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Research Article

Spatio - Temporal Assessment of Air Pollutants in Kochi City, Kerala, India

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Abstract: Kochi City is a fast growing industrial region where mounting civilization and urbanization has been affecting abruptly in diminishing the air quality of these atmospheric environments. Hence a systematic investigation have been undertaken to carry out the quality assessment emphasizing six transition sectors which are prominent sites with distinct topographical features covering the entire estuarine, riverine and coastal regions of the Cochin Aquatic System. The study recorded that one of the riverine site (R2) is exponentially showing enrichment in SO_2 concentration which can be speculated for severe industrial emissions and this site can described as the "Hot Spot Realm". The enrichment of NO_2 portrays the pollution source as through vehicular emissions. Regarding the temporal trend, vagueness exists throughout the analysis more than the spatial allocation trend. It is reflected from the analysis that both climatology and source effect plays significant role in pollutant dispersion. The Air Quality Index (AQI) values calculated for SO_2 and NO_2 gases pointed out that Kochi area is moderately polluted.

Keywords: Trace gases; Monitoring; Air Quality Index; Kochi.

INTRODUCTION

The prime area dealt with human beings recently is environmental pollution and its related health effects. Moreover, climatic distortion is a severe problem encountered by the biota nowadays. In the atmosphere aerosols (colloidal suspension of particulate matter and trace gases) are the major sinks of the pollutants, especially trace gases and these crucial species are to be evaluated since they create serious environmental havocs and deteriorate the ecosystem primarily to the biota which reflected in terms of health and climatic distortions. Urban air pollution due to vehicular emission[1, 2] contributed in the enhancement of constituents like Respirable Suspended Particulate Matter (RSPM), SO_2, NO_X and other organic and inorganic pollutants including trace metals which is a matter of grave concern and has adverse effects on human and environmental health[3,4,5,6,7].

Trace gases are chemical constituents found in low concentrations (makes up less than 1% by volume of the Earth's atmosphere) and they include, ozone (O_3), Nitrogen oxides including NO, NO_2 (NO_X), Carbon monoxide (CO), Sulphurdioxide (SO_2) and Ammonia (NH_3). Enhancement in anthropogenic activities in terms of developmental activities and hi-fi standard of living raised the pollution index in a geometric proportion for these obnoxious atmospheric trace gases which has resulted in global warming and acid rain[8] and subsequently noted a change in climate. Certainly these trace gases can exert considerable influence on a range of environmental distortion effects and health disorder. Reactive nitrogen compounds such as NO_2 and NH_3 plays a crucial role in various biogeochemical processes[9] such as the nutritional balance of the aquatic and terrestrial ecosystems via acid deposition[8]. As a whole, the trace gases impart profound effect on air quality[10,11,12,13].

Both anthropogenic and natural sources are comprehending for the distribution of these trace gases (SO_2, NO_2 and NH_3). Industries, automobiles and human intervention such as deforestation constitute the anthropogenic sources whereas atmospheric emissions via wind driven transportation, transformation (gas-to-particle conversion) and wet and dry deposition[10] comprise as natural sources. Microbial decomposition of organic waste materials is the main biological source of NH_3 in the troposphere and rarely natural sources include oceanic, soil, fire and plant emissions[14]. In addition to deterioration of material objects, trace gases create serious health disorders[15] which are mentioned as reproductive and developmental effects in terms of preterm birth[16,1,17]. These soluble gases in water causes health effects including cardiovascular deaths[18,19], respiratory problems such as asthma and bronchitis[20]. The oxidized nitrogen species deteriorate materials, cultural artifacts, vegetation and crops and has prime role in the formation of photochemical oxidants[21]. NH_3 has toxic effect to humans and due to the application as fish preservatives and is introduced through diet. The direct and indirect effect of aerosols on radiative forcing creates global climate change[12].

In the Indian context, most of the studies are dealt with trace metal distribution as an aerosol particulate matter constituent. It would be incomplete if the characterization of ambient aerosol is not facilitated in the marine scenario, Kochi-the Queen of Arabian Sea, experiencing tremendous industrial influxes. The spatio-temporal analysis with special reference to trace gases is also required to assess the source apportionment. Pertaining to the reality, Kochi City is a fast growing industrial region where mounting civilization and urbanization has been affecting in diminishing the air quality of the atmospheric environment. Cochin aquatic environment is progressively affected by marine pollution concomitant

through industrially related hazardous chemicals and municipal waste. The entire environment including atmosphere in this "Queen of Arabian Sea" is seriously polluted with particulate matter and trace gases[22].

Simultaneous measurements of aerosol optical depth and incoming global solar flux were carried out by[36] with a MICROTOPS-II Sun photometer and Eppley Precision Spectral Pyranometer over the premises of Pune in a field campaign mode during the period December 2010–May 2011 and observed that aerosol optical depth shows significant diurnal variability which is related to the prevalent meteorological conditions, surface-based nocturnal temperature inversion in the atmospheric boundary layer (ABL), and influx of aerosols from different source regions. Gogoi and coworkers[24] assessed the climate impact of aerosol black carbon (BC) over snow covered regions (through enhanced absorption of radiation as well as snow-albedo forcing), and in view of the increasing anthropogenic presence and their influence in the northern polar regions, continuous long term measurements of airborne black carbon have been undertaken from the Svalbard region of Norwegian Arctic over a period of 4-years (2010-2013) and have noticed a consistent spring time enhancement in black carbon concentrations, which was higher than the lowest black carbon concentrations in summer.

Besides Gogoi et.al.[24] analysed physical and optical properties of aerosols in a free tropospheric environment resulted from long-term observations over western trans-Himalayas including the absorption characteristics of aerosols over the northwestern region of India in the year, 2013 and identified distinct seasonal signatures of biomass burning aerosols and mineral dust.

The assimilative capacity of Kochi region was evaluated for providing assistance for the siting of environmental friendly industries by[25] to locate the air polluting industry. Kaushik and coworkers[27] assessed the ambient air quality of Haryana City and observed that the average ambient air concentrations of SO_2 and NO_2 were found below the permissible limits at all the centers. Besides, comparatively higher concentration of SO_2 was observed during winter seasons, which seems to be related with the enhanced combustion of fuel for space heating and relatively stable atmospheric conditions. Air Quality Index (AQI) prepared for the study sites shows that residential, sensitive and commercial areas were moderately to severely polluted which is a cause of concern for the residents of these cities. They added that the high levels of TSPM and SO_2 especially in winter are of major health concern because of their synergistic action. Moreover, Hisar city records a significant increase in the total number of hospital visits/admissions of the patients with acute respiratory diseases during winter season when the level of air pollutants was high.

Zabalza[26] in 2007 measured SO_2 and NO_2 and observed a winter time enhancement of the two species in two cities in Spain. Virkkula[27] in 2003 noticed that SO_2 and NO_2 concentration varied during the period 1992-2002 and located the source to the east and north east of the site. Ceron and coworkers[28] attempted an identification of ion sources in Mexico City and found that nitrate concentration exceeded the background level reported for coastal sites with significantly high correlation with sulphate concentration.

It is clear from literature that characterization of atmospheric pollutants in this industrial and marine niche, Kochi, Kerala, is seldom executed. Hence a systematic monitoring programme has been performed in the urban city of Kochi by assessing the spatio-temporal variability of trace gases. The study marks its significance in the pollution aspect of Kochi city, situated along the south western part of Indian subcontinent.

MATERIALS AND METHODS

Description of the Sampling Area and Air polluting sources: Kochi is an 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 criss crossed by backwaters, of which the most prominent is Vembanad Lake. Many portions of the region are water logged for most part of the year. 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. It is spread over an area 94.88 square km and is amplified in pollution from sources like heavy traffic, lithogenic debris, industrial outflows, local and international untreated effluent plants, solid waste, fabrication works, incomplete refuse burning and inevitable municipal wastes.

In addition to transport systems, the industrial polluters such as FACT and allied industries in the city such as Cominco Binani Zinc Ltd, Travancore Cochin Chemicals, FACT Udyogamandal, Ambalamugal, Hindustan Insecticides Ltd, Indian Rare Earths Ltd, ASCL Caprolactam, Cochin Refineries, Carbon and Chemicals and many small scale industries, shipyard related work accelerated the industrial growth in the area and engender to a tremendous boost in the economic budget of Kochi. Though fully urbanized, the solid waste management in this area is seemed to be improper.

It can be proclaimed that, this study is the first attempt to get the baseline data on aerosol trace gases in Kochi city and its counter parts prioritizing the dual character such as marine and land influence, though a number of investigations in recent years have shed light on the varied nature of biogeochemical characteristics of Cochin back waters[29-35].

Selection of Sampling Sites: The sampling site specifications chosen are ample enough to provide a complete appropriation about the declining air quality in Kochi. The sampling sites are marked in the site map (**Fig.1**).

Six transition zones which are prominent sites with distinct topographical features were selected, covering the entire estuarine, riverine and coastal regions. The hydrographic parameters and the atmospheric stability condition vary at these three sites due to the variability of pollutant dispersion pattern in the water, air and sediment phases. The selected six sites are in the vicinity of **estuarine, riverine and coastal areas** flanked over the aquatic realm. They are categorized in to these three different segments for the firm understanding on each specific site which has its own characteristic emanation.

The sites E1 ($9°95'$ N, $76°$ $29'$ E) and E2 ($9°98'$, $76°$ $26'$ E)   represent **estuarine sites** which is in the kerb side situated near the boat jetty of School of Marine Sciences campus and on the banks of Cochin back waters respectively. Diesel fuelled terrestrial and water traffic systems along with the harbour related activities are intensified in these scenarios. R1 ($9°33'$ N, $76°35'$ E) and R2 ($10°05'$ N, $76°$ $34'$ E) are the two **riverine sites**. At R1, automobiles are the major source for both particulate matter[36] 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 and augmented with industrial emissions. Insidious trace metals

originated from industries elevated the pollution level. Biomass burning and vehicular emissions concomitantly engender to a slight extend and confound to the deterioration of the environment enhancing the trace gas level. The **coastal sites** C1 ($9^058'$ N, 76^0 14' E) and C2 ($10^015'$ N, 76^0 17' E) makes the difference in the sea salt contamination in addition to emission of trace gases from the oceanic water bodies which is boomed in their pollutant discharge. The pollution sources for particulates and trace gases are fishery related activities and coconut husk retting in the coastal belt.
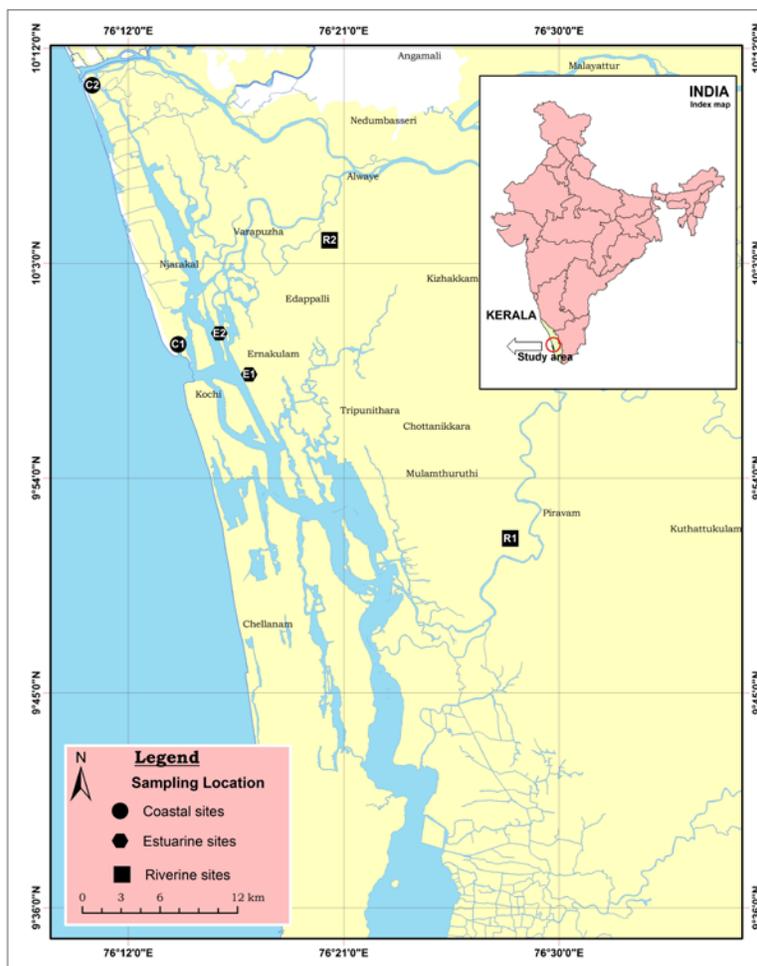

Figure 1: Map showing sampling locations in the study area.

Meteorology: Meteorological factors play vital role in air pollution studies particularly in pollutant transport irrespective of their entry into the environment. The climate is dominated by heavy rainfall during the southwest monsoon season and moderate rainfall during the post monsoon months. Being a coastal station, the city is influenced by the effects of land and sea breezes[28].

Air circulations are generally light to moderate throughout the year. Generally monsoons results in large amount of precipitation, high wind velocities and changes in wind direction. Abundance in precipitation resulted in scrubbing off pollutants. Further, wind velocities will drift away pollutant from sources and increase mixing processes. During winter, there is increased atmospheric stability, which in turn reduces

air parcel disposal and thus more stagnant air masses and cluttering of pollutants in any given area. The prevailing calm atmospheric conditions facilitate more stability to atmosphere and consequently diminished dispersion of generated pollutants and helps in buildup of pollutants in the vicinity of the pollutant sources[37]. A brief discussion of the meteorology experienced in this sampling period is illustrated in the (**Table 1**).

Table 1: Ambient Air Quality Standards by KSPCB.

Pollution	Annual Mean Concentration ($\mu g/m^3$)	
Level	Industrial	Residential
	SO_2 & NO_2	SO_2 & NO_2
Low (L)	0-40	0-30
Moderate (M)	0-80	30-60
High (H)	80-120	60-90
Critical (C)	>120	>90

The current study area flanked with industrial and marine remnants experienced the following meteorological status in the period of investigation. The premonsoon month in the first phase recorded a temperature range which falls in the range as 26-27°C (minimum) to 33-34°C (maximum) and in Phase II it ranged as 25-35°C. The post monsoon month noticed the temperature range as 22-24°C (minimum) and 31-33°C (maximum) in Phase 1 and 22-24°C (minimum) and 32-33°C (maximum) in Phase II. Wind rose plots are included as **Fig. 2.**
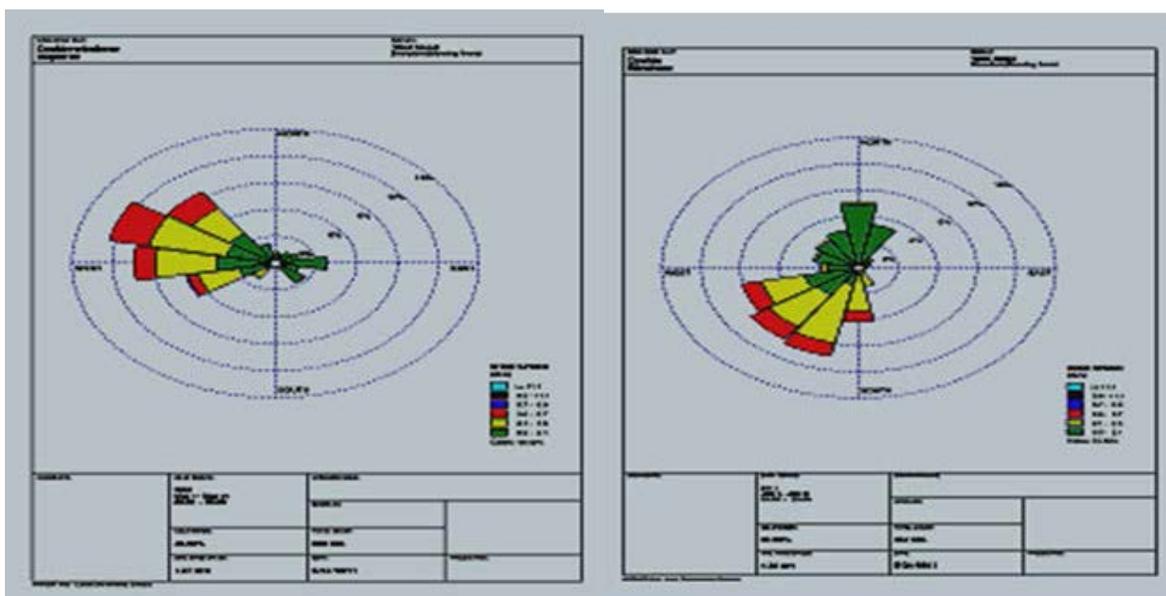

Figure 2: Wind rose plots showing-NW wind in May 2010 and SW wind in January 2011.

Relative humidity varied from 71-82% (premonsoon month) and it remains stagnant as 71% in phase I. Phase II marks the variability in humidity as 78-79% in premonsoon month and 68% in post monsoon period. Throughout the study period, the wind speed varied from 4.6 m/s (January 2011) - 6.7 m/s (May 2010). January 2011 and 2014 obtained seldom rainfall whereas it reaches a maximum of 331mm (October 2013). The meteorology experienced in the study period is configured as **Table 1**.

Sampling Equipment and Protocols: Trace gases in the ambient air were collected using High Volume Sampler (Envirotech, APM - 415). In this investigation two sampling phases are included in order to check the consistency in pollution trend after a two year gap. Hence the programme was split into Phase I and Phase II for checking the pollution index and concordance in pollution level. Phase I included the collection of samples with duplicate from six sites.

The period involved May 2010(pre-monsoon), January 2011(post-monsoon), May 2011(pre-monsoon) and November 2011(post-monsoon). The hot spots identified from Phase I analysis are E1, R2 and C1with respect to most of the analyte including trace gases. Hence the experiment was repeated as Phase II and samples with duplicate were collected from the above said hot spot sites (E1, R2 and C1) which are screened out as: one estuarine, riverine and coastal site in three months October 2013, January 2014 and March 2014. In the present work, day time sampling in between 10 am to 6 pm was performed and the sampling duration was fixed as three hours. The rate of flow was adjusted to 1.1 m^3/mt using a rotameter. Supporting data (meteorological data) including wind direction, wind speed, rain fall and temperature has been incorporated for interpreting the resulted inferences (**Table 1**).

Trace gases SO_2, NO_2 and NH_3 were collected from six sites (E1, E2, R1, R2, C1 and C2) with four samples with duplicate from all sites during Phase I and three sites (E1, R2 and C1) with three samples with duplicate from the respective sites during Phase II sampling periods, representing three distinct topographical regimes (estuarine, riverine and coastal).

Average of four samples in Phase I and three samples in Phase II are taken for assessing the air quality index at the respective sites. Gaseous pollutants are collected in impinger tubes (Midget impingers) having 35 ml capacity containing the characteristic absorbing media and the flow of sampling air through each impinger tubes can be controlled by individual system, connected to the manifold and the samples were preserved till analysis. Trace gases estimated are: SO_2, NO_2 and NH_3 referring standard colorimetric method. The estimates were calibrated against that of earlier published works[48,33].

Air Quality Standards and Air Quality Index (AQI): In India, the Central Pollution Control Board (CPCB) is the authority to assure the environmental pollutant level status and identifies four categories as: low, moderate, high and critical. The CPCB and NAAQ[38] insists the pollutant level for residential areas as 60 ($\mu g/m^3$) for three pollutants, SO_2, NO_2 and PM_{10}. The State Pollution Control Board in Kerala (KPCB) also monitors the air quality in different cities and displays their data at several locations or in local newspapers for each city for the benefit of the general public and used in this investigation appended in the **Tables 2 and 3**.

Table 2: Ambient air quality standards by CPCB, (NAAQ, 2009).

Pollutants	Time-weighted average	Concentration in ambient air		Sensitive Areas	Method of measurement
		Industrial Area	Residential Rural & other Areas		
Sulphur dioxide (S0$_2$)	Annual Average*	80 µg/m^3	60 µg/m^3	15 µg/m^3	Improved West and Geake Method -Ultraviolet Fluorescence
	24 hours**	120 µg/m^3	80 µg/m^3	30 µg/m^3	
Oxides of Nitrogen as (N0$_2$)	Annual Average*	80 µg/m^3	60 µg/m^3	15 µg/m^3	Jacob &Hochheiser Modified (Na-Arsentie) Method
	24 hours**	120 µg/m^3	80 µg/m^3	30 µg/m^3	Gas Phase Chemiluminescence
Ammonia (NH$_3$)	Annual Average*	0.1 µg/m^3	0.1 µg/m^3	0.1 µg/m^3	Indo- Phenol Blue Method.
	24 hours**	0.4 µg /m^3	0.4 µg /m^3	0.4 µg /m^3	

*Annual Arithmetic mean of minimum 104 measurements in a year taken twice a week 24 hourly at uniform interval.

**24 hourly/8 hourly values should be met 98% of the time in a year. However, 2% of the time, it may exceed but on two consecutive days.

Table 3: Meteorological Data collected during the sampling period.

Sampling Periods	Min Temp (°C)	Max Temp (°C)	Range of Temp (°C)	Relative Humidity (%)	Wind Speed (m/s)	Rainfall (mm)
May 2010	27	34	7	71	6.7	327
January 2011	22	31	9	71	4.6	0
May 2011	26	33	7	82	6.7	286
November 2011	24	33	9	71	4.8	108
October 2013	24	32	8	78	5.2	331
January 2014	22	33	11	68	4.6	0
March 2014	25	35	10	79	5.5	22

The air quality index (AQI) was calculated using the method suggested by[39] and is calculated by the formula

Q= (V/ V$_s$) x 100

Q = quality rating, V= the observed value of pollutant, V_s= standard value recommended for that pollutant. The standard value (V_s) recommended for NO_2 and SO_2 by NAAQ on 24/8 hourly sampling basis in residential areas is $80\mu g/m^3$. The calculation of AQI in the present investigation is based on this standard value which provides categorizing the sites based on air quality (**Table 4**).

Table 4: Air quality categories based on AQI.

Category	AQI of ambient air	Description of ambient air quality
I	Below 10	Very clean
II	Between 10-25	Clean
III	Between 25-50	Fairly clean
IV	Between 50-75	Moderately polluted
V	Between 75-100	Polluted
VI	Between 100-125	Heavily Polluted
VII	Above 125	Severely polluted

Analytical Methods for Quantification of Trace Gases: The samples in the absorbed medium are estimated colorimetrically using spectrophotometer (GENESYS- 10UV- Thermospectra). Sulphur dioxide is estimated on the basis of modified[40]. The gas is collected in an impinger containing 20 ml absorbing medium, sodium tetrachloromercurate. It is treated with sulphamic acid, acid bleached p-rosaniline hydrochloride converting to a dye and the absorbance is measured at 560 nm. Nitrogen dioxide is measured using modified Jacob and Hochheiser[41] method (1968) in which the gas is collected in alkaline sodium arsenite (20ml) and the colour development is effected by adding sulphanilamide and N (1-Napthyl ethylene diamine dihydrochloride) with the absorbance at 540 nm. Ammonia in ambient air is estimated by Indophenol-blue method[42]. Ammonia is collected by bubbling a measured volume of air through a dilute solution of sulphuric acid (20ml) to form ammonium sulphate and is analyzed colorimetrically by reaction with phenol and alkaline sodium hypochlorite to produce indophenols, measured at 630 nm on a spectrophotometer.

RESULTS AND DISCUSSION

The current study included the trace gases, which is the dispersion medium of the colloidal system, since trace gas-particulate equilibrium play a pivotal role in controlling the pollution hazard. Temporal and spatial distribution trend in the trace gases were encountered in four months (Phase I): May 2010, January 2011, May 2011 and November 2011 and it covers two post and two pre monsoon months. The spatial and temporal heterogeneity of the trace gases, SO_2, NO_2 and NH_3 which are determinants in P^H maintenance of the atmosphere and consequently ecosystem sustainability are explained herewith. From the wind direction plot (**Fig: 2**) it is observed that the prevailing wind at Kochi is easterlies which has profound influence on the dispersion of trace gases. Throughout the sampling period moderate precipitation were experienced. 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). In the present study period, it is noticed that thinning of monsoonal rain fall and spreading over the entire sampling period was noticed in Phase I. The experiment was stretched to Phase II for calibrating the analysis comprising three

months, October 2013, January 2014 and March 2014 selecting three hot spot sites E1, R2 and C1 constituting one estuarine, riverine and coastal sites respectively.

Distribution Profile of SO₂, NO₂ and NH₃ during Phase I sampling: Near surface aerosol was collected in the study in order to assess the air quality over the land and water surface. These could identify the hot spot area and for the subsequent validation towards health effects since the concentration of near surface aerosol is a measure of air quality and aerosol source strength at a particular location[43]. The overall inter-site comparison of data obtained for the concentration of trace gases revealed that the highest concentration of SO_2 gas is found at the riverine station R2 (126.9µg/m^3, May 2010) (**Table 5**) and the lowest concentrations at R1 (Below Detectable Limit, (BDL), May 2011) and C2 (BDL, January 2011).

Table 5: Concentrations of NO₂, SO₂ and NH₃ during Phase I sampling period.

Sampling period	Concentration of SO_2 (µg/m^3)					
Phase I	E1	E2	R1	R2	C1	C2
May, 2010	29.68	25.37	31.77	126.9	52.8	14.74
Jan, 2011	10.5	35.9	14.7	12.6	6.4	BDL
May, 2011	10.9	10.9	BDL	4.9	14.9	17.5
Nov,2011	13	1	0.5	0.5	4.1	1.5
Sampling period	Concentration of NO_2 (µg/m^3)					
Phase I	E1	E2	R1	R2	C1	C2
May, 2010	3.15	35.36	52.42	4.21	5.89	8.42
Jan, 2011	11.76	21.97	35.2	19.68	48.52	15.31
May, 2011	6.46	23	10.21	33.95	8.13	5.52
Nov,2011	2.7	14.9	26.14	37.45	23.74	35.09
Sampling period	Concentration of NH_3 (µg/m^3)					
Phase I	E1	E2	R1	R2	C1	C2
May, 2010	57.38	29.9	41.76	104.1	29.9	27.6
Jan, 2011	41.88	33.42	17.72	20.94	24.16	12.08
May, 2011	9.93	5.24	5.24	20.76	14.31	13
Nov,2011	80.9	18.52	21.34	37.04	80.75	13.69

The highest concentration of NO_2 is reported at R1 site (52.42µg/m^3, May 2010) and least concentration at E1 (2.70 µg/m^3, November 2011). Enrichment of NH_3 was found to be prominent at riverine station R2 (104.10µg/m^3, May 2010) whereas lesser concentration were detected in two sites E2 and R1 (5.24µg/m^3, May 2011). Periodic comparison of data regarding trace gases in each month portrays that in May 2010 riverine station R2 is enriched in SO_2 (126.9 µg/m^3) and NH_3 (104.1µg/m^3) whereas enrichment of NO_2 (52.42µg/m^3) is observed at the riverine station R1. During the sampling period January 2011 similar trend in enrichment for SO_2 (35.9µg/m^3) and NH_3 (41.88µg/m^3) was observed in estuarine stations E2 and E1 respectively; whereas NO_2 was enriched at the coastal station C1 (48.52 µg/m^3). In the month of May 2011, enrichment of SO_2 (17.5µg/m^3) and NH_3 (14.3 µg/m^3) is prominent at coastal sites C2 and C1 respectively. NO_2 significantly enriched in the riverine station R2 (33.9µg/m^3). November 2011 exhibited significant enrichment in SO_2 (13µg/m^3) at the estuarine site E1; NH_3 was observed to be enriched in both

estuarine station E1 (80.9µg/m^3) and coastal station C1 (80.75µg/m^3) whereas NO$_2$ elevation recorded at the riverine site R2 (37.45µg/m^3).

The Phase I data analysis revealed that among the estuarine sites sampled E1, the predominant dumping area of organic and inorganic waste, showed enrichment of SO$_2$ except in the month, January 2011. The annual average value (average of four sample concentrations) of SO$_2$ concentration at this spot, near Cochin backwaters, E1, was 16.02 µg/m^3. This concentration was closer to the annual average concentration, 19.9 µg/m^3 by Virkkula[45]. The concentration of SO$_2$ gas at the estuarine site, E2, is observed to be varying from the minimum value (1.0µg/m^3) in the month, November 2011 to the maximum (35.9µg/m^3) in the month, January 2011.The average value for the entire sampling period observed is 18.29µg/m^3. The two estuarine sites shows difference in seasonal trend in the month, January 2011 and depict the minimum at E1 and maximum at E2 **(Table 5)**. The observed trend can be associated to the difference in the dispersion rate, potential sources and atmospheric conditions. Analytical data for the concentration of NO$_2$ shows that at estuarine zone, E1, the maximum value (11.76µg/m^3) is reflected in the month, January 2011 and the minimum concentration (2.7µg/m^3) is noticed in the month, November 2011. The average value for the entire sampling period recorded for NO$_2$ concentration in this analysis is 6.019µg/m^3. E2 exemplifies the highest concentration (35.36µg/m^3) in the month, May 2010 and a diminished mass (14.9µg/m^3) in the month, November 2011. The average value for the entire Phase I sampling period (23.9µg/m^3) is noticed at the estuarine spot on the bank of Cochin Estuary. Ammonia concentration at E1 recorded is 80.9 µg/m^3 in the month, November 2011 and the least mass (9.93µg/m^3) noted in the month, May 2011. The average mass during the entire Phase I sampling period (47.515µg/m^3) is found in this estuarine zone. The estuarine spot, E2, is showing an elevated concentration of NH$_3$ as 33.42µg/m^3 in the month, January 2011. The highest loading (33.42µg/m^3) is observed in the post monsoon month, January 2011 and the lowest value (5.24µg/m^3) noted in the pre monsoon month, May 2011. Fishery export units and coconut husk degradation products and also from butcheries, cattle farms, sanitary units and sewage waste, provide excellent sources for ammonia gas at this site. The two estuarine spots, E1 and E2, are in the neighborhoods with similar type of pollution sources such as shipyard, industries and automobiles and are affected by the same type of pollutants. The bio waste from hotels and ships add to the gaseous pollution load in this area which substantiate the obtained results. Among the estuarine sites, E1 is more prone to SO$_2$ and NH$_3$ pollution whereas enrichment of NO$_2$ was observed at E2 (**Table 5**).

Riverine stations (R1 & R2) in the present study experiences considerable pollution from automobile emissions in addition to other sources such as agricultural farm lands. At R2, the enrichment in SO$_2$ (126.9µg/m^3) was noticed in the month, May 2010. This riverine site marks least mass (0.51 µg/m^3) in the post monsoon month, November 2011, similar to E2. **Table 5** indicates the maximum and minimum range of SO$_2$ as BDL (R1) in the month, May 2011 to 126.9µg/m^3 (R2) in the month, May 2010 respectively. The average concentration during the entire Phase I sampling period in riverine stations observed is 11.74 µg/m^3, which is less than that present in the estuarine zone, E1 and E2. Similar decrease in post monsoon month was noted by Kaushik[27] an investigation conducted at Haryana. The summer month, fallen in the pre monsoon period, is comparatively dry (experiences summer shower) than the post monsoon month which experiences abundant monsoonal rain fall. As known, most of the atmospheric gases are soluble in water and the major transformation pathway is photochemical in origin. The lowest concentration at R1 site in the month, May 2011 can be endorsed to the extensive gas to particle

conversion in the kerb site where the only and major source is vehicular exhausts. Moreover, enhanced fossil fuel combustion can contribute much to the pollution event.

The overall data analysis with respect to SO_2 portrays enrichment in riverine/industrial site at R2 than at R1. The highest mass of NO_2 observed is $52.42\mu g/m^3$ in the month, May 2010 and a lowest concentration $(10.2\mu g/m^3)$ is noticed in the month, May 2011 at R1. The average concentration during the entire Phase I $(30.99\mu g/m^3)$ is noted in the present case. The enhanced concentration can be ascribed to the low rate of photochemical destruction. The industrial location, R2, exhibits maximum NO_2 concentration of $(37.45\mu g/m^3)$ in the month, November 2011 and a minimum value $(4.2\mu g/m^3)$ in the month, May 2010. The average concentration measured during the entire Phase I sampling is $23.82\mu g/m^3$. These two riverine sites differ in temporal maximum as May 2010 and November 2011 respectively as the enhancement period. The spatial enhancement order for NO_2 concentration can be depicted as R1 > R2. The range of NH_3 which shows predominantly biogenic in origin than industrial input follows the range as: 5.24 - $41.76\mu g/m^3$ at the riverine zone, R1 (**Table 5**). A maximum concentration of NH_3 (R2, $104.1\mu g/m^3$) is noticed in the month, May 2010 and minimum concentration $(5.24\mu g/m^3)$ in the month, May 2011. The average value during the entire Phase I sampling period observed is $21.55\mu g/m^3$. The high degree of fertilizer application containing NH_3 may be the endorsement for the elevation noticed in the respective months. A pre monsoon increment and post monsoon decline is reflected exhibiting clear temporal trend. The data shows that a maximum concentration of NH_3 is noted in the month, May 2010 $(104.1\mu g/m^3)$.

In coastal zone, the second coastal site, C2, exhibits a lower range than C1 for SO_2 concentrations. Emission from potential sources such as water transport can endorse to the above observed fact. At the coastal site, C2, the range is Below Detectable Limit (BDL) in the month, January 2011 and $17.5\mu g/m^3$ in the month, May 2011 and the average concentration during the entire phase I sampling period is $8.435\mu g/m^3$ (**Table 5**). The spatial allocation range with respect to SO_2 at the coastal zone is in the order C1 > C2. NO_2 concentration in the coastal site, C1, depicts the enriched quantity $(48.52\mu g/m^3)$ in the month, January 2011 and a minimum $(5.89 \mu g/m^3)$ in the month, May 2010 (**Table 6**).

Table 6: Concentrations of NO_2, SO_2 and NH_3 during Phase II sampling period.

Sampling period	Concentration of SO_2 ($\mu g/m^3$)		
Phase II	E1	R2	C1
Oct, 2013	BDL	33.08	BDL
Jan, 2014	117.2	102.9	91
Mar, 2014	167.4	BDL	BDL
Sampling period	Concentration of NO_2 ($\mu g/m^3$)		
Phase II	E1	R2	C1
Oct, 2013	BDL	BDL	7.38
Jan, 2014	BDL	20	BDL
Mar, 2014	20	20	20
Sampling period	Concentration of NH_3 ($\mu g/m^3$)		
Phase II	E1	R2	C1
Oct, 2013	38.8	47.8	81
Jan, 2014	61.14	24.22	119.8
Mar, 2014	81.4	43.4	62.4

The average concentration during Phase I (17.01 µg/m^3) is reflected with respect to NO$_2$ at the coastal zone, C1, with enhanced coastal activity. At the second coastal site, C2, a peak value (35.09 µg/m^3) is noticed in the month, November 2011 and a lowest value of (5.52 µg/m^3) is registered in the summer month, May 2011. The two coastal sites are related with the maximum (C2) and minimum (C1) falls in the same month, November 2011 and an average concentration value for NO$_2$ (16.08 µg/m^3) is noticed at C2 station. NH$_3$ concentration reflected the fact that at the coastal spot, C2 with almost same source pattern as that exhibited at C1. This second coastal site, C2 is exhibiting the concentration (27.6 µg/m^3) in the month, May 2010 and a decline (12.08µg/m^3) in the month, January 2011.

The trace gas, NH$_3$ concentration varies from 12.08 µg/m^3 in the month, January 2011to 27.6µg/m^3 in the month, May 2010 (**Table 5**). The seasonal pollution trend at C1 and C2 are reversely related. The average ammonia concentration noted is 16.5925µg/m^3 at C2. The average evaluated at C1 amount to 37.28µg/m^3 and the concentration range falls as 14.31µg/m^3 (May 2011) – 80.75µg/m^3 (November 2011).

The highest range in this coastal site (C1 > C2) may be due to injection of this gas through potential sources such as bio-waste degeneration and emission from meat processing units, cattle fields and sanitary areas.

Distribution Profile of SO$_2$, NO$_2$ and NH$_3$ during Phase II sampling: From the results outweighed in Phase I, a severe source impact was reflected rather than atmospheric conditions. Therefore, in order to verify concordance in temporal variability for trace gas concentration, the experiment was extended to Phase II by selecting three sampling sites (E1, R2 and C1) with prominent (hot spots) characteristics such as estuarine, riverine and coastal regime respectively and period as: October 2013, January 2014 and March 2014. Before the start of sampling in Phase II, heavy rain fall occurred and this contributed much towards the sweeping off traces gases[44]. This drift in air pollutants by frontal rain fall were perceived throughout the three sampling periods.

The variability in distribution pattern of trace gases in Phase II is illustrated in **Table 6** which clearly depicts the following observations. C1, the coastal site, is least concentrated with respect to SO$_2$ in Phase II (**Table 6**). The estuarine site, E1, recorded maximum SO$_2$ concentration (167.4 µg/m^3) during the Phase II. During January 2014 sampling, three stations (E1, R2 and C1), showed significant quantities of SO$_2$ gas. No significant variations (ranging from 0- 20µg/m^3) were observed for NO$_2$ during Phase II sampling scenario, since most of the stations exhibited lesser amount of NO$_2$.

The concentrations of NH$_3$ were found to be elevated as found during the Phase I sampling. The highest concentration of NH$_3$ was observed at the coastal site C1 (119.8µg/m^3) similar to that in the case of Phase I which substantiate the source characteristics (**Table 1**) prevailing in this site. AQI provides information about the air quality (**Table 4**). In the present investigation AQI was calculated for SO$_2$ and NO$_2$ alone (**Table 7 & 8**) since concentration of NH$_3$ showed irregular variations in its concentration.

The AQI for SO$_2$ reveals that in Phase I sampling most of the sites belong to the Category III (Fairly clean) and Category IV (Moderately Polluted) except R2 (158.63µg/m^3) in the month, May 2010 which shows a severe pollution (Category VII). R2 is an industrially clustered site which is severely polluted by the industrial emissions. AQI values for NO$_2$ also reveals that sampling sites belong to fairly clean (Category III) to moderate pollution (Category IV). The highest pollution was pointed out in riverine station R1 which justify the vehicular emission of NO$_2$.

Table 7: Air quality Index calculated during Phase I sampling period.

Sampling period Phase I	AQI calculated for SO_2					
	E1	E2	R1	R2	C1	C2
May, 2010	37.1	31.71	39.71	158.63	66	18.43
Jan, 2011	13.13	44.88	18.38	15.75	8	0
May, 2011	13.62	13.62	0	6.12	18.625	21.87
Nov, 2011	16.25	1.25	0.625	0.62	5.125	1.875
Sampling period Phase I	AQI calculated for NO_2					
	E1	E2	R1	R2	C1	C2
May, 2010	3.94	44.2	65.53	5.26	7.36	10.53
Jan, 2011	14.7	27.46	44	24.6	60.65	19.14
May, 2011	8.08	28.75	12.76	42.44	10.16	6.9
Nov, 2011	3.38	18.63	32.68	46.81	29.68	43.86

Table 8: Air quality Index calculated during Phase II sampling period.

Sampling Period	AQI calculated for SO_2		
Phase II	E1	R2	C1
Oct, 2013	0	41.35	0
Jan, 2014	146.5	128.62	113.75
Mar, 2014	209.25	0	0
Sampling Period	AQI calculated for NO_2		
Phase II	E1	R2	C1
Oct, 2013	0	0	9.22
Jan, 2014	0	25	0
Mar, 2014	25	25	25

AQI values during January 2014 (Phase II) sampling revealed an enrichment of SO_2 in the estuarine station (E1) and riverine station (R2) and they belong to the Category VII (severely polluted). The C1 site is also included under the heavily polluted Category VI. The AQI values for NO_2 were found to be in between Category I and II, which may be due to the sweeping or dilution of the NO_2, an easily photo-chemically changing constituent.

CONCLUSION

Enrichment of trace gases disturb the climatic condition in an area directly and indirectly and affect the health condition of the biosphere. The exceeding concentration may disrupt the climatic pattern also. The present study comprehended that the concentration of SO_2 (126.9 µg/m^3) and NO_2 (52.42 µg/m^3) is considerably high in the Phase I sampling period. The enrichment of these two gases in Phase I attributes

to the pollution through both industrial and vehicular emissions. Though source effect is more prevalent in Phase I analysis and it is clear that atmospheric condition plays vital role in dispersing the pollutants which is reflected from the abrupt change in concentration of nitrogen dioxide in Phase II. The organic degradation products emanating from sources like fishery export units, coconut husk degradation products ,butcheries, cattle farms, sanitary and sewage waste execute to enrichment of NH_3 concentration (Phase I -104.1 µg/m^3 & Phase II-119.8 µg/m^3) during both the phases of sampling. Sudden decrease in NO_2 concentration during Phase II sampling period may be due to the monsoonal rainfall affected. Among the estuarine sites, in Phase I, E1 is heavily loaded with trace gases. The industrial site, R2, is identified as the hot spot (Phase I) with respect to various trace gases and is more polluted than the other riverine site, R1. It is clear from the current analysis that among the coastal sites, C1, is more polluted than C2. The AQI values for SO_2 and NO_2 gases serve to point out Kochi area as moderately polluted which could pose health risk either alone or in combination with other pollutants. In comparison with the respective standards, the overall AQI is high which indicates possible threat to the residents in these localities and remedial measures should be adopted in the coming future.

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