Original Article

Formation of Atmospheric Sulfate under Elevated PM_{10} Concentration in Kanpur City: A Case Study

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Abstract

The study was primarily initiated to understand consistently low levels of SO_2 in a few cities in India in spite of rising SO_2 emissions. A literature review suggested a good possibility of chemical transformation of SO_2 to SO_4. Thus, the objective of research was modified as to understand the formation of SO_4 as a function of SO_2, and other constituents of atmosphere such as PM_{10}, water content, Ca, and pH. For this purpose, air quality monitoring was conducted at five locations (during 2013-14) representing various land-use patterns in the city of Kanpur, India. It was found that the sulfate levels were considerably high (2.77-43.6 $\mu g/m^3$) compared to levels in a few cities in the USA (1.9-3.6 $\mu g/m^3$ [13]; 15.7-18.4 $\mu g/m^3$, [1]; 4.0-14 $\mu g/m^3$ [7] and UK (3.2-9.0 $\mu g/m^3$ [11]). The high SO_4 levels provided a plausible explanation for low SO_2 concentration levels in the city of Kanpur. It was concluded that high levels of PM_{10}, Ca (acts as a catalyst for SO_2 oxidation) and high pH in atmosphere provide conductive environment for oxidation of SO_2 and eventual formation of SO_4.

Keywords: Sulfur dioxide, Sulfate, PM_{10}, Calcium, pH.

Introduction

Although sulfur dioxide (SO_2) emission levels in Indian urban centers continue to rise due to lack of legislative controls and unprecedented urbanization/ industrialization, the ambient SO_2 levels have remained well below acceptable levels. Moreover, there is little variation in air concentration of SO_2 both spatially and temporally (CPCB, 2004) [5]. Figure 1 presents number of times the 4-hour SO_2 concentration measurements (of National Ambient Air Quality Monitoring Program of India) stayed in a particular range over 220 locations spread over 80 cities in India in the year 1998.

It is clear from Fig. 1 that the ambient SO_2 pollution is very low, and generally in the range that is found in clean atmosphere (2.6-26 $\mu g/m^3$) [15]. The reason(s) for low concentration levels, individually or jointly include: (i) inaccurate SO_2 sampling/ analysis, (ii) significant physical scavenging (dry/wet deposition) and (iii) chemical transformation to SO_4. The possibility of SO_2 getting absorbed on the filter paper was also examined. It was found for several samples that the atmospheric concentrations of SO_2 with and without filter paper were almost the same. Since the national air quality monitoring program is operated under strict quality control and scavenging process not important close to the source, the plausible reason is the third one that SO_2 is chemically transformed. One of the important migration pathways of SO_2 includes transformation to SO_4 particulate through gas/ liquid phase reactions [4]. If it is believed that SO_2 is transformed to SO_4, the present SO_2 levels are not true indicators of sulfur pollution in the ambient air and there is a need to study sulfate levels too.

Once SO_2 is converted into SO_4, atmospheric particulate provides opportunity for SO_4 adsorption. The sixteen-year long landmark study in six US cities on health effects of pollutants by Dockery et al [7] has established that sulfate-rich fine particles show higher mortality than other particles in the atmosphere.

In order to address the issue of low SO_2 concentrations in Indian cities and considering the adverse health effects of sulfate, it was decided to examine sulfate levels in the city of Kanpur, India. The city of Kanpur has a population of about 3.2 million and is situated in north-central part of India (longitude 88° 22' E and latitude 26° 26' N).

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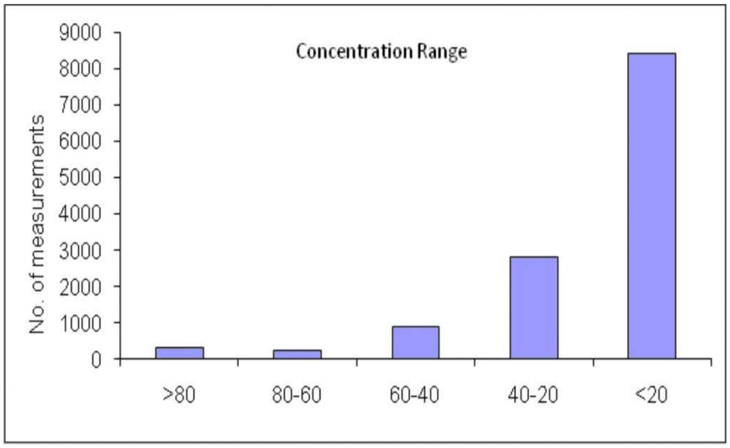

Figure 1.Distribution of SO_2 Concentration in India, 1998

The overall objective of this study was to examine SO_4 levels in the city of Kanpur under varying urban land-use patterns and formation of SO_4 particulate in presence of other constituents of the atmosphere such as, PM_{10} Ca, pH (of collected PM10), NH_3, and atmospheric water content.

Migration Pathways of Sulfur Dioxide to Sulfate

In overall analysis, sulfur dioxide slowly becomes oxidized and hydrolyzed to form sulfuric acid. The oxidation rate tends to limit the acid formation process; the oxidation can occur either in the gas phase or in a condensed phase within water drops. The gas phase oxidation tends to be slow and in the absence of catalyst or highly reactive species (OH, HO_2 or RO_2, O_3) does not occur at a significant rate [14]. The reaction within water drops is catalyzed by the presence of certain trace compounds [8], provided the pH is above 5. At higher pH, the oxidation occurs at a significant rate without the presence of catalysts [14]. The sulfate formation rates are extremely small except for high pH [3]. Apparently the oxidation of sulfite ion limits the rate of oxidation and the concentration of this ion is very small at low pH. Moreover, the oxidation itself produces proton and in the absence of substances, which neutralize the acid as it is formed, such as alkaline particles, ammonia, etc., the sulfate production rate is quenched, as the system becomes more acidic [14]. The dissolution of atmospheric ammonia and role of alkaline particles removes excess protons and in this way, is an effective but indirect ‘catalyst’ for sulfate production.

The brief literature review presented here suggests that oxidation of SO_2 to SO_3 is an important step which eventually leads to SO_4 formation. The atmospheric reactions are quite complex and it is difficult to determine/ estimate the extent (significance) of one reaction over another.

The literature survey does indicate that the important environmental parameters (physical and chemical) on which sulfate formation depends include SO_2, particulate (PM_{10}), Ca (as a catalyst and as acid neutralizing ion), pH, NH_3 and water content and perhaps other catalysts. In order to assess sulfate quantity and to understand role of other environmental parameters in sulfate formation, it was decided to measure these parameters in the field.

Study of Ambient Air SO_4 Levels (Outside India)

There is no study in the literature to indicate SO_4 ambient air levels in Indian cities. However, there are a few studies in literature, which quote sulfate concentration in USA and UK [1, 7, 11, 13].

Sandberg et al. [13] reported five-year mean for SO_4 as 2.68 $\mu g/m^3$ for San Francisco Bay area; the annual average varied between 1.9 to 3.6 $\mu g/m^3$ and SO_2 levels were reported between 5 and 20 $\mu g/m^3$. The peak values of SO_4 varied between 7.7 to 22 $\mu g/m^3$ for the period from 1969 to 1973. Altshuller [1] studied the sulfate levels in various regions of US. For East Coast, the two-year average levels of SO_2 varied between 66 $\mu g/m^3$ (1969-71) to 147 $\mu g/m^3$ (1963-65) and the SO_4 levels varied from 15.7 $\mu g/m^3$ (1969-71) to 18.4 $\mu g/m^3$ (1963-65). The study by Altshuller [1] reported higher values of SO_4 as compared to values reported by Sandberg et al. [13]. The two studies mentioned above also indicate that SO_4 and SO_2 levels were correlated and the East Coast area was more polluted in terms of both SO_2 and SO_4 levels in 1960s and 1970s.

The other study by Quarg [11], although has not shown the SO_2 levels, does indicate SO_4 levels in various urban areas in UK which range from 3.22 to 9.0 $\mu g/m^3$. It may be noted that SO_4 levels in UK and some of the cities in USA are comparable.

Study Area and Field Study

As stated in the introduction, the study area for this research was the city of Kanpur, India. The present annual (2013) SO_2 concentrations levels at four different locations in Kanpur showed low levels with very little variations (16.17±6.17, 16.71±6.11, 17.38±6.56, 16.66±6.11 $\mu g/m^3$). These levels are very low for the size of city and emission quantities. The low levels of SO_2 in Kanpur are similar to SO_2 levels in other cities in India, as discussed in introduction. The major sources of SO_2 emissions in the study area include industrial, vehicular and other combustion processes. A study by CPCB [6] estimated total SO_2 emissions as 42,758 kg/d in the city. The major SO_2 contributions are from a coal-based 200 MW thermal power plant (industries), and from 250,000 vehicles plying on the road.

For this study, the following five locations have been taken throughout the city (Fig. 2) for ambient air quality measurements.

1. GT Road (GT) (road side);
2. Agricultural University (AU) (residential area);
3. Naveen Market (Navee) (commercial area);
4. Lajpat Nagar (Laj) (industrial area);
5. IIT Kanpur (IIT) (clean area, control site)

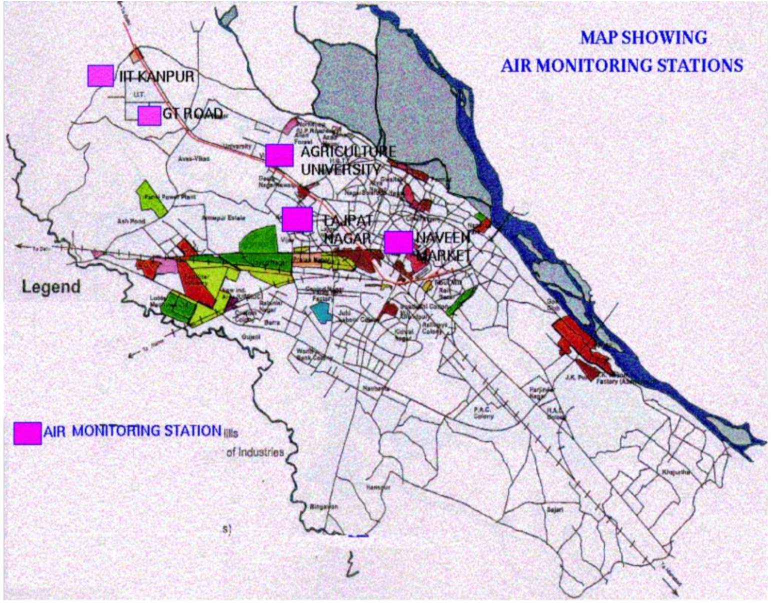

Figure 2.Air Monitoring Stations in Kanpur, India

Materials and Methods

In view of literature survey, the following parameters have been studied in the field.

1. SO_4
2. SO_2
3. PM_{10}
4. Ca (of collected PM_{10})
5. pH (of collected PM_{10})
6. Ammonia (NH_3)
7. Water content

The water used for all chemical analyses was ultrapure distilled water, and all chemicals were of analytical reagent grade. All filters used for collecting the particulate matter were glass microfiber filters (size 20.3×25.4 cm) of Whatman company.

Instruments Used and Their Specifications

- High volume sampler capable of measuring PM10 (APM 620, Envirotech)
- Handy sampler (Envirotech, New Delhi)-Battery operated sampler for gaseous sampling only
- Flame photometer (No. 128, Systronics India)

Sampling and Measurement Procedure

- PM_{10}: Gravimetrically using the high volume sampler
- Sulfur dioxide: Absorption in Tetrachlromercurate and spectrophotometrical analysis following the method given in *Air Sampling and Analysis* [9].
- Sulfate: Extraction and analysis as per *Air Sampling and Analysis* [9].
- pH: Extraction for pH of collected PM_{10} as per ASTM [2] method and pH-meter analysis.
- Calcium: Extraction using acid digestion and analysis on atomic absorption spectrophotometer.
- Water content: Data obtained from Indian Air Force Meteorological Station, Chakeri, Kanpur.
- Ammonia: Data obtained from NEERI, Kanpur, for the days of monitoring.

Preliminary Results

Ca and SO_4 Levels in Soil (at Control Site)

Before initiating the field study, four soil samples were taken at different locations at the control site (i.e., IIT Kanpur) to know about the background level of Ca and SO_4 in the unpolluted soil. It may be mentioned that the SO_4 levels in the soil were insignificant (0.2735±0.01907 mg/g), whereas Ca levels were significant (2.51±1.466 mg/g). It suggests that the SO_4 levels in atmosphere are not likely to be caused by soil dust, and all SO_4 levels in atmosphere can be attributed to secondary formation from SO_2. The average ratio of SO_4/Ca in soil was 0.11 (range 0.07 to 0.29).

Soil SO_4 Levels at GT Road

The high-volume sampler was kept at the roadside for sampling at the GT Road (about 3 m away from the edge of the road). Since GT Road is heavily polluted in terms of emissions from diesel-driven vehicles, SO_4 levels in soil were also measured (0.741±0.08 mg/g) at this site. This was done to assess if the SO_4 levels at this site could be of soil origin.

Overall Results

The results obtained for the parameters studied at various sampling locations are summarized in Table 1.

Statistics	SO_4 $\mu g/m^3$	SO_2 $\mu g\ /m^3$	PM_{10} $\mu g\ /m^3$	Ca $\mu g\ /m^3$	Water Cont., %	pH	NH_3* $\mu g\ /m^3$
IIT Kanpur (No. of samples=16)							
Mean±SD	3.4±.7	5.44±1.58	62±11.22	7.52±0.09	1.99±0.411	8.5±09	
GT Road (No. of samples=7)							
Mean±SD	26.8±9.2	28.6±9.9	401±60.28	20.17±9.1	1.48±0.016	8.6±08	-
Agricultural University (No. of samples=15)							
Mean±SD	14.9±1.9	11.0±2.7	226±141.5	8.0±29	1.67±0.294	8.56±.07	85.1±13.1
Naveen Market (No. of samples=15)							
Mean±SD	15.5±2.2	14.6±3.8	281±169.9	8.35±2.9	1.67±0.29	8.60±.09	92.8±16.2
Lajpat Nagar (No. of samples=15)							
Mean±SD	20. ±4.2	17.73±4.38	384±138.6	11.59±2.7	1.66±0.29	8.60±.07	88.8±18.5

*Data taken from NEERI (National Environmental Engineering Reassert Institute), Kanpur

Table 1.Air Quality Monitoring Results

Results and Discussion

Location Specific

IIT-Kanpur: This is a clean site (with almost negligible emissions) as indicated by the low levels of both SO2 and PM10. SO4 levels are also low but higher than what could be expected given the extremely low SO_2 concentrations. The pH of PM_{10} collected on the filter paper remained constant all through in the range from 8.4 to 8.7. The alkaline pH can be attributed to soil, which is rich in Ca.

Although pollution levels are low, the SO_4 levels at this site are however, comparable with annual levels (1.9-3.6 $\mu g/m^3$) reported in San Francisco Bay Area [13]. However, the average SO_2 levels in San Fransisco Bay Area were higher by a factor 2-4 compared to this site. It suggests that even at this clean site, SO_4 levels are higher than what could be expected given the low SO_2 concentrations.

GT Road: This location is found to be the most polluted for obvious reasons. This site is influenced by emissions from heavy traffic, mostly diesel-driven vehicles. These vehicles emit considerable amount of both SO_2 and PM_{10} leading to higher ambient SO_2 (16.73-46.25 $\mu g/m^3$) and PM_{10} levels (272-445 $\mu g/m^3$). The calcium content at this site is also high (11.38-37.4 $\mu g/m^3$). But it may be noted that the Ca content as compared to PM_{10} levels has reduced (in comparison to IIT Kanpur site) suggesting that PM_{10} is not being contributed significantly from the road side dust and it has its origin perhaps from vehicular emissions.

Agricultural University: This is a residential area. The SO_2 (7.0-18.0 $\mu g/m^3$) and PM_{10} (71.46-335.83 $\mu g/m^3$) levels are lower than those at GT Road. SO_4 (12.14-18.92 $\mu g/m^3$) levels are higher than what could be expected given the low SO_2 concentrations. The calcium content (4.07-14.42 $\mu g/m^3$) at this site is in expected range for the obtained PM_{10} concentrations. The pH of PM_{10} collected on the filter paper remained constant all through in the range from 8.5 to 8.7.

Naveen Market: This is a commercial area. The SO_2 levels (8.0-21.0 $\mu g/m^3$) although expected to be higher than residential area, show no significant change (compared to Agricultural University). PM_{10} (114.22-634.68 $\mu g/m^3$) levels are much higher when compared to Agricultural University site. The SO_4 (12.08-18.90 $\mu g/m^3$) levels are higher than those obtained at Agricultural University; one can argue that lower SO_2 levels can be explained by higher sulfate levels (i.e., conversion of SO_2 to SO_4). The calcium content at this site was found to be in the range 4.37-13.77 $\mu g/m^3$. The pH of PM_{10} collected on the filter paper remained constant all through in the range of 8.4 to 8.7.

Lajpat Nagar: This is an industrial area showing significant pollution (in relative sense) for all pollutants. The SO_2 (12.5-29.0 $\mu g/m^3$), PM_{10} (221.77-650.73 $\mu g/m^3$) and SO_4 (11.54-23.32 $\mu g/m^3$) levels are higher and comparable with the pollution levels at GT Road. The calcium content at this site (6.07-16.74 $\mu g/m^3$) is higher than in other areas as PM_{10} levels are also high. The pH of PM_{10} collected on the filter paper remained constant all through in the range from 8.5 to 8.7.

A few findings can be drawn if one looks at the obtained results in totality; these findings are described below.

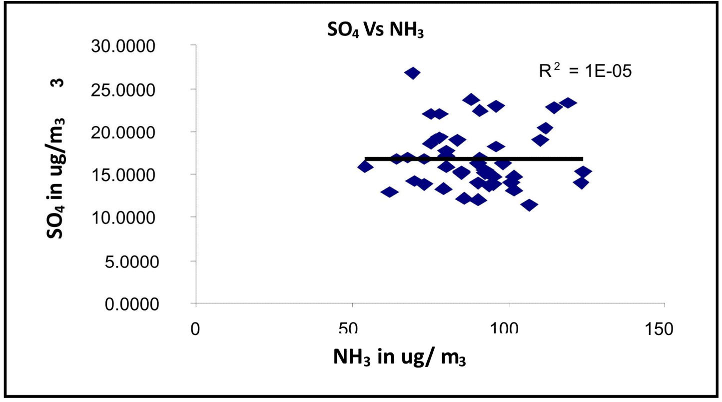

Figure 3.SO_4 vs NH_3

NH_3 vs Sulfate

As reported in Table 1, the NH_3 levels in the ambient air for the same days when monitoring was conducted (for this study) were obtained from NEERI, Kanpur. Figure 3 shows the scatter plot of NH_3 and SO_4. This can be seen that these two constituents of atmosphere seem to have no relation. This finding matches with results reported by Samara et al. [12] for wet precipitation in Thessaloniki, Greece, during the period 1989-90. They found that ammonium ions are poorly correlated with SO_4^{-2} while they are better correlated with NO_3^- and suggested that ammonia gas reacts with nitric acid aerosol to form NH_4NO_3. Similar conclusions about calcium association with sulfates and ammonium association with nitrates have also been reported for other places [10, 12].

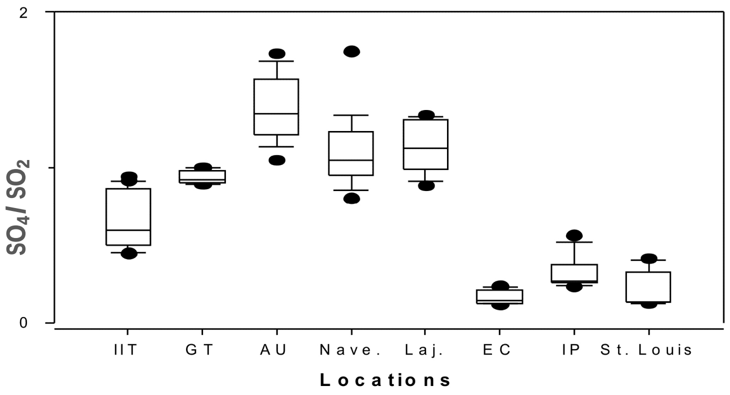

Figure 4.SO_4 to SO_2 Ratio at Various Locations (This Study) and Sandberg et al. [13] and Altshuller [1]

SO_2 vs Sulfate

It has been found that at all locations the SO_2 to SO_4 conversion is much higher than what has been reported by Sandberg et al. [13] (at St. Louis) and Altshuller [1] (at East Coast and Indianapolis). Figure 4 presents the comparative SO_2 to SO_4 ratio for various locations of this study and those reported by Sandberg et al. [13] and Altshuller [1]. Figure 4 clearly indicates that conversion of SO_2 to SO_4 is significant in the study area. In fact, the absolute sulfate levels at the sites of this study are also higher than those found by Sandberg et al. [13] and Altshuller [1].

The question, which needs to be answered at this point, is why is the situation so different in the study area? For this purpose, the correlation between various parameters is examined (Table 2). The correlation table shows that sulfate levels positively correlate with SO_2, PM_{10}, and Ca, which are present in plenty in the atmosphere of Kanpur. It may be mentioned that Ca acts not only as pH raiser but also has been reported to be a catalyst in SO_2 oxidation (Hoffman and Jacob, 1984). The other significant reason for higher sulfate conversion is the high pH. Whatever may be the mode of oxidation of SO_2 to SO_3, the oxidation increases with increase in pH [3]. The high levels of PM_{10} in the study area provide opportunity for SO_4 to get adsorbed and the PM_{10} particles may also contain various catalysts, which enhance the oxidation of SO_2. It can thus be concluded that the atmospheric conditions in the study area are conducive for sulfate formation and there are enough evidence and reasons to believe that SO_4 formation is quite significant in the study area.

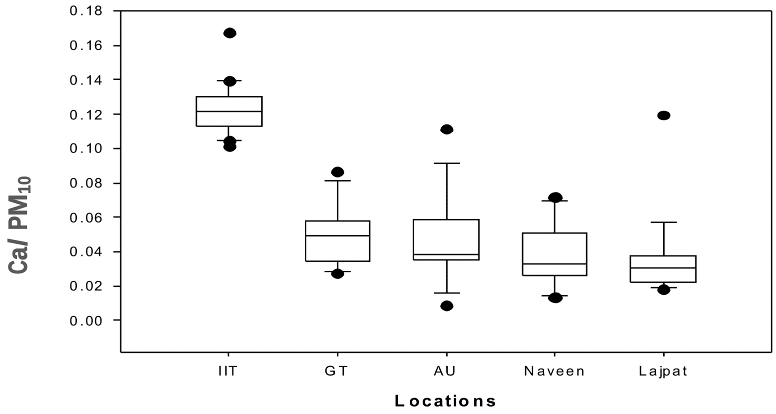

Figure 5.Ca to PM_{10} Ratio at Various Locations

PM_{10} vs Calcium

Figure 5 presents the comparative representation of PM_{10} to Ca ratios for various locations. This figure clearly indicates that PM_{10} to Ca ratio is higher at all locations other than at IIT Kanpur (unpolluted site). If one takes Ca as the indicative species of soil dust, it can be argued that contribution to PM_{10} is largely from sources other than soil (i.e., anthropogenic sources). With the same argument, it can be said that the control site (IIT Kanpur) is influenced mostly by soil dust.

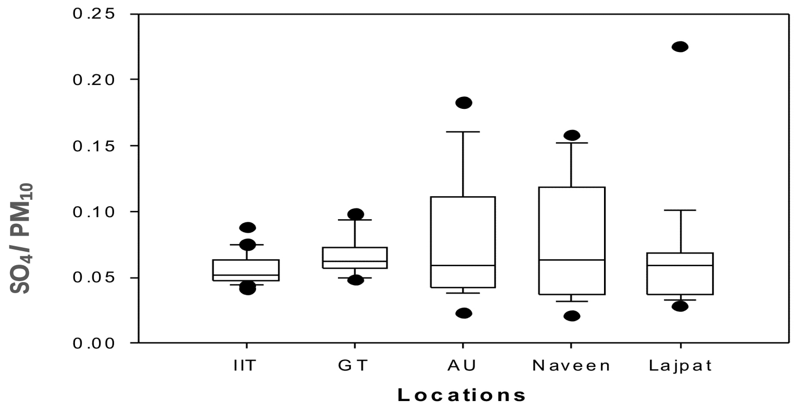

Figure 6.SO_4/ PM_{10} at Various Locations

SO_4 vs Particulate Matter

Figure 6 presents the comparative ratio of SO_4 to PM_{10} at various locations. This figure indicates that SO_4 to PM_{10} ratio is similar at all locations with exception at Agricultural University. This indicates positive correlation between SO_4 and PM_{10} levels; this behavior of SO_4 and PM_{10} correlation is explained while discussing SO_2 versus SO_4.

	SO_4	SO_2	PM_{10}	Ca	W/c	PH
SO_4	1.00					
SO_2	0.93	1.00				
PM_{10}	0.64	0.55	1.00			
Ca	0.61	0.67	0.49	1.00		
w/c	–.36	–0.26	–0.19	–0.04	1.00	
pH	0.00	0.03	0.08	0.11	–0.10	1.00

Table 2.Correlation Matrix

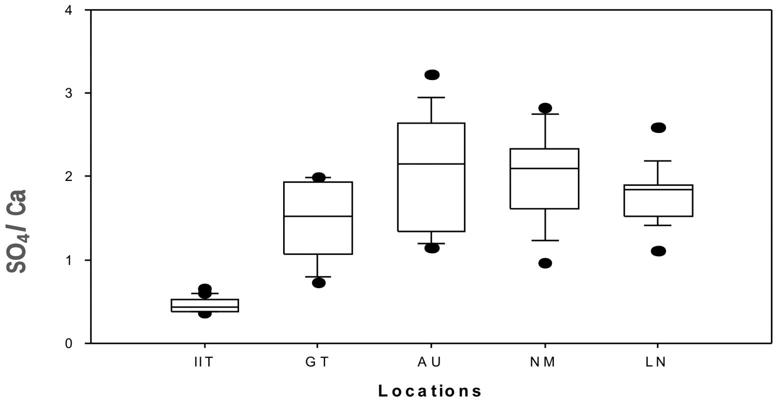

Figure 7.SO_4 to Ca Ratio at Various Locations

SO_4 vs Calcium

Figure 7 presents the comparative ratio of SO_4 to Ca at various locations. This figure indicates that SO_4 to Ca ratio is similar at all locations with exception at IIT Kanpur. This indicates positive correlation between SO_4 and Ca. This behavior is expected as Ca raises the pH as well as acts as catalyst for oxidation of SO_2 to SO_3.

Since water content and pH do not correlate with SO_4, their ratios with SO_4 are not discussed here. This insignificant correlation is more due to narrow ranges of pH (8.2-8.6) and water content found in the study is than other scientific reasoning.

Conclusions

It was found that in the study area of city of Kanpur, in spite of reasonably high SO_2 emission, the SO_2 levels were low. This unusual finding is explainable with the fact that corresponding SO_4 levels are high all the same. This suggests that SO_2 level alone in the ambient air is not true indicator of sulfur pollution in general and particularly in Kanpur and, therefore, sulfate measurement should become additional pollutant parameter for monitoring. The regular SO_4 measurement has commenced since July 2006 in Kanpur city. Sulfate levels correlate positively with SO_2, PM_{10} and Ca. The high levels of PM_{10} in the study area provide opportunity for SO_4

to get adsorbed and Ca raises the pH (>8) making the overall environment conducive for sulfate formation. Since health effects of sulfate are well known, the pollution control agencies were advised to measure sulfate and be not complacent with low SO_2 levels,

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