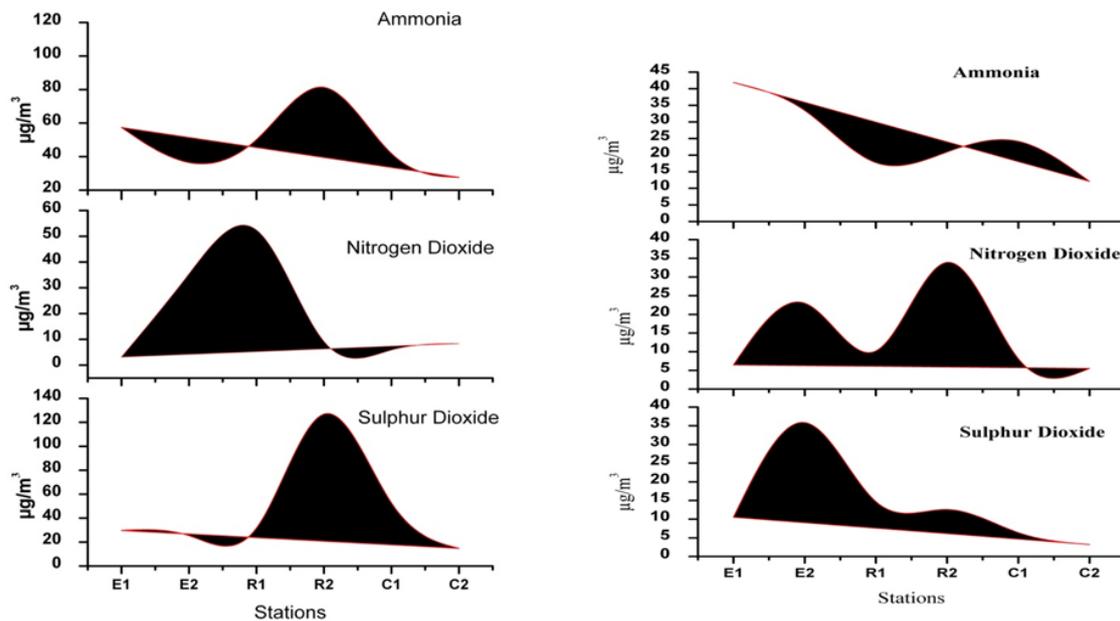


Figure 5. Variation of Trace Gases in Summer and Winter

3.2. Quantification of Gases

The main sources of atmospheric acidity are the gaseous emissions of SO_2 and NO_2 , generated by civil and industrial activities [18]. In the atmosphere, both SO_2 and NO_x are subjected to chemical transformation by oxidants, which lead to formation of sulphuric acid containing aerosol and gaseous HNO_3 [19]. These two products then react further under typical conditions with NH_3 and have a neutralizing effect producing both sulphate and nitrate in the aerosol phase as ammonium sulphate and ammonium nitrate. These chemicals can be deposited to the earth's surface by either dry or wet deposition process and the chemical transformation process can be referred to as gas-to-particle conversion and involves many factors, viz. meteorological parameters, site characteristics. [6]. The present study reveals the elevated concentration of SO_2 in the winter season. The average concentrations of SO_2 at the commercial city centers Sydney, Prague, Cairo, Frankfurt, Tokyo, Nairobi and Manila are 62.6, 154.3, 39.0, 80.7, 55.1, 214.8 and 56.5 $\mu\text{g}/\text{m}^3$ respectively [25]. A peak value of 126 $\mu\text{g}/\text{m}^3$ is observed at site R2 in winter season. The industrial belt zones which release SO_2 into the atmosphere as a byproduct is the major reason. The mean concentration varies from 6.4 $\mu\text{g}/\text{m}^3$ to 35.9 $\mu\text{g}/\text{m}^3$ (summer) and 14.74 $\mu\text{g}/\text{m}^3$ to 126.9 $\mu\text{g}/\text{m}^3$ (winter). NO_2

in winter and summer season is found high at R1 and R2. The mean NO_2 concentration reported for the cosmopolitan cities like Delhi, Calcutta, Chennai, Mumbai are 37.4, 167.4, 16.2 and 30.7 $\mu\text{g}/\text{m}^3$ respectively [4]. In the present study site the concentration varies from 6.46 $\mu\text{g}/\text{m}^3$ to 23 $\mu\text{g}/\text{m}^3$ (summer) and 3.15 $\mu\text{g}/\text{m}^3$ to 52.48 $\mu\text{g}/\text{m}^3$ in winter. The site, R1, rural in action hitherto, there is a major roadway connecting to different districts and busy with vehicular traffic throughout the times. The study behavior by Avnish Chauhan [2] also proposes that the concentrations of pollutants are higher in winter. NH_3 is the most prevalent gaseous base found in the atmosphere, and is, therefore, fundamental in determining the overall acidity of, precipitation, cloud-water and atmospheric aerosols [14,15,22]. NH_3 is emitted by a variety of sources such as soil, sludge, animal waste, automobiles and agricultural processes [20]. Ammonia decreases in the order $\text{E1} > \text{E2} > \text{C1} > \text{R2} > \text{R1} > \text{C2}$ in the summer season. The site, E1 encompasses estuarine character along with harbor activities are foregoing. Biogenic waste enhances the richness of ammonia in the estuarine premises. The major transport of ammonia and sulphur to the industrial site R2 is through water ways from the Wellington Island, a place near to E1. Hence ammonia can be distributed entirely over the available space and might be one of the reasons for its high

fortification in respective site. Conversely in winter, ammonia is considerably high at R2 (Figure 5). Some of the major thriving industries which manufacture ammonia, caprolactum, ammonium Sulphate, urea, sulphuric acid etc are located near to this site. In winter due to low temperature, the dispersal may be low and in all the sites ammonia is profoundly enhanced in this season. The comparatively higher temperature though frequent rain can cause dissociation and volatilization of ammonium salts enriching the environment. The site R2 which is in an industrial belt is experimentally proved to be heavily polluted in winter which is in accordance with our expectation.

3.3. Quantification of Trace Metals

The measured metal concentrations are graphically presented in Figure 6. The winter season represents the maximum concentration of trace metals. It might be due to persistent ground level inversion conditions during this time. Organic and inorganically bound species both in particulate and soluble form intensify the existing dangerous situation. The concentration of Cd and Pb are below the detectable limit, however Pb is observed at an average of $0.03\mu\text{g}/\text{m}^3$ in all the sites during the summer season. The low value shows the control adaptive measures taken for Pb. The major source of Pb to the atmosphere comprises from petrol combustion. The non-leaded petrol is using now-a-days which reduces the amount of Pb considerably. A slight detection in summer

can be attributed to emission of Pb into the atmosphere over past decades which have initiated to considerable increase of Pb in soil along the road side. [3,13]. Fe and Al vary from 0.38 to $0.84\mu\text{g}/\text{m}^3$ and 0.17 to $1.81\mu\text{g}/\text{m}^3$ in summer. The winter season with concentration (Fe) 1.5 to $109.85\mu\text{g}/\text{m}^3$ and (Al) 3.67 to $155.3\mu\text{g}/\text{m}^3$ shows a high input of these metals. Fe and Al have both crustal and anthropogenic point sources. Earlier reports show that the crustal elements are found to have high concentration in summer [1]. Al levels are elevated in summer than Fe especially in site E2. The site topography enlightens the fact that one of the largest container terminal (Vallarpadam Terminal Container) resides near to it and is commissioned in 2010. Frequent construction works are taking place and prevailing W-NW windblown in the season might have a role in dispersing the pollutants. The winter season representing a higher input can be attributed for the stable conditions and low dispersion rates but at the same time anthropogenic activities are intense and construction related work in the harbor areas leads to aggregation of pollutants in and around the place where the source is located. Similar type of observations have been reported [1,11]. Zn varies from 0.05 to 0.38 (summer) and 0.75 to 4.36 (winter). The spatial distribution of copper is enhanced in summer season than in winter. This fortification is high in site E2 ($0.58\mu\text{g}/\text{m}^3$) and may be due to coal ash resuspension [3] and from industrial sources.

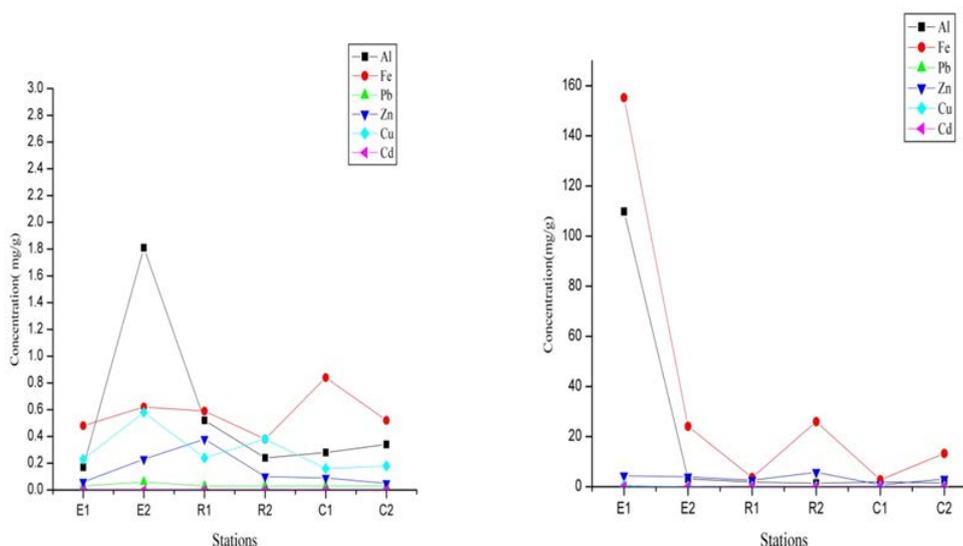


Figure 6. Variation of Trace metals in Summer and Winter

3.4. Enrichment factor (EF)

The distribution of trace elements vary from place to place, depending upon the regions selected. However it is possible to predict whether the given element is enhanced or reduced using a parameter called Enrichment Factor (EF). The Enrichment Factor is the ratio of the concentration of any trace metal or ion to Fe in the sample divided by the corresponding ratio in crustal material [23]. If the $EF < 10$, trace metal in aerosol has crustal origin and if vice versa they are derived from some other sources. The enrichment factor is calculated for each metal, using iron as the normalizing element. $EF = (C_{\text{metal}} / C_{\text{iron}})_{\text{spm}} / (C_{\text{metal}} / C_{\text{iron}})_{\text{crust}}$, where EF is the enrichment factor, $(C_{\text{metal}} / C_{\text{iron}})_{\text{spm}}$ is the ratio of concentration

of metal to concentration of iron in aerosol, and $(C_{\text{metal}} / C_{\text{iron}})_{\text{crust}}$ is the ratio of the metal to iron in the earth crust. The results of EF factor reveal that except Al all other elements have EF values greater than 10. This indicates other than aluminum; rest of all elements has significant anthropogenic sources. The order of EF values are in the order $\text{Cu} > \text{Zn} > \text{Pb} > \text{Al}$. The Enrichment factors for elements at the site R2 are found to be higher especially in winter season. The atmospheric stability in winter compared to summer facilitate the pollutants, especially hygroscopic, adhesive type and deliquescent, to remain as an aggregation. The site R2 is an industrial belt area, covering small and large scale industries which are run by state and centralized organizations. This region can be considered to be a cesspool of toxic metals surrounding in ambient air.

Table 2. Correlation Analysis of Trace Metals in summer and winter

	Al	Fe	Pb	Zn	Cu
Al	1				
Fe	0.19052	1			
Pb	0.981739	0.151286	1		
Zn	0.448388	0.148173	0.296987	1	
Cu	0.843872	-0.22317	0.875543	0.304284	1
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4. Conclusion

The behavioral pattern of PM₁₀ and trace gases at Kochi in two prominent seasons is monitored. The values figured to be more enriching in winter is due to pollutants emitted from various sources that get trapped in troposphere due to temperature inversions and a special situation arising with the advection of pollutant containing sea salt. The industrial belt site is more pronounced on gaseous pollutants and particulate matter loading and is more pronounced at estuarine sites rather than the other two zones. The science of statistics is put into operation to the parameters monitored in order to establish the relationship between the pollutants. The correlation analysis and ANOVA are performed on the data set accomplished. The results are tabulated in Table 2. Season wise correlations of metals shows positive between Fe and Al (0.98) where as all other metals are trivial. Conversely metal to metal correlation shows a positive nature existing between Pb and Al in summer (0.98), Cu and Al (0.96) and Cu and Fe (0.97) in the winter season. The gases are also processed similarly and found to be insignificant. The ANOVA analysis showed that there is no spatial and season wise correlation among the trace gases and pollutants. The meteorological conditions together with the sites specifications have played a turnaround amalgamation in distributing these pollutants into the atmosphere.

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