

SOURCES OF SULFUR DIOXIDE IN THE SUMMERTIME NW-IGP

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A dissertation submitted for the partial fulfillment of BS-MS dual degree in Science



Indian Institute of Science Education and Research Mohali
November 2014.

[Geben Sie Text ein]

Certificate of Examination

This is to certify that the dissertation titled “Sources of SO₂ in the NW-IGP” submitted by Ms. Gursharanjeet Sandhu (Reg. No. MS09055) for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Dated: November 25, 2014

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Baerbal Sinha at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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Dated: 25 November, 2014

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Baerbal Sinha

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Notation (Abbreviations)

1. DMS- dimethyl sulfide
2. ppt- part per trillion
3. ppm –parts per million
4. ppbv –parts per billion per volume
5. NW-IGP – North-West Indo-Gangetic plane
6. kt/yr – kilotonnes per year
7. Tg – Teragrams
8. Gg – Gigagrams

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Abstract

The aim of the project was to analyze the sources of emission of sulfur dioxide in my campus IISER Mohali using the Model 43i Thermo Scientific SO₂ Analyzer. This instrument is specifically used for continuous and real time measurements of SO₂. The analysis was carried out considering the simultaneous presence of tracers CO, M42 (Acetonitrile) and NO_x. The tracers helped to eliminate certain sources and were useful in establishing concrete results. The results are obtained in terms of observed average of SO₂ mixing ratios and identification of the sources.

Chapter 1

Introduction

Sulfur dioxide (SO_2) is one of a group of highly reactive gasses known as “oxides of sulfur.” It consists of one atom of sulfur bonded to two atoms of oxygen and is a strongly acidic smelling non-flammable gas. It occurs in five oxidation states -2, 0,+2,+4,+6. Its chemical reactivity is inversely related to its oxidation states. Water solubility of sulfur species increases with oxidation state. Reduced sulfur compounds (preferentially occur in gas phase) with oxidation state -2 or -1 are oxidized by hydroxyl radical with resulting atmospheric lifetimes of a few days. Whereas, S (VI) compounds often tend to be found in particles or droplets.

SO_2 is not a greenhouse gas but it is a precursor of atmospheric (H_2SO_4) and sulfate aerosol.

1.1 Sources of SO_2

1.1.1 The global SO_2 budget

Sulfur dioxide enters the atmosphere as a result of both natural phenomena and anthropogenic activities, *e.g.*:

- Fossil fuel combustion at power plants and other industries (72%)^[1] (i.e.. burning of coal, oil, natural gas and waste)
- Oxidation of DMS from oceans (19%)^[1]
- Volcanic eruption (7%)^[1]
- Biomass burning (2%)^[1]

Other major sources include as extracting metal from sulfide ores, and the burning of high sulfur containing fuels by large ships and non-road equipment. Coal burning is the only largest man-made source of sulfur dioxide accounting for about 50% of annual global emissions, with oil burning accounting for a further 25 to 30%.^[1] Oceanic phytoplankton (19.6Tg yr⁻¹ as DMS), volcanoes (5.5Tg yr⁻¹ as SO₂) and biomass burning (1.2Tg yr⁻¹ as SO₂).^[2] also contribute to the SO₂ budget. DMS (dimethyl sulfide) is the largest natural contributor to global sulfur flux.

1.1.2 The anthropogenic SO₂ emissions with special focus on emissions from India and China

Figure 1 shows the estimates of global SO₂ emissions from the year 1990 till the year 2011. This graph is based on GAINS (Greenhouse gas-air pollution Interactions and Synergies) model which was used to calculate land-based anthropogenic emissions. Global emissions peaked in the early 1970's and decreased until 2000^[3] after western countries introduced flue gas desulfurization in power plants to combat acid rain. But recently Klimont et.al 2011 estimated that emissions again started growing rapidly since the year 2000 due to the growing number of coal fired power plants in India and China and reached a high in 2006. Global SO₂ emissions

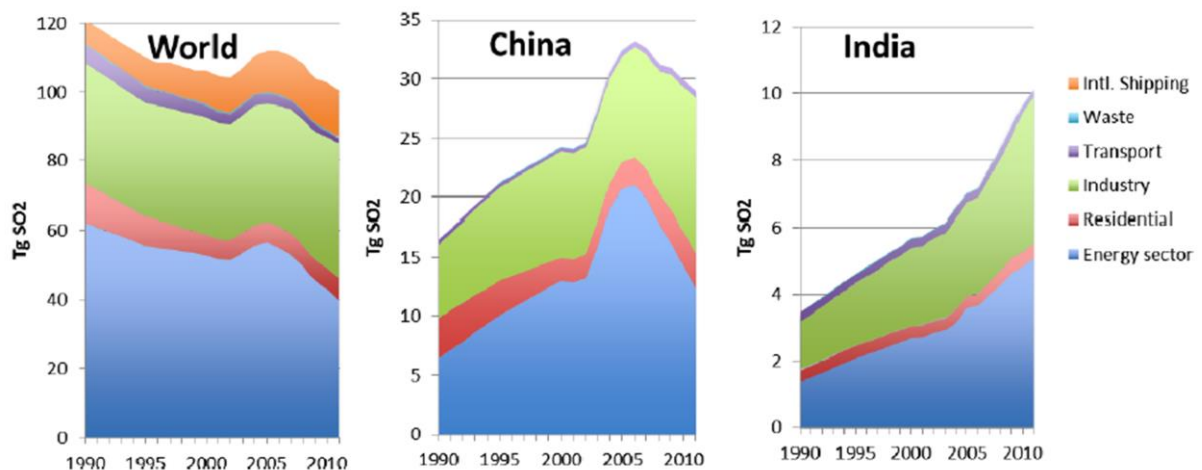


Figure1. Sectorial trend in global, China and Indian SO₂ emissions since 1990, TgSO₂. Here, India is about 1/3 of China and China 1/3 of world emissions ^[4]

finally started declining from 2006 onwards. The modeled decrease after 2006 is largely due to the fact that government agencies in China claim they are retrofitting coal fired power plants with flue gas desulfurization units. The models continuing increase in India is blamed on a complete absence of technology aimed at controlling flue gas emissions in Indian power plants.

Emissions were calculated at different levels like country-wise, regionally as well as sector wise. Emissions in China were estimated to be high in 2006 at around 33Tg SO₂ and declined till 2011 because of increased emission controlled operations like installation of FGD (Flue-gas desulfurization) plants in the electric power generation sector. According to Klimont et al. (2013) SO₂ emission in the Chinese energy sector goes from 60% in 2005 down to 40% of the total in 2010; a reduction of about 30% . But China still continues to be the largest contributor to global SO₂ emissions in terms of absolute numbers. On the other hand, Lu et.al 2011 did the similar analysis for SO₂ emissions and concluded the power sector as major contributor in emission reductions and but also showed a significant increment of about 40% from 2005 by 2010 in industrial sector. The second largest emitter in Asia according to the model is India where according to these sources there is no reduction in SO₂ emissions in India which is mainly because of consumption of coal in power sector and no emission controlled operations started likewise in China. Emissions have grown by 40% since 2005 (here Lu et.al showed a little faster growth rate). According to policy makers in India, Indian coal is low in sulfur content and has an extremely high ash content (45%) ^[5]. Therefore, technology aimed at reducing sulfur emission is not that urgently required. The main problem associated with domestic coal is the high ash content and most in-stack technology is aimed at reducing fly ash emissions.

Lu et al. estimated SO₂ emission in China were 34.0Tg in 2006 and decreased to 30.8Tg in 2010. From power sector there was drastic reduction to 21% in 2010 but also increase in industry sector emissions to 66% in the same year. And residential always varied between 6%-13%. Now, if we talk about India, then according to Lu et al. (2011) emission has increased by 70% to 8.81Tg in 2010. Here, power plant is the main source of SO₂ which contributes 59% (5.2Tg) in 2010 to the total emissions. Sector-wise contribution is like this: An industry gives approx. 34%, residential gives approx. 6% and transportation is approx. 3%. Coal consumption contributes approx. 69% which is smaller than that of China (>89%). So, as these two countries are the two

major contributors to anthropogenic sulfur budget, results indicate emission growth of SO₂ in China was 27% between 1990- 2010 and in India was 70% for the same years.

Globally, since 2000, contribution of Asia has increased from 41% to 52% while that of North America and Europe, declined from 38% to 25%. So, because of North America and Europe there is net decrease in global emissions. ^{[3], [4]}. Now, we can refer the table mentioned below, which compares different emission inventories.

Table1: Left side: Comparison of the global SO₂ budget according to different sources (in TgSO₂). Right side: Comparison of different emission inventories for India according to different sources

Year	Klimont 2005	Lee 2006	Smith 2005	year	Lu 2000 (Gg/yr)	Ohara 2000 (Gg/yr)	Klimont 2000 (GgSO ₂)	Smith 2000 (GgSO ₂)
Fossil fuel on land	----	103.1	----	Power plants	3251	3084	----	----
Energy sector	56.7	----	----	Industry	1973	2133	----	----
Residential	5.8	----	----	Transport	225	199	----	----
Industry	34.1	----	----	Domestic	321	725	----	----
Transport	2.9	----	----	Coal	3779	3520	----	----
Waste	0.3	----	----	Oil	1732	1754	----	----
Int. shipping	12.0	9.4	12.1	Others	175	278	----	----
Biomass burning	4.0	2.4	4.0	Process	----	241	----	----
Volcanoes	----	13.1	----	Biofuel	84	348	----	----
DMS(dimethylsulfide)	----	42.1	----	Total	5819	6140	5674	5363
Total anthropogenicSO ₂	115.1	112.5	115.5					
Total natural SO ₂	----	57.6	----					

1.1.3 Contrasting satellite top down SO₂ emissions with model inventories (Geos-Chem)

Here figure2 shows, SO₂ column on right side as calculated by GEOS-CHEM model. We can see the yellow dot in Pakistan which means model considers having substantial emission in that particular area of Pakistan. While on the left hand side, we see SO₂ column as retrieved from the satellite minus what model considers to being present in terms of SO₂ column. The blue color in this case is showing that the difference is negative because the model has more SO₂ column than

what the satellite observes in the real world. Therefore, question arises here!! That which source

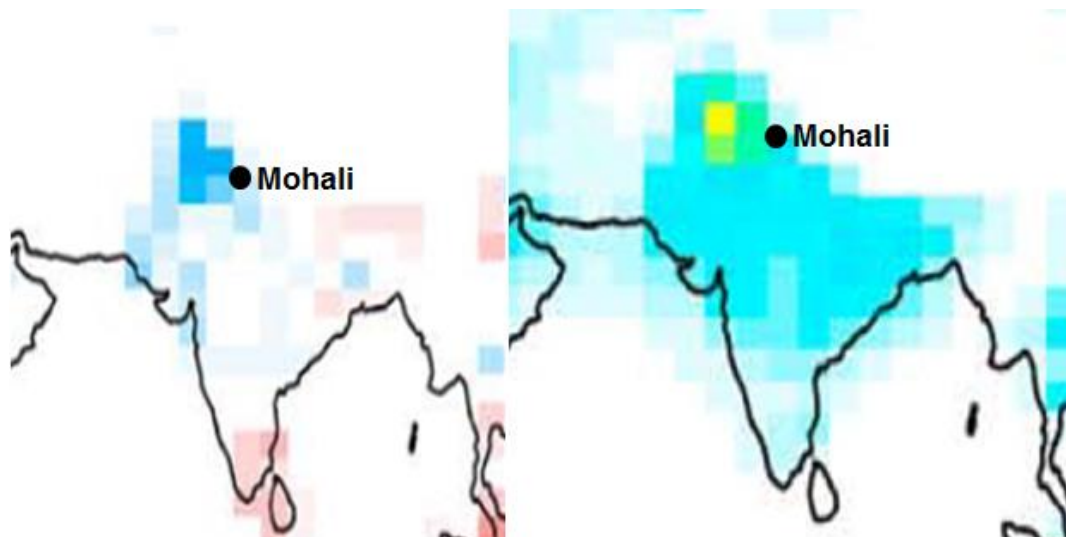


Figure2. Left: Top-down (SCIAMACHY) – Bottom-up (GEOS-CHEM). Right: Anthropogenic column of GEOS-CHEM model ^[10]

is overestimated in the model? Here we can also see the light blue shade in few places which indicate that whatever source is present in more than one place is overestimate. So, model also overestimates the Indian emissions than Pakistan. Since, we are down-wind of the place where model overestimates strongly the actual emissions. We can use our data to investigate.

First thing we have to see, whether emission inventory in this particular model is unusually high. There we see in the table shown on left hand side, that anthropogenic emissions is estimated by Lee 2011 is the lowest among all recently published global emission inventories. So, if the lowest one is overestimating here that means the others would be more overestimating. If we compare the Table1 on the right hand side, the Indian emissions in regional emission inventories are higher compare to Indian emissions in global emission inventories and most emission are blamed on domestic coal and burning of heavy oil and in this thesis we will address the question whether these recently proposed emission inventories accurate or whether they are overestimating the Indian SO₂ emissions for certain sections.

1.1.4 Emissions ratios for the most important sources of SO₂ in India

As already discussed that power sector is major source of SO₂ in India;

So, sectorial emissions in 2000 in India are as follows in Table2 (in kty⁻¹). ^[6]

	SO ₂	NO _x	CO	SO ₂ /NO _x	SO ₂ /CO
Power plant (coal)	2865	1543	936	1.857	3.061
(oil)	216	185	71	1.167	3.042
(others)	3	81	262	0.037	0.011
Industry (coal)	490	249	4088	1.968	0.120
(oil)	1339	228	160	5.873	8.369
(others)	63	161	6978	0.391	0.009
(process)	241	0	1461		0.165
Transport (oil)	199	1564	7093	0.127	0.028
(others)	0	0	0		
Domestic (coal)	165	45	2253	0.267	0.073
(biofuel)	348	618	56058	6.214	0.006
(others)	212	56	22	3.786	9.636

Therefore, total emissions in India are:

$$\text{SO}_2 = 6141, \text{NO}_x = 4730 \text{ and } \text{CO} = 79382^{[6]} \text{ (in kty}^{-1}\text{)}.$$

Here, we calculate emission ratios of SO₂ to other pollutants as these can be helpful in constraining sources. Emission ratio is due to nature of the fuel as well as due to nature of the combustion. The sulfur content of the fuel is very important to determining SO₂ emission provided there is enough oxygen in the combustion to convert all the sulfur in the fuel to SO₂.

NO_x emissions are typically proportional to the combustion temperature as a higher temperature flame has more energy to break the N₂ bond and consequently lead to higher NO emissions.

CO emissions are usually driven by the combustion efficiency. In a very efficient combustion more carbon in the fuel will be converted to CO₂. If however, the flame in oxygen deprived then CO emission will be higher.

We can see that when we look at emission ratio SO_2/CO then coal-fired power plants supposedly had a very high emission ratio because according to the emission inventory coal does contain a lot of sulfur and no control technology is in place. Also the combustion in the power plant is supposedly very efficient; therefore, CO emissions are low. The coal burned by industrial users will have a low SO_2/CO emission ratio because CO emissions are higher and sulphur content of industrial coal is less.

The lowest emission ratios are associated with domestic biofuel. Fuel supposedly contains very little sulfur and combustion is highly inefficient.

The NO_x on the other hand will be low when there is inefficient combustion. This can be clearly seen for SO_2/NO_x ratio in domestic biofuel sector. According to emission inventories the NO_x emission from the sector are very low because of low flame temperature while CO emissions are high due to an oxygen deprived flame.

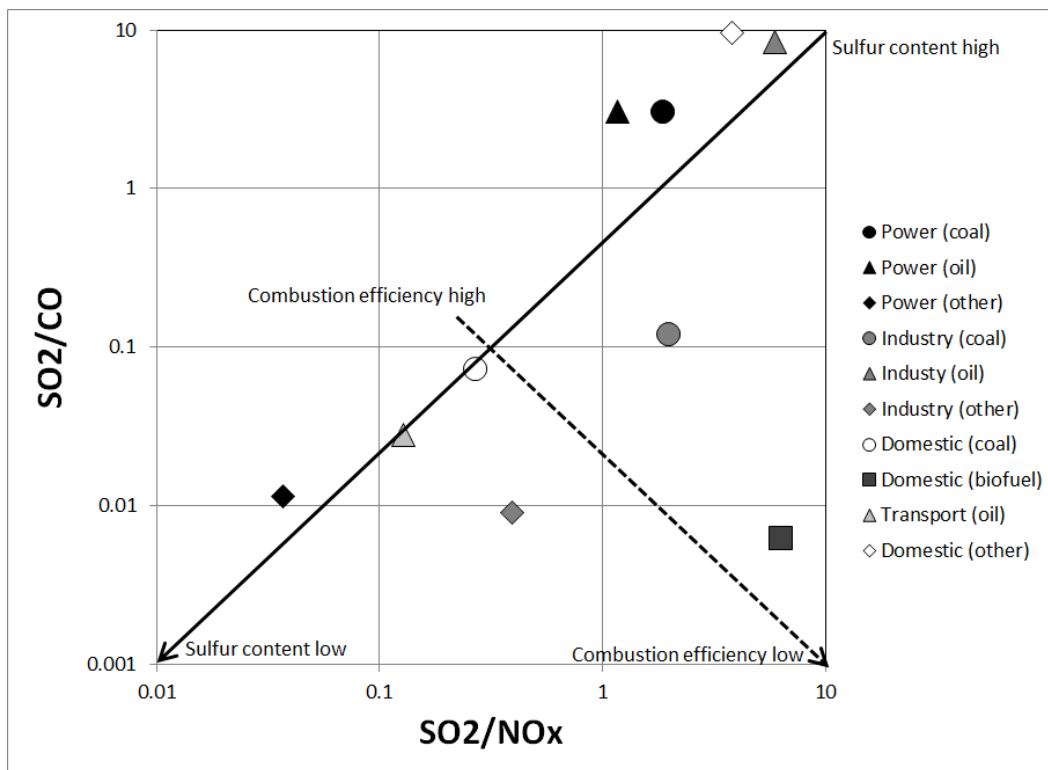


Figure3. Combustion efficiency diagram for the different fuels

1.2 Sinks of SO₂

Sulfur dioxide and sulfate are removed from the atmosphere via dry deposition, wet deposition and oxidation to sulfate.

1.2.1 Dry deposition

Dry deposition is the transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation. It is usually characterized by a deposition velocity, V_g . The net flux of a species to the surface is proportional to the concentration of that species in air, [S]. The deposition velocity is just the proportionality constant relating flux to the concentration.

$$F = -V_g[S]$$

Where; flux [F] is amount of the species deposited per unit area per second in a geographical location.

{Here, negative sign is because of flux taken negatively towards the surface}.

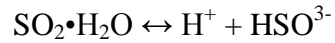
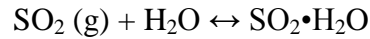
Factors that govern dry deposition are:

Atmospheric turbulence, chemical properties of depositing species and nature of surface itself. SO₂ is one of the gases that is reasonably efficiently removed from the atmosphere by dry deposition.

1.2.2 Wet deposition

When clouds are present, the removal of SO₂ can be enhanced even beyond that attributable to dry deposition. In wet deposition the species must be brought into the presence of condensed water. In addition to meteorological factors, parameters such as solubility of the pollutant in ice snow and rain and how this varies with temperature and pH and the size of the water droplets; for example, snow may scavenge some species more efficiently than rain. The rate of wet deposition of a pollutant is taken as λC , where C is the concentration and λ is known as washout coefficient which is further proportional to the precipitation intensity.

Absorption of SO₂ in water results in-



Uptake of SO₂ is governed by Henry's law and usually followed by oxidation. However, the fraction of dissolved SO₂ that rains out before reacting is subjected to wet deposition. Most SO₂, however is first oxidized to sulfate and then removed by wet deposition.

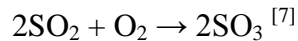
1.2.3 Oxidation to sulfate

SO₂ reacts under tropospheric conditions via;

Gas phase and aqueous phase processes and via heterogeneous or photochemical reactions on the surface of particles and is oxidized to S (VI).

1.2.3.1 Gas phase reactions

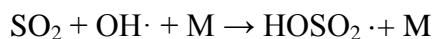
SO₂ has strong tendency to react with oxygen in air:

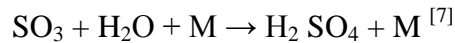
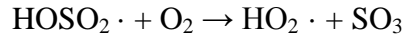


The rate of this reaction is so slow under catalyst-free conditions in the gas-phase that it can be totally neglected as a source of atmospheric SO₃.

Gas phase oxidation pathway:

Primary oxidants for atmospheric oxidation of SO₂ on global scale are: OH, H₂O₂ and O₃. The most important gas phase reaction of SO₂ in the ambient atmosphere is oxidation by hydroxyl radicals (OH). The final step of this multi-step reaction is H₂SO₄ (g), which then becomes aerosols through photo-chemical gas-to- particle conversion.





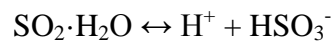
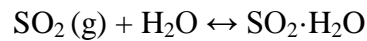
The lifetime of SO₂ based on above reaction, at atmospheric levels of OH is about one week.

1.2.3.2 Aqueous phase reactions

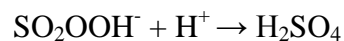
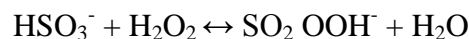
While SO₂ reacts much more slowly with OH than does NO₂, SO₂ dissolves readily in the suspended liquid droplets in the atmosphere and thus prone to form acid rain. Aqueous phase sulfate formation involves dissolution of SO₂ followed by acid-base dissociation of SO₂·H₂O to HSO₃⁻ (pK_a=1.9) and SO₃²⁻ (pK_a=7.2).^[8]

Aqueous phase oxidation pathway:

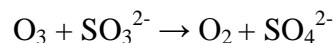
Absorption of SO₂ in water results in-



Uptake into aqueous phase is usually followed by one the following terminating oxidation reactions where oxidation of S (IV) takes place by dissolved H₂O₂^[8]



And dissolved O₃.



1.2.3.3 Heterogeneous and photochemical reactions on particle surfaces

SO₂ can also attached to dust and soot particles in the atmosphere where it is usually oxidized through reaction pathways catalyzed by the surface of the particles.

1.3 Previous measurements of SO₂ in summertime India

SO₂ has been measured for different sites in the same city for eight cities in Haryana. The sites have been classified as residential, sensitive, commercial and industrial (Table 3).

Table3: Results for the June 2000 are shown (in µg/m³) in the table. The location of the measurement sites in Panchkula are indicated in the figure 4 below. ^[11]

	Bhiwani	Gurgaon	Faridabad	Sonepat	Panipat	Y.Nagar	Panchkula	Hisar
(Residential)	6.4	18.8	7.5	5.1	10.2	30.3	6.2	13.8
(Sensitive)	2.4	18.9	5.4	14.2	5.4	7.4	7.6	24.5
(Commercial)	7.1	21.5	14.2	16.7	16.6	9.4	8.7	29.3
(Industrial)	6.5	9.4	41.9	17.0	16.9	43.1	30.3	36.1

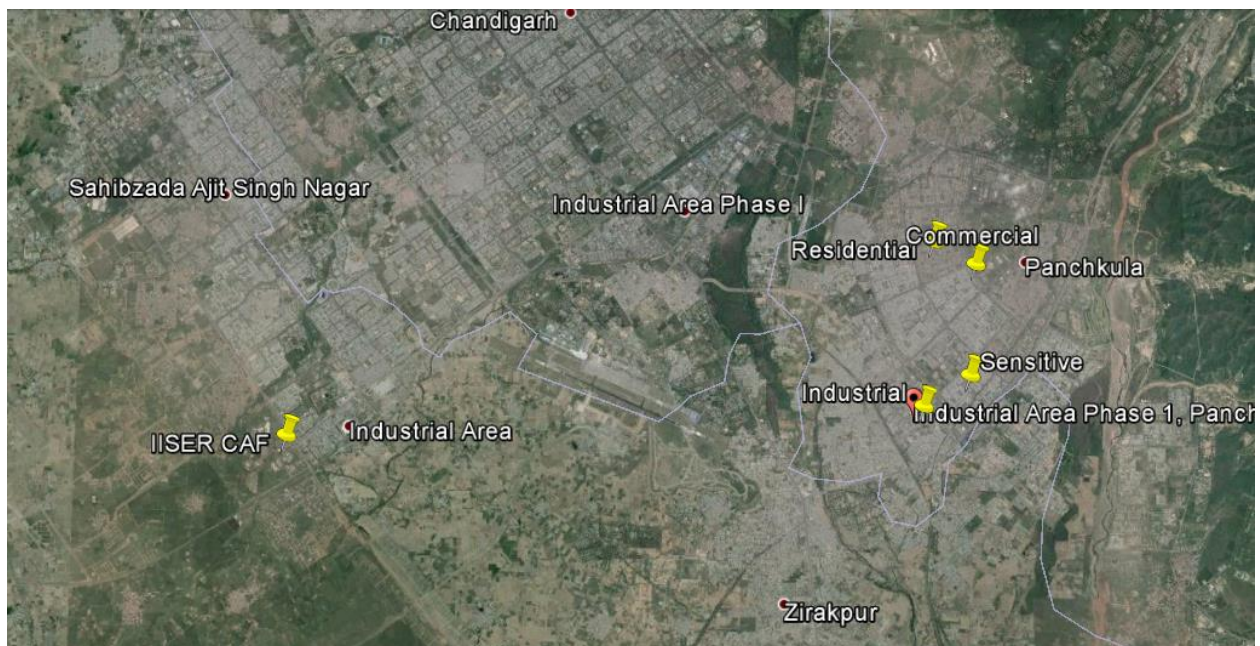


Figure4. Map for the different sites for which SO₂ mixing ratios for the month of June have been reported in Panchkula ^[11]

We can see that in general, that highest SO₂ is observed at the industrial site within each city. This is true for six out of eight cities. Overall the highest SO₂ levels have been seen in Faridabad, Yamuna Nagar, Panchkula and Hisar. Out of these Yamuna Nagar has 600MW thermal power plant called Deen Bhandhu Chotu Ram. Faridabad use to have very old 160MW thermal power plant which has been decommissioned by now and the Rajiv Gandhi thermal power plant is located in a village near Hisar. However thermal power plants do not seem to be good explanatory factor for higher SO₂ levels because there is no thermal power plant near Panchkula while there is a total of 2000MW installed capacity in Panipat which has low SO₂ levels. Therefore, high SO₂ levels near the surface seem to be driven by industrially rather than power plant emission. This is easy to understand as power plants typically release the stack emission at an altitude of 100-275 metres (a.g.l) and therefore distributed emission over wider area and are outside the nocturnal boundary layer whenever there is an inversion that leads to high local pollutant concentration.

It is also interesting to note that there are substantial differences between the value measured at different sites in the same city even if they are only located few kilometres apart. This indicates that the emissions are either very rapidly diluted or rapidly lost.

Table4: Measurements shown for SO₂ in and around the metropolitan areas of Lahore ^[12]

Sampling Sites	(in ug/m ³)	Educational institutes	Hospitals	Parks
main road crossing				
Chouburji Chowk	193	FC college 149	Shalimar hospital 174	Ghazhafi stadium 94
GPO Chowk	194	GC U/Nasir Bagh 151	Children hospital 172	Bab-e-Jinnah 93
Chearing cross	193	UET 145	Jinnah hospital 175	Shahi fort/hozori bagh 97
Niazi Chowk	194	GC edu college TS 150	Mayo hospital 167	Shalimar bagh 96
Ghari Shahu	191	FJ college 142		Gulshan-e-Iqbal 98
Bhatti Chowk	197			Model town park 92
Shlimar Chowk	196			Race course 93
Railway station	192			
Multan chunghi	204	Industrial	Residential	Suburban
Rang Mahal	196			
Defense Chowk	192	CCL/ASSMY township 111	Shahdara town 144	Begum kot 70
Kalma Chowk	194		Faisal town 148	Harbanspura 72
Akbar Chowk	201		Model town 149	Shauket Khanum 73
Thokar	190		Ichra 141	
Yateem Khana	199		Johar town 149	
Muslim Town	200		Wapda town 150	
Campus bridge	198		Sant nagar 154	
Kanchi	200		Bagh ban pura 145	
Fortress stadium	196			
Yadgar	192			

Average comes out to be:

1. Traffic intersection= 196

2. Educational Institutes= 147

3. Hospitals= 172

4. Industrial=111

5. Residential=147

6. Parks=95

7. Suburban=72

We have seen in section 1.1.3 that SO₂ emissions over Pakistan are extremely high. Measurement from Lahore indicates that found near highest surface SO₂ is found near busy traffic intersection followed by educational institutes and residential neighbourhoods, lower values are recorded in urban parks and lowest ones are found in sub-urban sites. This clearly indicates that sulphur content of fuel which efficiently regulated in India is very poorly regulated in Pakistan and the car in Pakistan still burns diesel with high sulphur content. We also see in the experimental data that SO₂ is rapidly lost or diluted with increasing distance from the source.

Table5: SO₂ measured in 2003 (April-June) in Kullu valley is shown below ^[13]

Season	Mohal (Kullu)in $\mu\text{g}/\text{m}^3$	Kothi (Manali)in $\mu\text{g}/\text{m}^3$
Summer(Apr-June)	19	12

In Mohal during summers they have $19\mu\text{g}/\text{m}^3$ SO₂ and in Kothi (Manali) they have $12\mu\text{g}/\text{m}^3$ SO₂. Mohal is a valley site near the road near Beas river valley and some SO₂ may be coming from the traffic here, whereas Manali is high altitude site where most of the pollutants would not be local.

Chapter 2

Materials and Methods

2.1 Site description

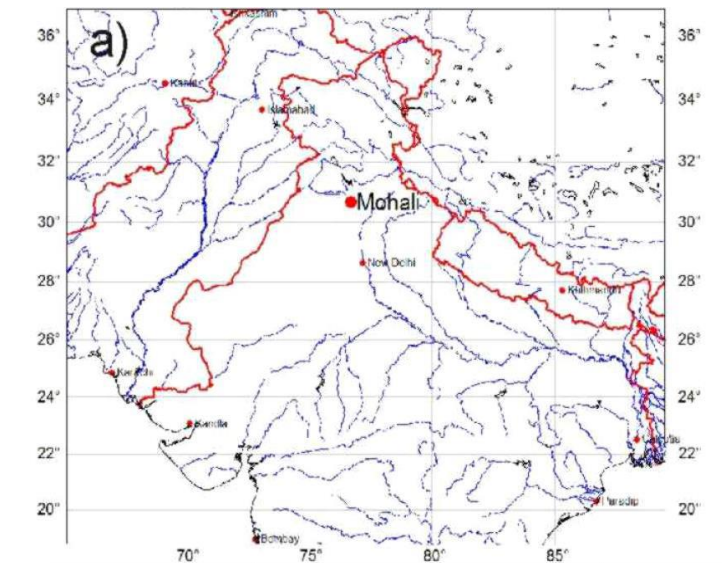


Figure 5(a). Location of the city of Mohali in the north west Indo– Gangetic plain (30.667 N,76.729 E,310ma.s.l.) {Reproduced from ^[14]}

This figure shows the location of the city of Mohali in the North West Indo–Gangetic plain in the Indian state of Punjab where greater than 80% land use is agricultural. The measurement facility is housed inside the campus of the Indian Institute of Science Education and Research (IISER), a suburban site (30.667_ N–76.729_ E, 310ma.s.l.) several kilometers away from the city centers of Mohali, Chandigarh and Panchkula which are the nearest neighboring cities shown in figure 1 (b).



Figure 5(b). Closest map of our site at IISER Mohali. { Reproduced from ^[14] }

Some neighboring potential point sources shown in figure are Guru Hargobind thermal power plant, Guru Gobind Singh thermal power plant, Diesel power plant Ambala and Deen bhandhu chottu ram power plant.

Meteorology of the pre- monsoon season in which the observations are made.

As the period of the observations was March to July so, in that period an ITCZ (Inter tropical convergence zone) layer shifts above towards north. So, the prevalent wind directions are mostly westerlies.

Table6: Table of meteorology of summer 2013.

PARAMETERS	AVERAGE	Median
Temperature [°C]	27.5	27.3
Relative humidity%	40	38.1
Solar radiation [W/m ²]	452.5	489.8

2.2 Measurement of SO₂ at the IISER Mohali ambient air quality station

2.2.1 Instrumentation

The instrument used for measuring SO₂ is based on pulsed fluorescence technology and measures the amount of sulfur dioxide in the air up to 10ppm. The pulsing of the UV source lamp serves to increase the optical intensity. Reflective band pass filters are used instead of transmission filters as they are less subjected to photochemical degradation and more selective in wavelength isolation, which in turn results in long term stability and increased detection specificity.



Figure 6(a). SO₂ analyzer (Model 43i Thermo Scientific) ^[15]

PRINCIPLE: This model operates on the principle that sulfur dioxide molecules absorb UV light and become excited at one wavelength (214nm), then decay to lower energy state emitting UV light at different wavelength (330nm).^[16]



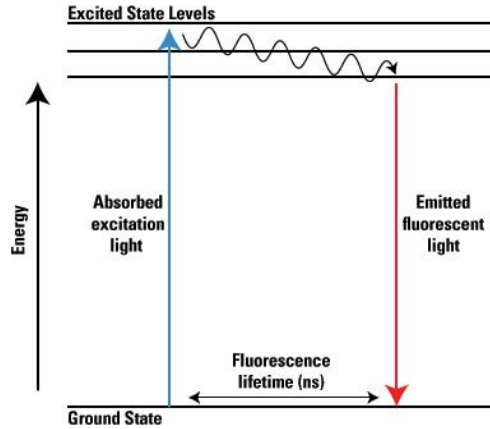


Figure7. Basic fluorescence diagram ^[17]

HOW DOES IT WORK (Figure 6a)?

Firstly, the sample is drawn into analyzer through sample bulkhead then sample flows through hydrocarbon kicker where all the hydrocarbons are removed and sulfur dioxide molecules remain unaffected. The sample then flows through fluorescence chamber where the pulsating UV light which is focuses by condensing lens into mirror assembly excite the molecules. The mirror assembly contains four mirrors that reflect the wavelength needed to excite the sulfur dioxide molecules. After excitation these molecules decayed to lower energy by emitting UV light which is proportional to the sulfur dioxide concentration. Then the UV light emission from these molecules is detected by the photomultiplier tube (PMT). There is photo-detector located at the back of the fluorescence chamber which continuously monitors the pulsating UV light source. As the sample leaves the optical chamber it passes through a flow sensor, a capillary and the shell side of the hydrocarbon kicker. The sample then flows through the pump and finally exhausted through an exhaust of the analyzer which in returns outputs the sulfur dioxide concentration to the screen and the system connected to it.

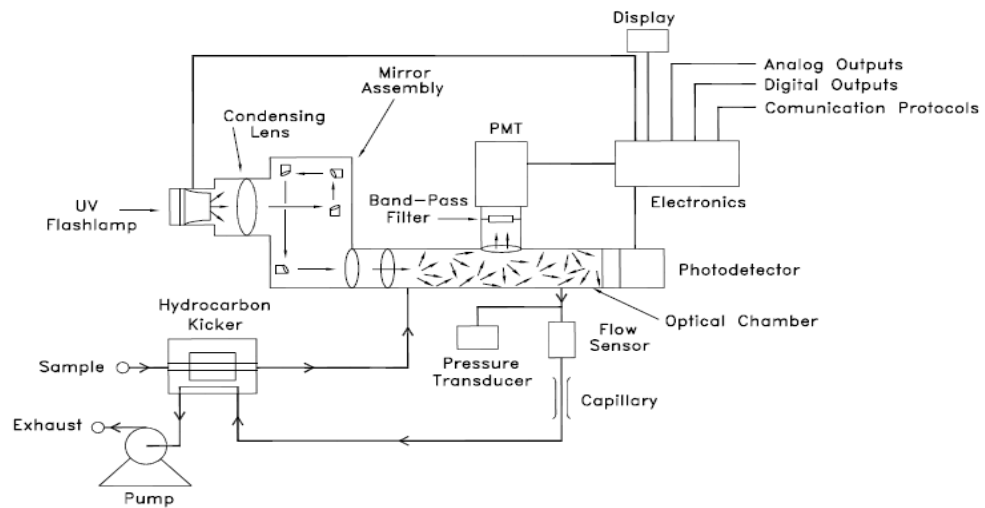


Figure 6(b). Flow diagram of SO₂ analyzer^[15]

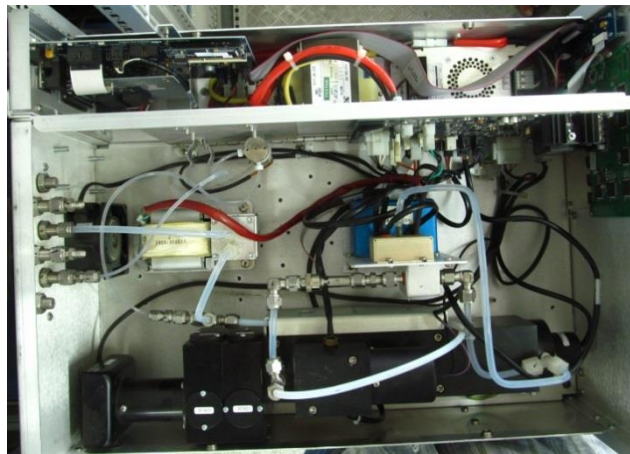


Figure 6(c). SO₂ analyzer (an internal view)

Hardware:

- Hydrocarbon kicker: It removes hydrocarbons from the gas stream while leaving the SO₂ concentration unaffected. It operates on a permeation principle using differential pressure to force hydrocarbon molecules to pass through the tube wall. This pressure is created across the tube wall as sample gas passes through capillary tube which reduces its pressure. The sample gas is then fed to the shell side of the kicker.

- **Optics:** This section provides the light source for the fluorescence reaction and optimizes the reaction with a system of lenses and mirrors. It includes a flash lamp, condensing lens, mirror assembly and light baffle.
- *Flash –lamp:* It provides the UV light source that causes the fluorescence reaction in the SO₂ molecules.
- *Condensing lens:* It focuses light from flash lamp into the mirror assembly.
- *Mirror assembly:* A set of eight mirrors reflect only those wavelengths used in SO₂ exciting molecules. This reflection filtering causes the radiation reaching the detection chamber to lifetime intensity and stability.
- *Light baffle:* It helps in keeping the stray light from entering the detection volume.
- **Trigger pack:** In whole trigger assembly, flash lamp is used which pulses the UV flash lamp at a rate of 10 times per second for improved signal-to-ratio and long-term stability mainly for reasons:

High optical intensity, long-term stability, long-life, small size, low power requirements and chopped signal processing (no dark current drifts).
- **Reaction chamber:** In this chamber, pulsating light from the flash lamp excites the SO₂ molecules. A condenser lens collects and focuses light from fluorescing SO₂ molecules onto the mirror assembly.
- **Band pass filter:** It restricts the light reaching from PMT to SO₂ fluorescence wavelength.
- **Photomultiplier tube:** It converts optical energy from the reaction to an electrical signal which further is sent to an input board which transmits it to the processor.
- **Photo detector:** It is located in the fluorescence chamber and continuously monitors the pulsating UV flash lamp. This photo detector is connected to a circuit that automatically compensates for fluctuations in flash lamp output.

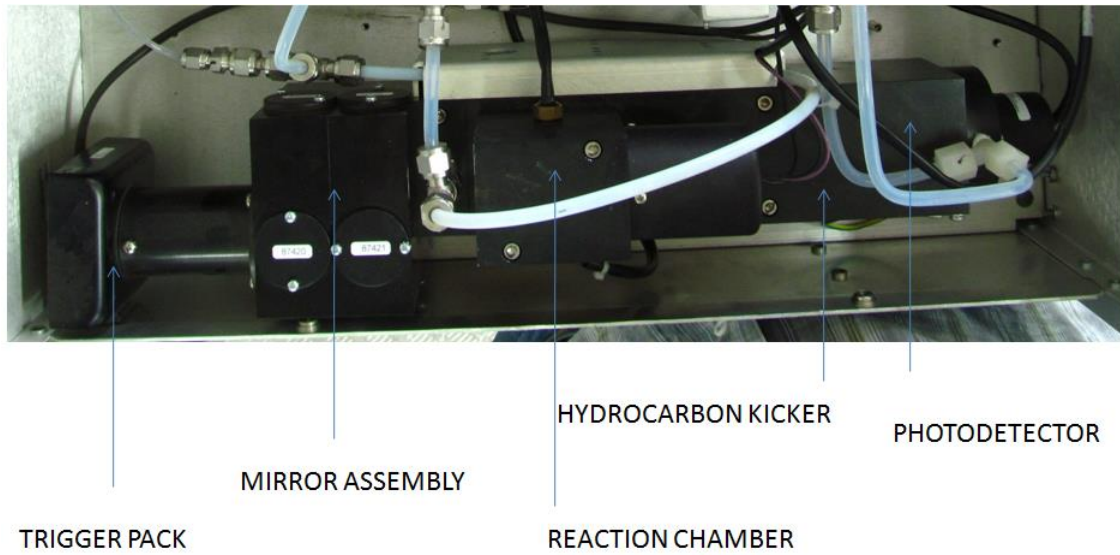


Figure 6(d). View of internal parts of the SO₂ analyzer

- Flow sensor: It is used to measure the flow of sample gas.
- Pressure transducer: It measures the pressure of reaction chamber.
- Capillary: The capillary along with the pump is used to control flow in the sample line.
- Vacuum pump: It draws out the reactive gases of the reaction chamber.

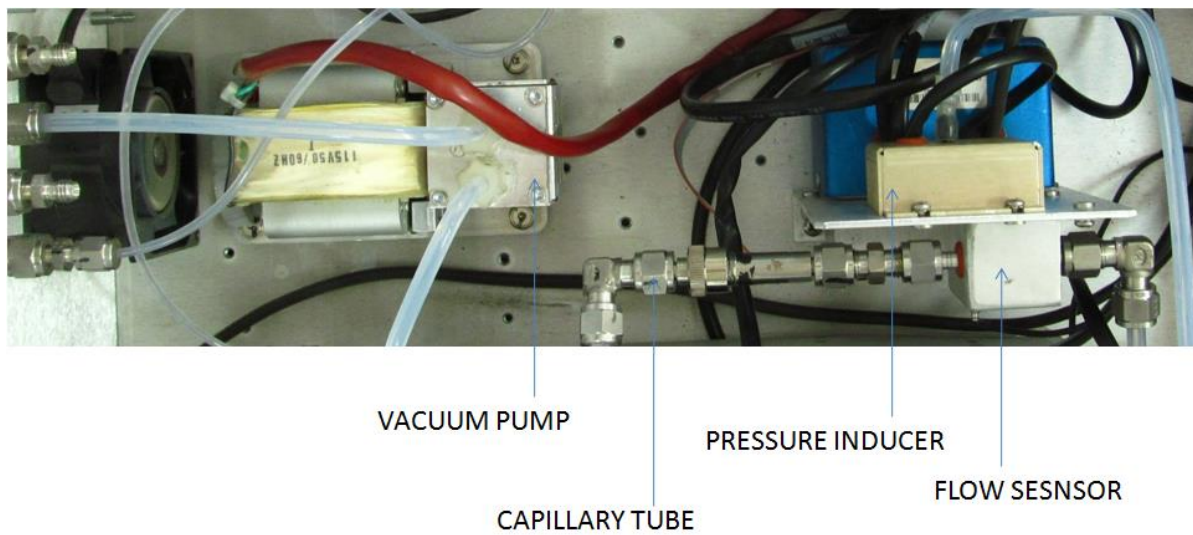


Figure 6(e). View of internal parts of SO₂ analyzer

2.2.2 Instrument, maintenance and calibration

Diagnostic check is to be done every day. (Table7: Table of diagnostic checks performed by me)

Date	Internal temp	Chamber Pressure temp	Flow	Lamp int.	
4/7/13	31.8	45.1	758.3	0.353	92%
8/8/13	32.2	44.9	760.3	0	92%
10/8/13	35.8	45	761	0	92%
17/8/13	33	44.9	760.7	0	92%
20/8/13	36.1	44.9	763.4	0.514	93%
21/8/13	40.7	45.3	762.4	0.514	92%
26/8/13	37.5	45	760	0.518	93%
30/8/13	32.8	45.1	765.4	0.521	91%
14/9/13	32.3	44.9	766.4	0.431	92%
16/9/13	34.3	44.9	762.4	0.426	92%
20/9/13	40.3	45	762	0.425	91%
21/9/13	33.3	45.1	766.4	0.431	96%
23/9/13	37	45.1	761	0.424	92%
26/9/13	38.4	45	765.4	0.427	92%
27/9/13	38.1	45.3	764	0.429	92%
28/9/13	33.5	44.9	764.4	0.429	92%
30/9/13	31.4	45	767.1	0.431	92%
1/10/13	31.7	45.1	769.1	0.431	90%
3/10/13	39.6	45.3	765.1	0.427	92%
4/10/13	39.1	45.3	766.4	0.427	91%

5/10/13	34.6	45.2	764	0.428	92%
9/10/13	28.9	44.9	772.1	0.435	92%
12/10/13	37.5	45.2	772.5	0.433	90%
22/10/13	34.7	45.1	770.1	0.431	92%
25/10/13	38	45.3	770.8	0.429	92%

In the above table under flow column, reading is shown zero which means at that time flow sensor got some problem and has stopped working. To ensure that the instrument continues to run smoothly a senior PhD student checked the actual flow regularly with a bubble flow meter.

Instrument specifications for: SO₂ diagnostics!

1. Internal temperature =15-45°C
2. Chamber temperature =43-47°C
3. Pressure =400-100mmHg
4. Sample flow =0.29-0.75 L/min
5. Lamp intensity =40-100%
6. Lamp voltage =900-1200 V

Calibration of SO₂ analyzer! Zero is to be done every week and five points span is to be done every month.

Table8: Table of zero drift values calibration of sulfur dioxide for calibrations performed by me.

Date	zero drift
4/7/2013	0.03
15/7/2013	-0.02
18/7/2013	-2.33
24/7/2013	0.07
8/8/2013	0.31
10/8/2013	1.71
17/8/2013	1.49
21/8/2013	2.37
30/8/103	1.74
20/9/2013	1.26
28/9/2013	1.29
4/10/2013	1.35
12/10/2013	1.4
22/10/2013	1.19

Five points span Calibration performed by me on 10/08/2013.

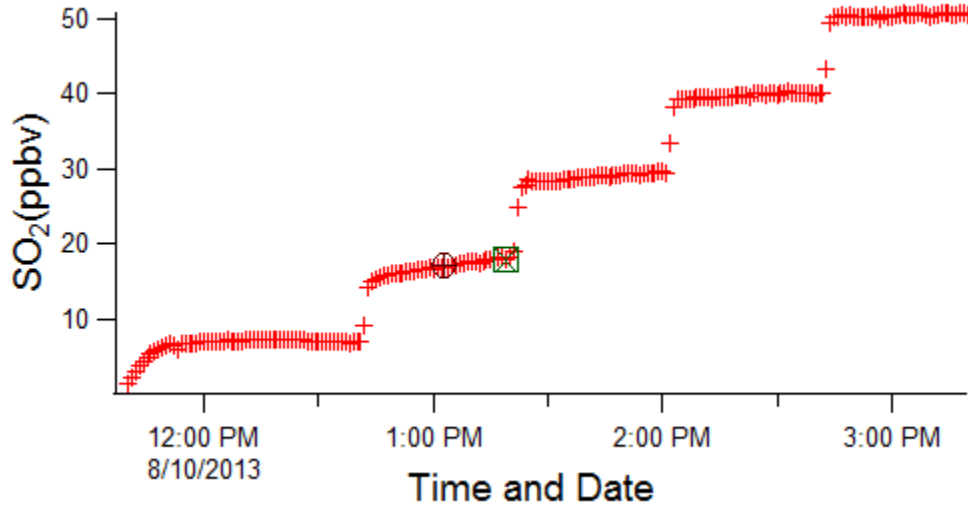


Figure 8(a). Five point span calibration plot of SO₂ gas analyzer

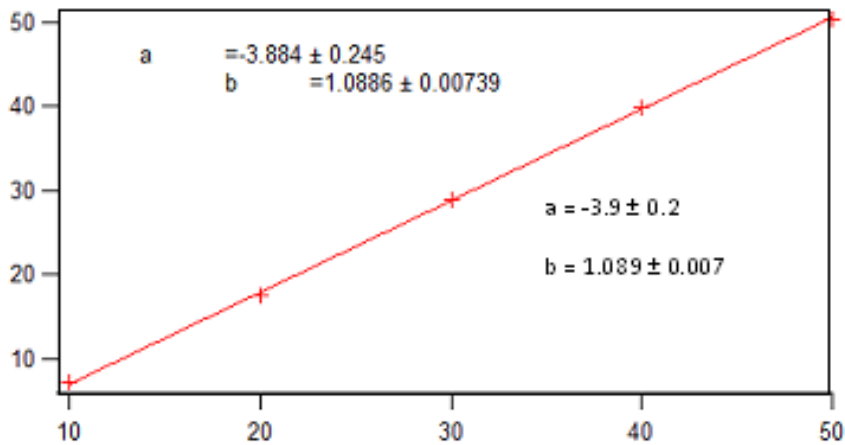


Figure 8(b). Calibration plot of SO₂ concentration introduced vs. measured

2.3 Data processing and calculations

2.3.1 Determining mean, median quarter values and standard deviation

MEAN: The mean is the average of the numbers. To calculate mean we simply add up all the numbers, then divide by how many numbers there are.

$$\text{Case 1: } (5+16+8+7+11+10+13+18+19+9+7)/11=11.2$$

MEDIAN VALUES: The median corresponds to the mean but is used in robust statistics. Robust statistics is applied to datasets that can have outliers occasionally. Let us assume that in the example above during a pollution plume a value of 80 was measured. The mean will change drastically, so will the standard deviation

$$\text{Case 2 } (5+16+8+7+11+10+13+18+19+9+7+80)/9 =16.9$$

To combat this effect of screwing the statistics with a single outlier, the median is introduced.

To calculate the median, we need to start by ordering our data means to put in a numerical order, if they are not in order already. Then find the median of the data. The median divides the data into two halves. If we have the even number of values, so the median would be the average of two middle values and if we have the odd number of values then the first median would be the actual data point.

In Case 1 the sorted numbers are 5,7,7,8,9,10,11,13,16,18,19 (total 11 numbers) and the median is the middle value

$$\text{Median} =10$$

In Case 2 the sorted numbers are 5,7,7,8,9,10,11,13,16,18,19,80 (total 12 numbers) and the median is the average of two middle values

$$\text{Median} = (10+11)/2=10.5$$

If we apply ordinary statistics then the mean changes by $16.9-11.2=5.7$ just because of a single plume, while in reality most of the time there is no plume and most measurements (9 out of 12) reported values bellow 16.9.

When we apply robust statistics, the median changes by $10.5-10=0.5$ in the same dataset. The median is hardly affected by events that occur only occasionally, which is why generally in atmospheric science we use robust statistics and prefer using the median over using the mean.

QUATER VALUES: For very much the same reasons in atmospheric sciences we prefer using **quarter values** (robust statistics) over using **quartile** (conventional statistics). Quartiles are calculated using the mean and standard deviation of a dataset. In contrast quarter values are obtained just like the median by sorting the data points.

To determine the quarter value we have to divide data into quarters. For this we first divide the data into two and then we have to find median of these two halves.

If we refer to Case 1 above the sorted numbers are 5,7,7,8,9,10,11,13,16,18,19 (total 11 numbers) and the median is the middle value (Median =10) The first half is made up of the following numbers: 5,7,7,8,9 (5 numbers) and the lower quarter value (Q_l) is the middle value $Q_l=7$. The second half is made up of the numbers 11,13,16,18,19.(5 numbers) and the upper quarter value (Q_u) is the middle value $Q_u=16$

In Case 2 the sorted numbers are 5,7,7,8,9,10,11,13,16,18,19,80 (total 12 numbers) and the median is the average of two middle values Median $=\frac{10+11}{2}=10.5$. The first half is made up of the following numbers: 5,7,7,8,9,10 (6 numbers) and the lower quarter value (Q_l) is the average of two middle values $Q_l=\frac{7+8}{2}=7.5$. The second half is made up of the numbers 11, 13, 16, 18, 19, 80. (6 numbers) and the upper quarter value (Q_u) is the is the average of two middle values $Q_u=\frac{16+18}{2}=17$.

STANDARD DEVIATION: It is a measure of how spread out numbers is.

First we have to calculate the difference of each data point from the mean and square the result of each. Then after, we have to calculate the mean of these values and take the square root. If we stick with the two cases outlined above

Then for case 1: $(5+16+8+7+11+10+13+18+19+9+7)/11=11.2$

Now,

$$5 - 11.2 = -6.2$$

$$16 - 11.2 = 4.8$$

$$8 - 11.2 = -3.2$$

$$7 - 11.2 = -4.2$$

$$11 - 11.2 = -0.2;$$

$$10 - 11.2 = -1.2$$

$$13 - 11.2 = 1.8$$

$$18 - 11.2 = 6.8$$

$$19 - 11.2 = 7.8$$

$$9 - 11.2 = -2.2$$

$$7 - 11.2 = -4.2$$

$$(-6.2)^2 + 4.8^2 + (-3.2)^2 + (-2.2)^2 + (-0.2)^2 + (-1.2)^2 + 1.8^2 + 6.8^2 + 7.8^2 + (-2.2)^2 + (-4.2)^2 = 210.8$$

$$210.8 / 11 = 19.17$$

$\sqrt{19.17} = 4.4$ is the standard deviation.

Then for case 2: $(5+16+8+7+11+10+13+18+19+9+7+80)/11=16.9$

Now,

$$5 - 16.9 = -11.9$$

$$16 - 16.9 = -0.9$$

$$8 - 16.9 = -8.9$$

$$7 - 16.9 = -9.9$$

$$11 - 16.9 = -5.9;$$

$$10 - 16.9 = -6.9$$

$$13 - 16.9 = -3.9$$

$$18 - 16.9 = 1.1$$

$$19 - 16.9 = 2.1$$

$$9 - 16.9 = -7.9$$

$$7 - 16.9 = -9.9$$

$$80 - 16.9 = 63.1$$

$$(-11.9)^2 + (-0.9)^2 + (-8.9)^2 + (-9.9)^2 + (-5.9)^2 + (-6.9)^2 + (-3.9)^2 + 1.1^2 + 2.1^2 + (-7.9)^2 + (-9.9)^2 + 63.1^2 = 4564.9$$

$$4564.9 / 12 = 380.4$$

$\sqrt{380.4} = 19.5$ is the standard deviation.

It can be seen very clearly, that the standard deviation is affected even much more by a single outlier. Therefore, instead of depicting ambient data as average and standard deviation we generally prefer to depict it using box and whisker plots.

2.3.2 Making a diel box and whisker plot

Let us assume we want to answer the question which values of SO₂ are generally measured between 7 and 8 am in the morning and how do they compare to values measured at noon or between 7 and 8 pm in the evening. To address such a question we make a diel box and whisker plot. A box and whisker plot is a compact way to depict all the statistical parameters with statistical parameters of a particular sample.

It depicts the median as a horizontal line and draws a box using the upper and the lower quarter values to determine the outline. It depicts as lower whiskers the value above which 90% of the data lies and as upper whisker the value below which 90% of the data lies. For our case 1 above (5+16+8+7+11+10+13+18+19+9+7), the horizontal line will be drawn at 10 the box will outline 7 and 16 and the whiskers will reach till 7 and till 18 (10 out of 11 numbers (91%) are either greater than or equal to 7 or less than or equal to 18). For our case 2 above (5+16+8+7+11+10+13+18+19+9+7+80), the horizontal line will be drawn at 10.5 the box will outline 7.5 and 17 and the whiskers will reach till 7 and till 19 (11 out of 12 numbers (92%) are either greater than or equal to 7 or less than or equal to 19).

The example demonstrates that a single outlier will not affect how the data is depicted and hence this type of plot is useful to show the typical values.

In contrast if he had used conventional statistics (average \pm 2 times standard deviation) to depict the ambient variability, then in case 1 we would have a marker at 11.2 and whiskers that reach from 2.4 to 20, whereas in case 2 the marker would be at 16.9 and the whiskers would reach from -22.1 to 55.9, which has clearly very little to do with the normal variability of the dataset.

2.3.3 Calculating the analytical uncertainty and determining the detection limit

Table9: Calculating the precision error for each dilution point of the 5 point calibration

POINT	Concentration introduced	Average	Standard deviation	Precision error%(2sigma)
1	10	7.1	0.1	2.8
2	20	17.6	0.4	4.5
3	30	28.9	0.4	2.8
4	40	39.8	0.3	1.5
5	50	50.4	0.2	0.8

Here, standard deviation calculated is the precision error (in %) of the instrument by using formula: 2σ i.e. $\text{standard deviation} \times 100 / \text{average of dilution point}$.

And for accuracy error (in %) we take slope into account. For that, subtract our slope from 1 and then multiply with 100 would give us an accuracy error. And here it is 8.9 %.

Detection limit: According to the user manual the detection limit is 1 ppb.

Chapter 3

Results and Discussion

Analysis of summer data (2013)

During summer 2013 the average observed SO₂ mixing ratio was 4.8 ppbv.

With a standard deviation of 5.4 ppbv. The median of SO₂ ratio was 3.1 ppbv.

Time series plot: It comprises methods for analyzing time series data in order to extract meaningful statistics and other characteristics of the .Figure 9 shows a simple plot of SO₂ mixing ratio as a function of the date and time on which the measurement was obtained. Now, in this graph there are some outliers (Outlier - It is an observation that is numerically distant from rest of the data).

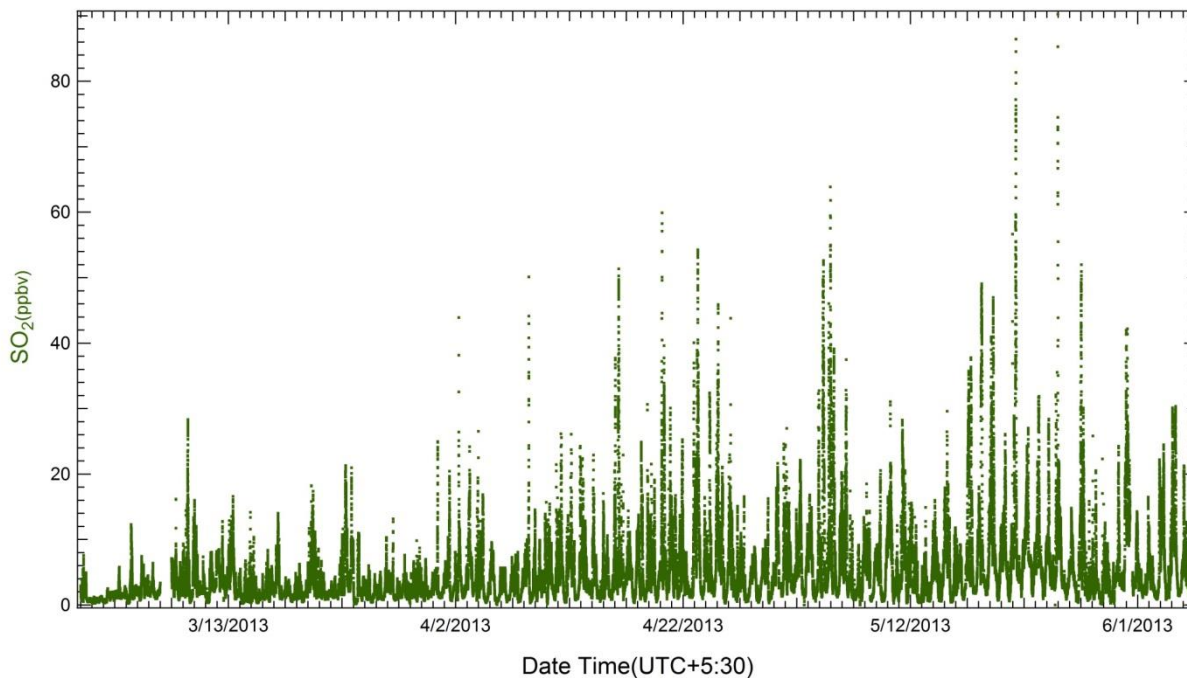


Figure9. Time series plot of summer 2013

This plot shows that the peak starts rising from April. We suspect the SO₂ might be coming from biomass combustion, as wheat residue burning takes place in this period.

So, to proceed further and sort this problem out we use Diel-box and whiskers plot. The box plot is a quick way to examine one or more sets of data graphically through their quartiles (different ranges of the box). These boxes have lines extending vertically from the boxes known as whiskers indicating the variability outside the upper and lower quartiles. In this plot, the top and bottom of the box are always first and third quartiles and the band inside the box is always the second quartile (i.e. median). Box represents that how much values are dispersed.

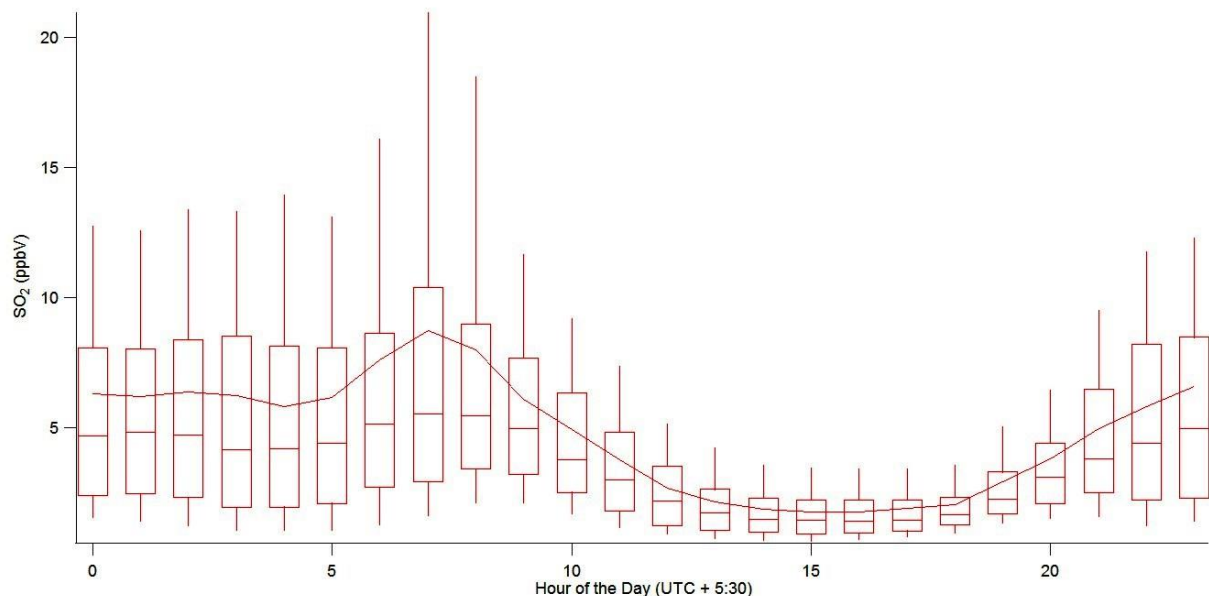


Figure10. Diel box and whiskers plot of summer 2013

This plot shows that all the high peaks are during morning time and there are outliers too. In morning time, concentration is high around 7:00- 8:00a.m as PBL layer is at less height. Same is the case during night time. In day time PBL (planetary boundary layer) height is more therefore, more is the volume, thus concentration is minimum. So, highest mixing ratios can be seen at around 7:00-8:00 a.m. Now, if we take crop residue burning into our consideration then we cannot conclude much from diel cycle about crop residue burning as this activity typically happens in the afternoon or evening.

Wind rose plot: Wind rose is a graphic tool used by the meteorologists to define the wind speed and wind direction of a particular location. It shows the frequencies of wind blowing from particular direction over a specific period of time.

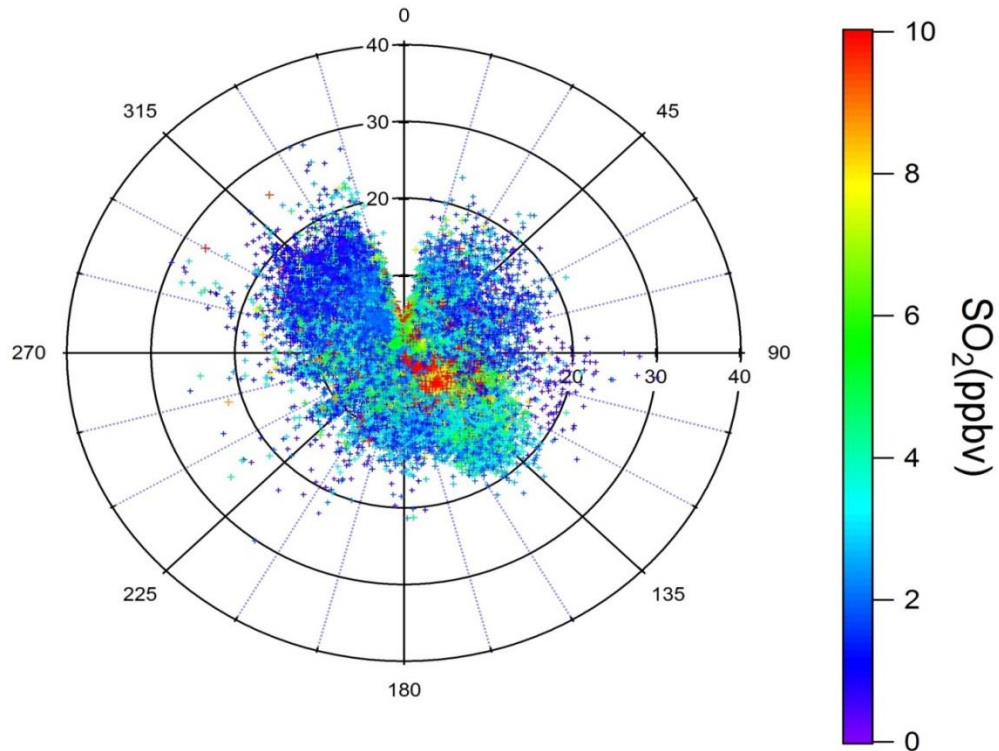


Figure11. Wind rose plot of summer 2013

Here, we can see the direction of our source coming from a particular region. Here sulfur dioxide is coming from the north direction but also we can see the high concentration in the south east direction. Reason being for these emissions could be the power plants or industries in those areas. So we need to investigate using further tracers as this contradicts our earlier hypothesis. M42 would be suitable to investigate the hypothesis of biomass combustion as it a very specific biomass combustion marker. Other tracer like CO would be suitable to constrain the combustion

efficiency of our source. It is high if combustion occurs under oxygen depleted conditions. Hence, it can be a marker for an inefficient combustion.

Correlation plots

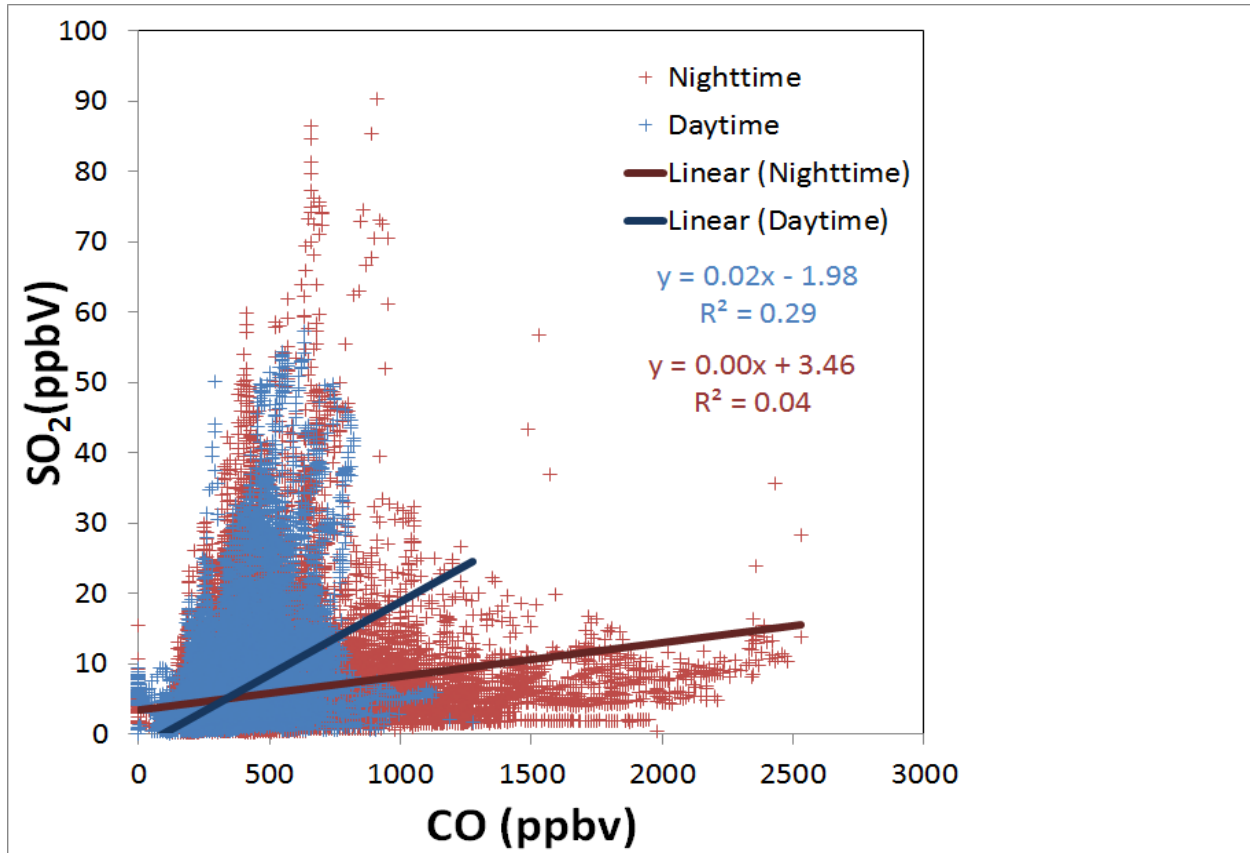


Figure12. Correlation plot of SO₂ vs.CO

In this figure, I am trying to correlate the sources of SO₂ and CO which is depending upon the R² value. So, if we see here, the values are quite different which means one single source type cannot explain the observations. For good correlation value should be the 1 or 0.9. CO is emitted from all forms of combustion. It is particularly high if the combustion occurs under oxygen depleted conditions else CO₂ would come out. Hence, it can be used as marker for low temperature – inefficient combustion.

When we look at this plot we found that there are at least two different sources. Here points seem to describe a triangle hence there are two sources at least. One source has very high CO and low

SO₂ and other has much high SO₂ and low CO. Since it makes no sense to calculate a line fit through this data. We instead estimate the SO₂/CO emission ratio of our two sources visually. One of them has approximately 10 ppbv on 2500 ppbv of CO. The other one has approximately 90 ppbv of SO₂ on 1000 ppbv of CO. Now, we calculate SO₂ for CO emission ratio for each data point which give each of this estimated emission ratio and uncertainty of 50% and split our dataset into several different datasets by filtering. One should have same emission ratio as source1 i.e. ± 50% and the second data that has same emission ratio as source2 i.e. ±50%. At this stage we don't look at data that have emission ratio that fall in between. But after filtering our data, we actually found that there is another source which also has distinct SO₂/CO emission ratio which is even much lower than source 1. We called it as source3 and further plotted it in Figure13, 14 and 15.

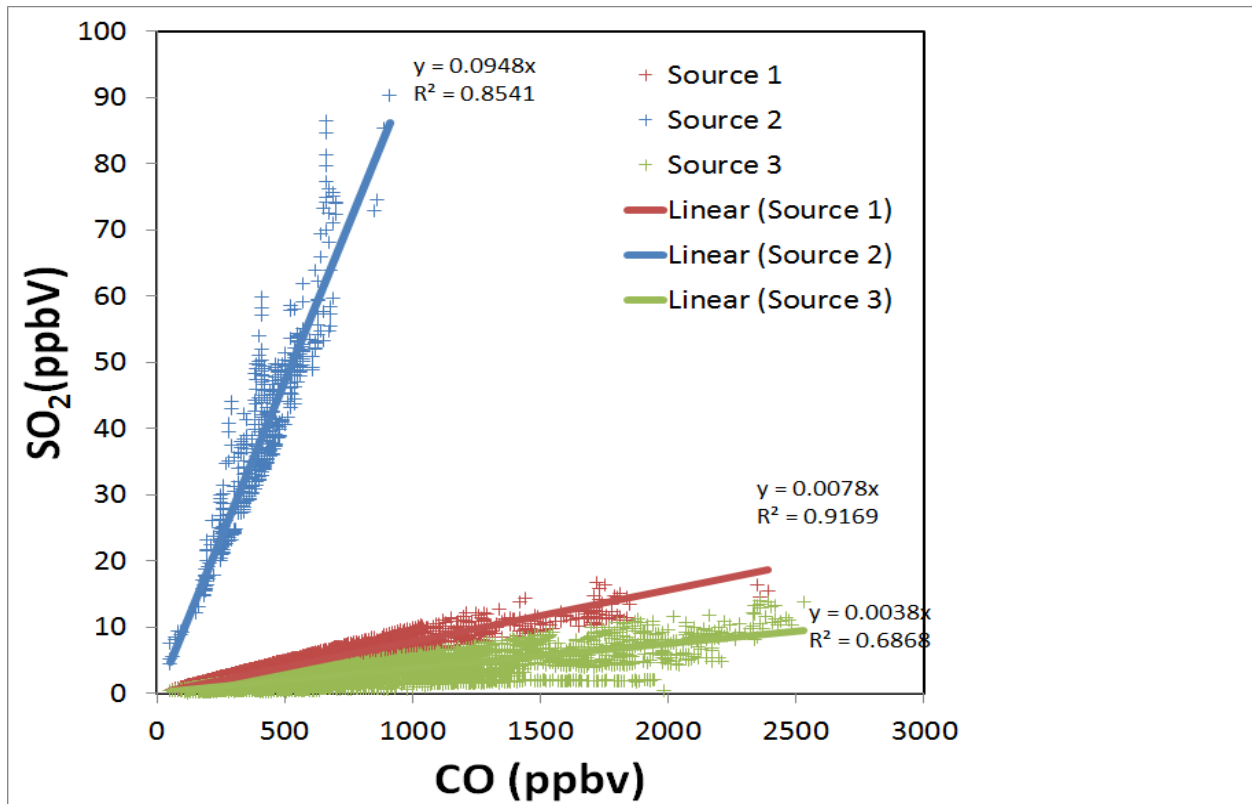


Figure13: Correlation plot of SO₂ vs. CO with three different sources

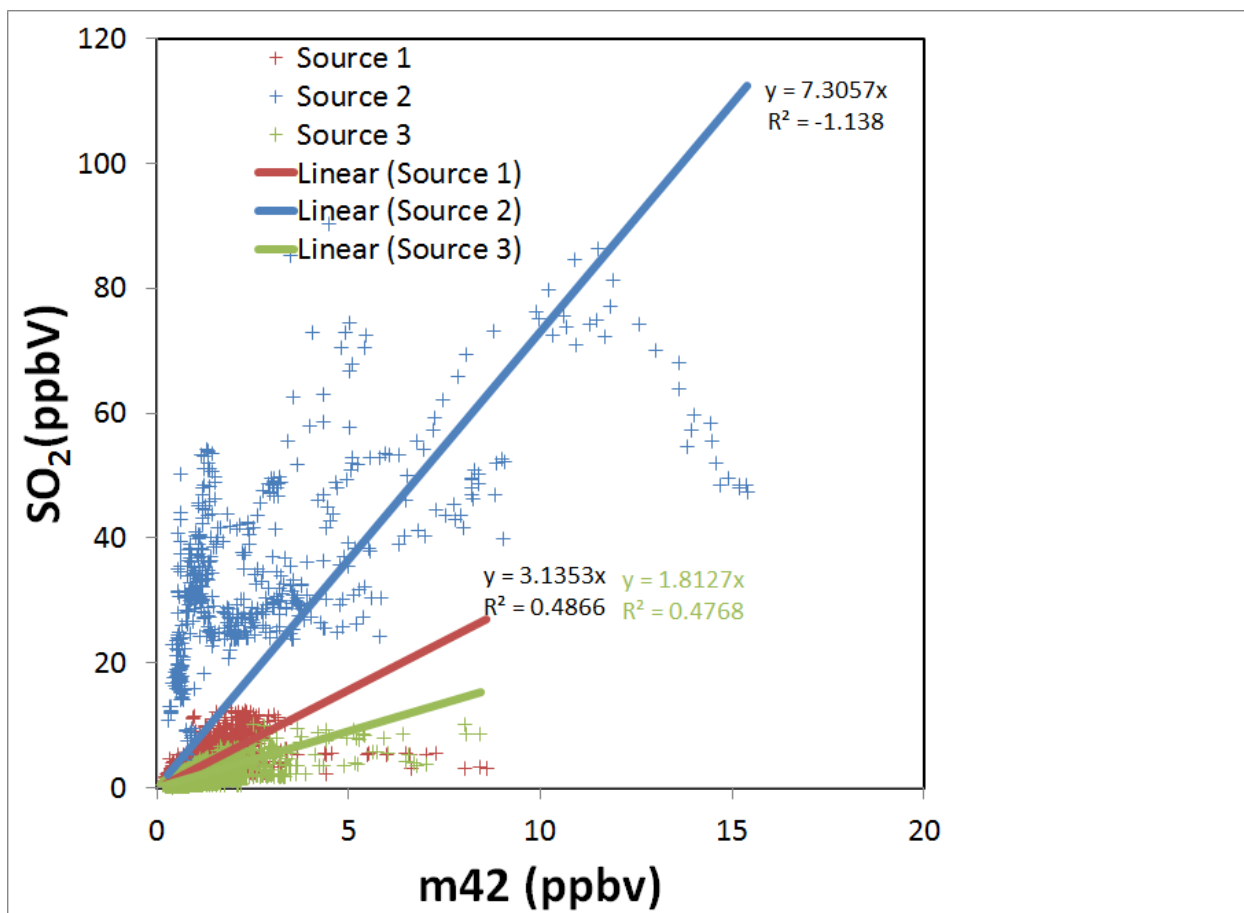


Figure14. Correlation plot of SO₂ vs. m42

Now, we have sources1 and source3. Source 1 and 3 have some correlation i.e. m42 (acetonitrile) which is a very specific biomass combustion marker. In above figure, we can see that source 2 doesn't have decent R with m42 but source1 and source3 correlates very well so they could be biomass combustion.

We also look at the correlation of our sources with NO_x. NO_x emissions are related to combustion temperature of the source. The higher the combustion temperature the higher is NO₂ coming out. Since, in order to produce NO_x the N₂ bond in the ambient air has to be broken in the fire. Traffic (spark temperature of combustion engine approx. 2000-4000K) has the highest emissions per amount of fuel burned. Next come power plants and industries > 1000-1200 °C temperature in the fire. Inefficient small fires produce correspondingly less NO_x. Here; we can

see that all of our sources have low R, but still we see different slopes. Source2 has the steepest slope which means highest combustion temperature NO_x .

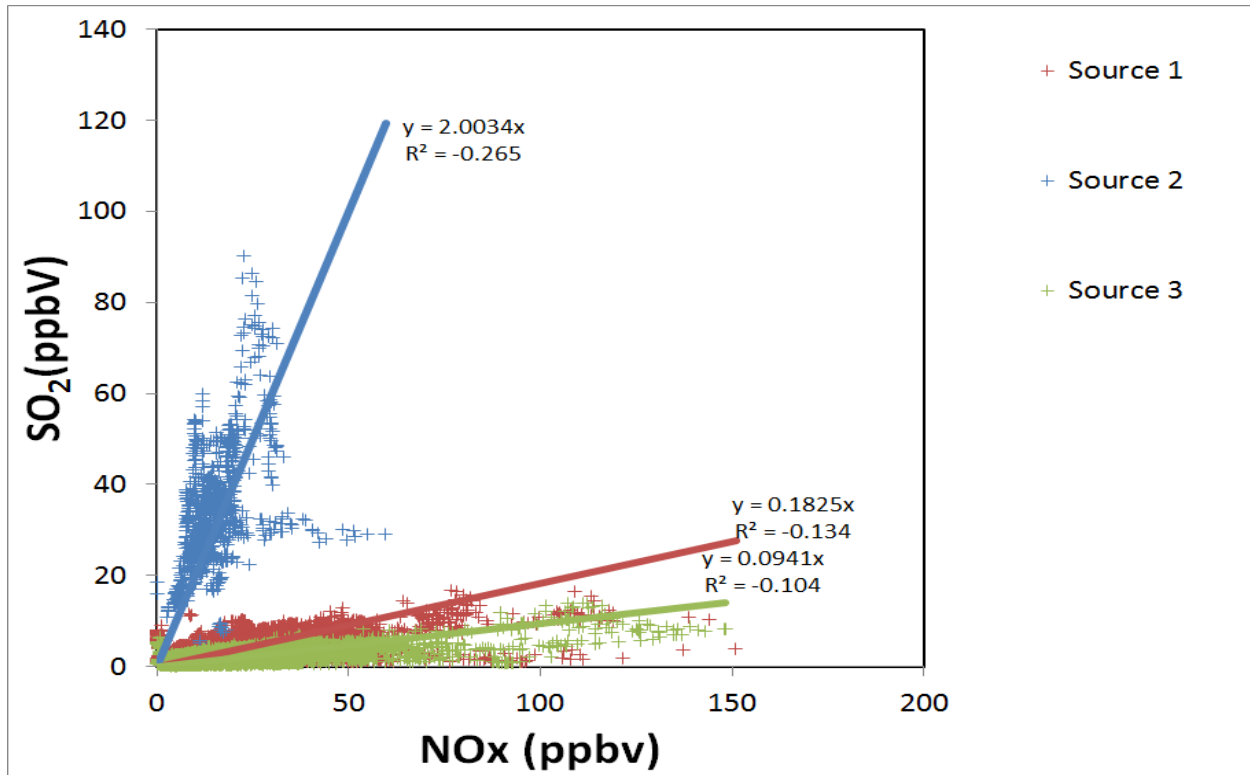


Figure15. Correlation plot of SO_2 vs. NO_x

Now, we use the slope of figure 13 and figure 15 to plot our sources into the sulphur content combustion efficiency diagram that we drew up based on the emission inventory (Figure 16).

In Figure 16, as we plotted three of our sources together with other sources from the emission inventory.

Source 1 and 3 had good correlation with acetonitrile and we can see that they also seem to have low sulfur content. So these could be biomass emissions. However, according to emission inventory biofuel has very poor combustion efficiency while our sources have a far more efficient combustion.

Source 2 falls very close to "industrial coal" and had no correlation with acetonitrile so these could be coal emissions.

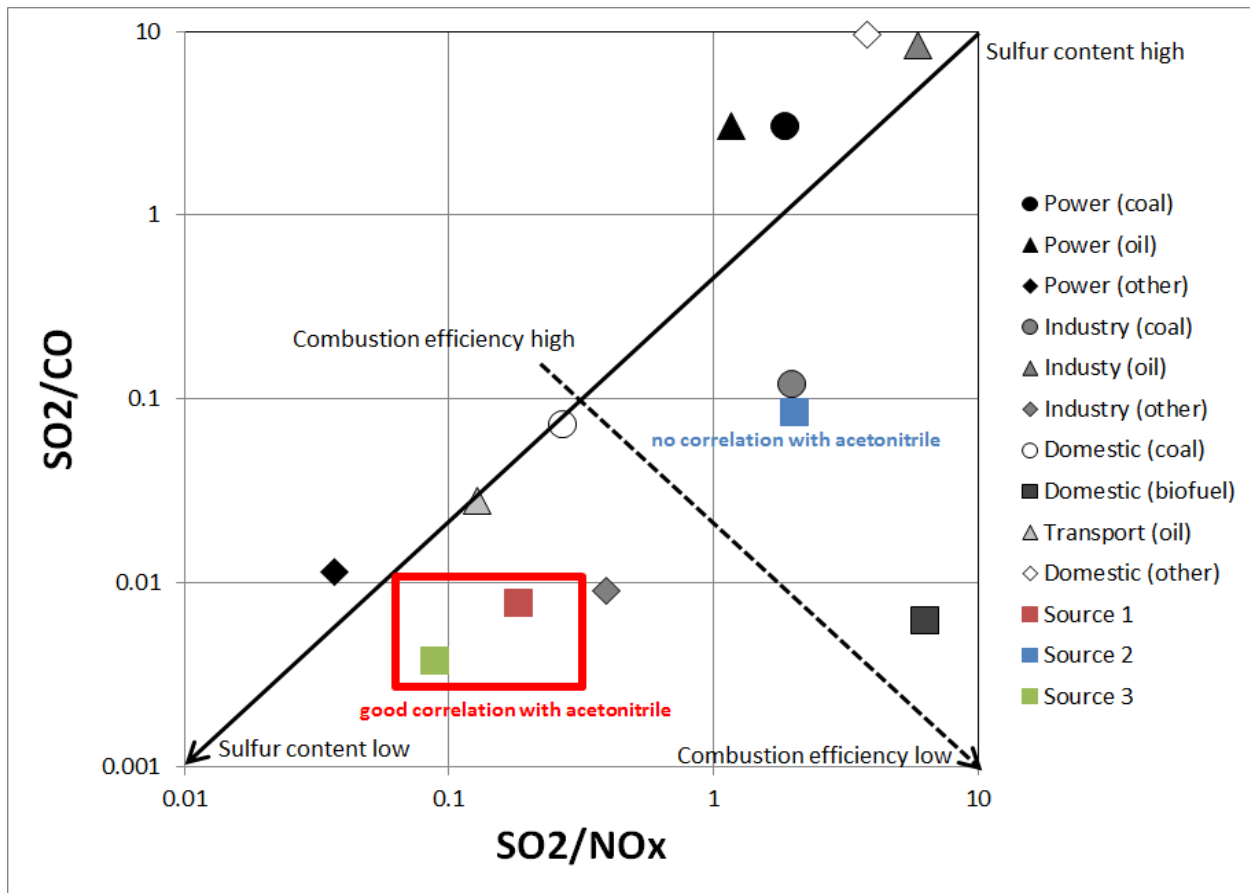


Figure16. Combustion efficiency diagram for different fuels with three different sources plotted in the same graph.

To constrain better, what the sources could be we plot diel box and whisker plots and wind rose plots for all sources separately.

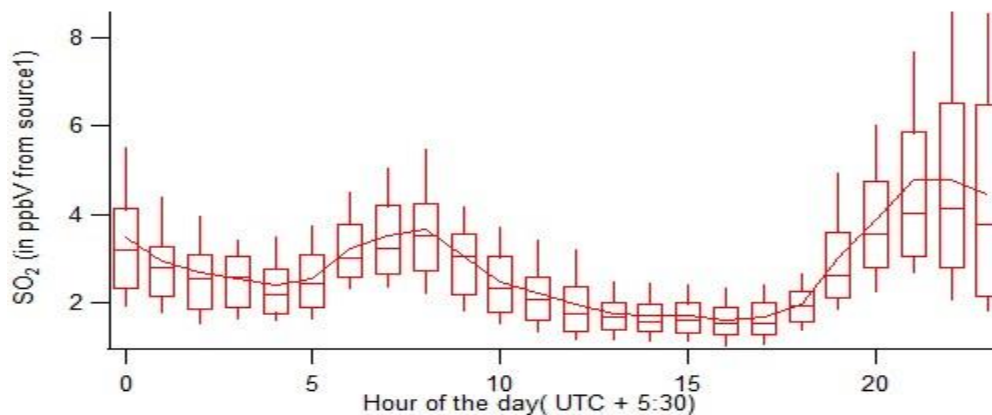


Figure17. Diel-box and whiskers plot for source1

Here, if we see then it is clear that it has bimodal peak. There are two peaks we see one in the morning and another one in the evening. It has something to do with diurnal variation activity. So we conclude from these two peaks shown that there could be garbage burning or domestic biomass use or some other form of biomass combustion with diurnal variations in emission strength.

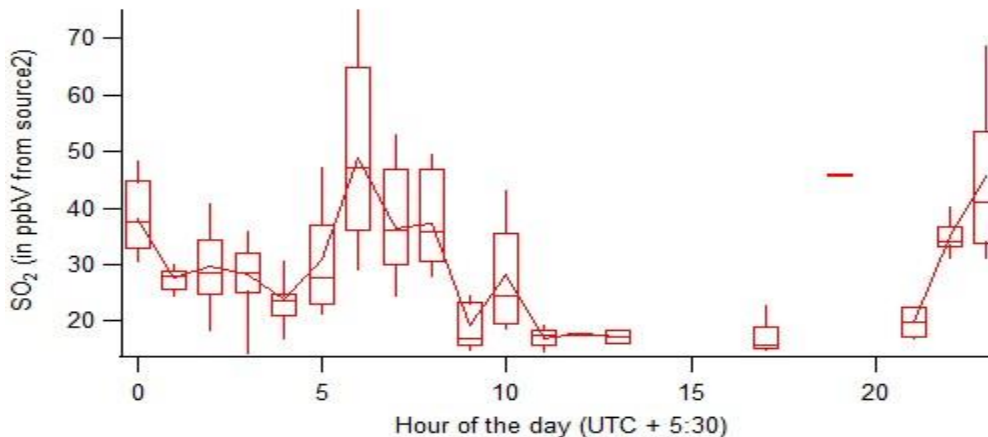


Figure18. Diel-box and whiskers plot for source2

Source 2 we capture predominantly at night. We don't capture it in a daytime. So, there could be two possibilities: one is either activity occurs only at night or SO₂ sinks during the day lead to us not capturing the high SO₂ /CO ratio during the day. If source has high sulfur content in the daytime SO₂ gets lost so rapidly that we never get the SO₂/CO emission ratio in the day. One distinct feature of this source is that we see sharp peak due to breaking of boundary layer in the morning time. This could mean the emissions occur above the nocturnal boundary layer.

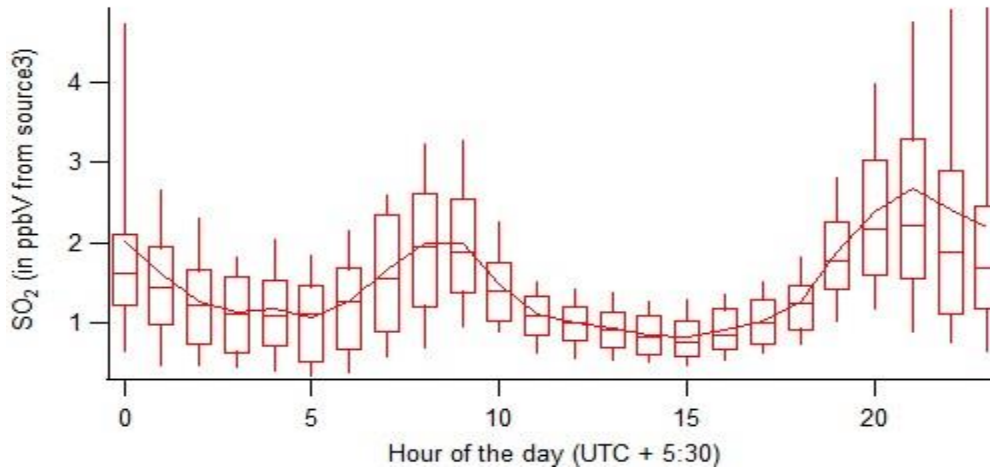


Figure19. Diel-box and whiskers plot for source3

For source 3 we also see the diurnal activity pattern. One peak in the morning between 8-9 hours and other one in the night time between 20-21 hours. We can conclude a little from here that traffic component possibly mixed with garbage burning. To clearly investigate further, what the sources are we made wind rose plots for all our three sources.

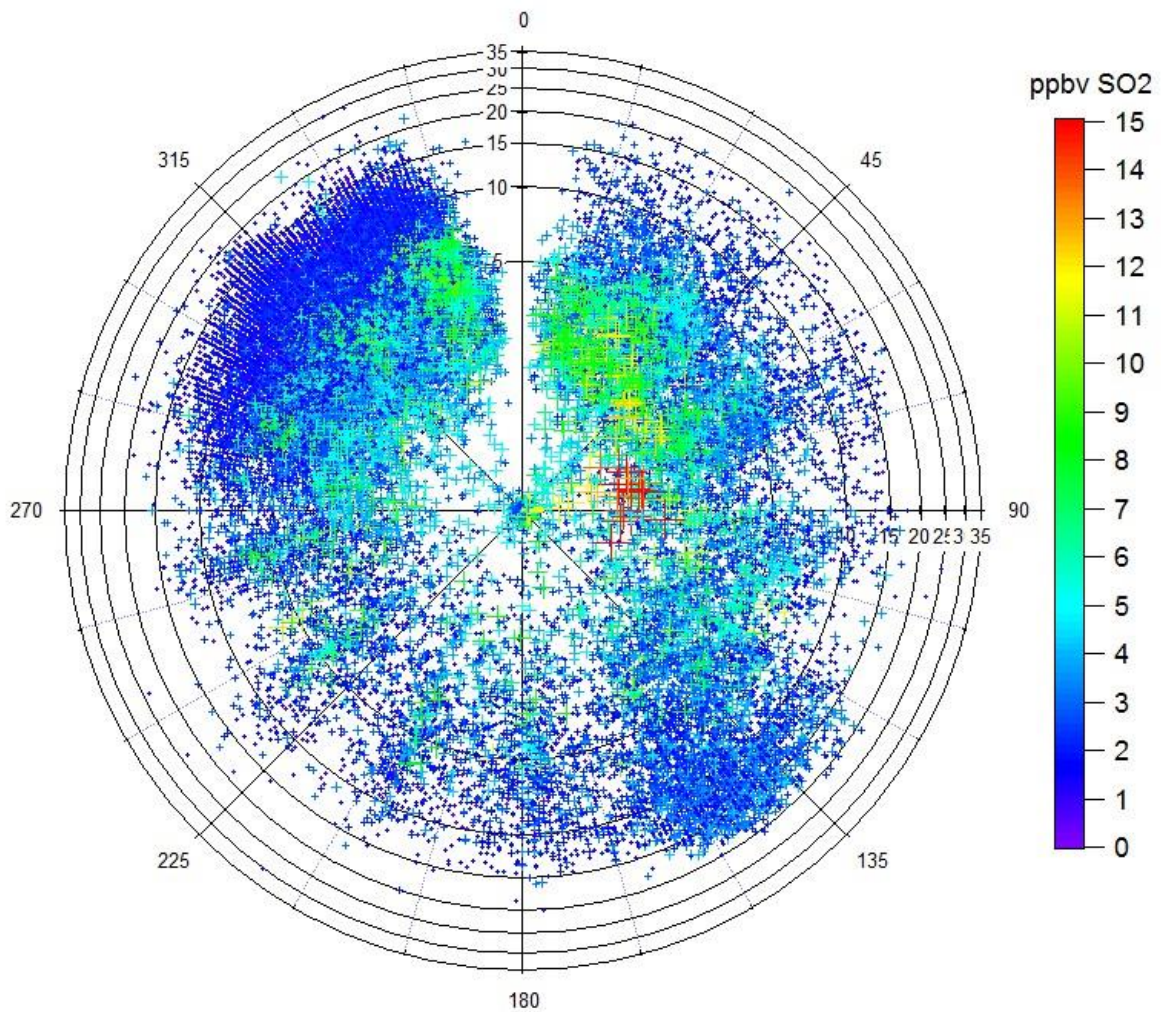


Figure20. Wind-rose plot for source1

When we look at this we can see the points are spread everywhere over the place. Higher values can be seen from 70-90° at very low wind speed. So here we have one potential local source which could be domestic biofuel use in the mid-day meal kitchen right across the street. Of course domestic biofuel use is ubiquitous so the similar emissions reach us from all over the place.

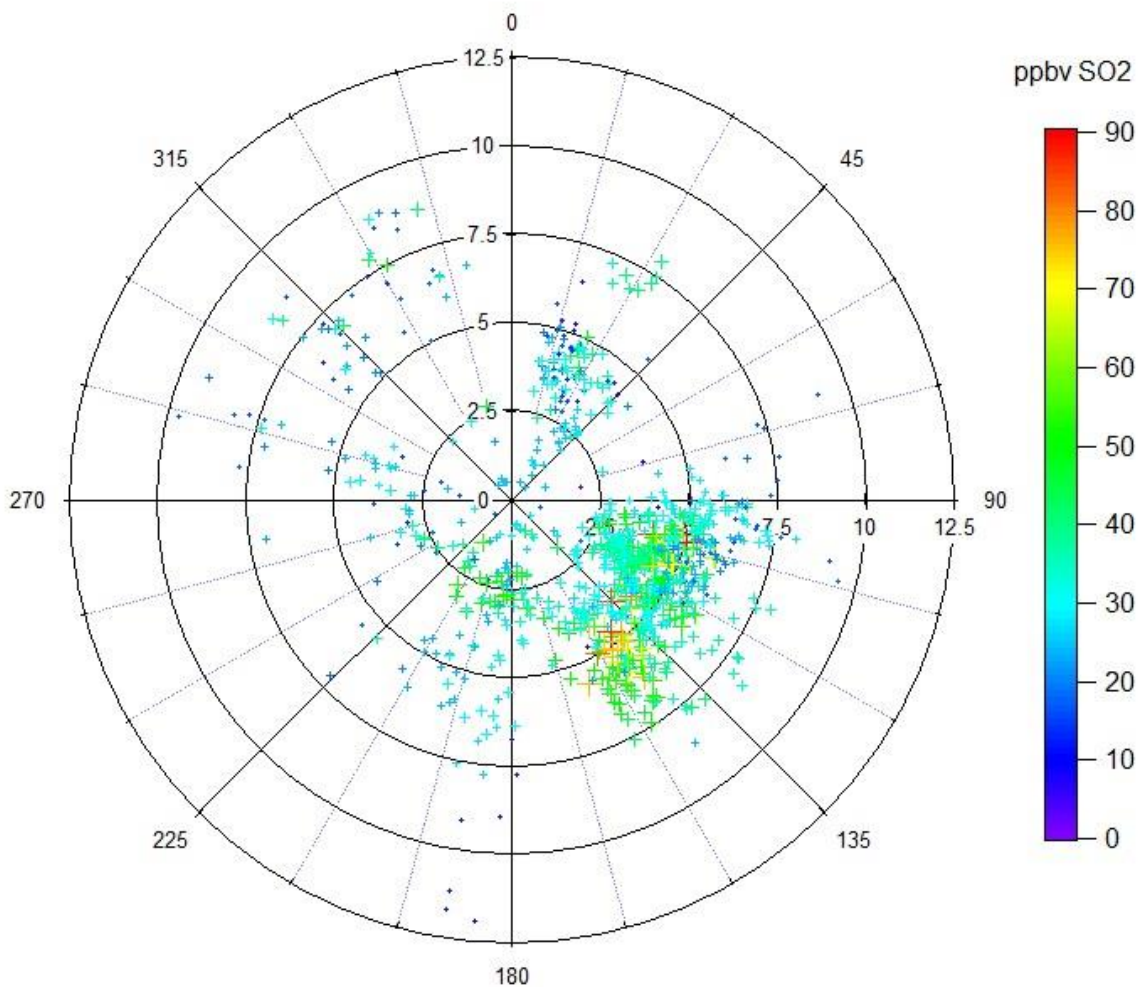


Figure21. Wind-rose plot for source2

In this figure there is distinctively a cluster around 135° where we have Yamuna Nagar coal-fired power plant is located. So it could power plant.

Since our wind rose shows a cluster of high observation values in two distinct directions, the source is likely to be a point source (industry/ power plant). SO_2/NO_x emission ratio for what we believe could be industrial coal in an emission inventory as well as in our data set too.

To check whether the source2 is the source that emits above the nocturnal boundary layer and is hence a power plant we have filtered Yamuna Nagar and made the diel-box and whisker plot. The sharp peak between 6-7 am confirms that this is the source that contributes high SO_2 in the morning when the nocturnal boundary layer breaks if the wind direction is from this sector and

the nocturnal boundary layer has been shallow on that day. Whenever the nocturnal boundary layer is so high that emissions occur within the boundary layer, emissions from this source reach as starting from the evening after the boundary layer establishes and mixing values gradually decrease throughout the night with the growth of the nocturnal boundary layer due to radiative cooling. The stack height of Deen Bandhu Chotu Ram power plant is 275 m.

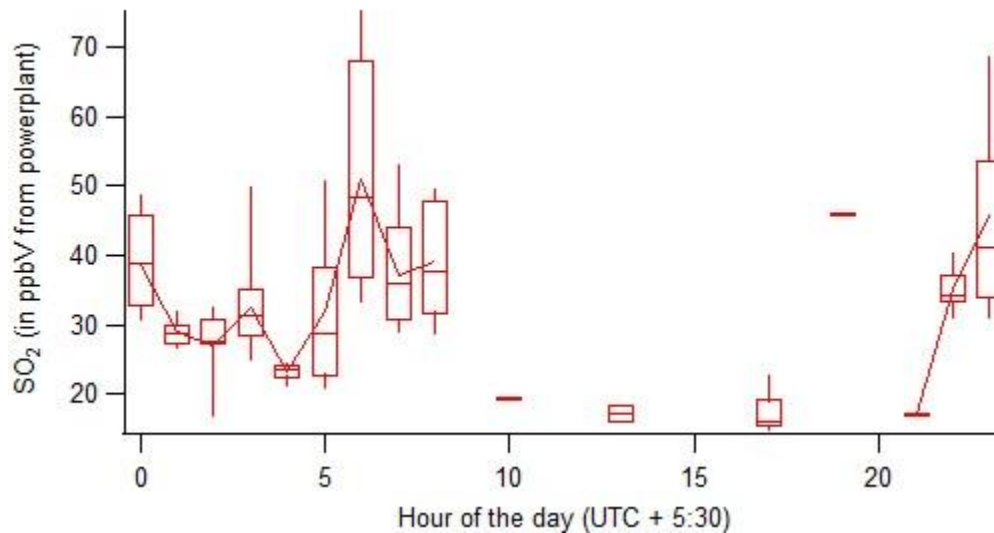


Figure22. Diel-box and whisker plot for source2 (which we investigated as a coal including power plants).

Emission inventory claims coal-fired power plants has lot of sulfur content where in reality we don't see any difference between industrial coal and power plant coal. So, SO₂ from the power sector is likely overestimated in the current emission inventories.

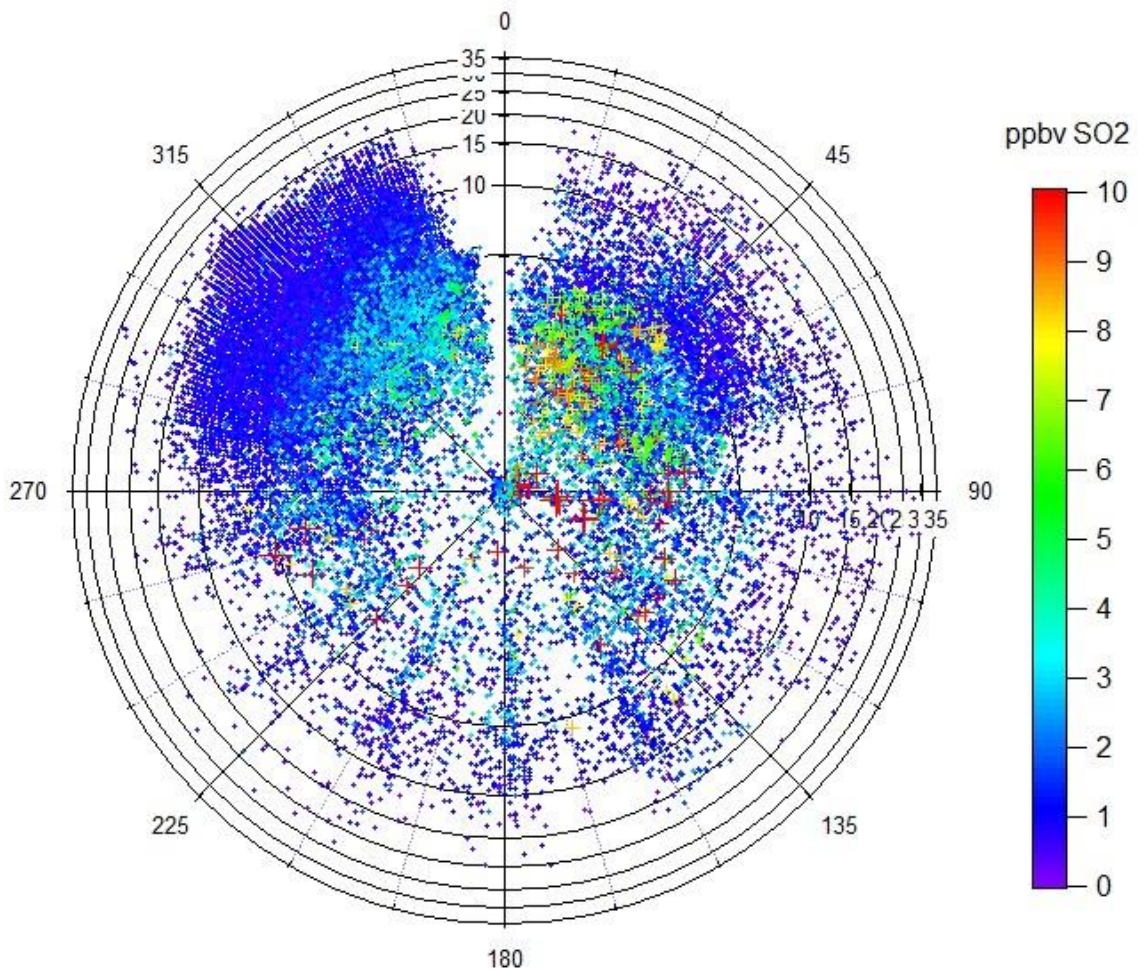


Figure23. Wind-rose plot for the source3

We can see occasional high values for all wind direction in particular at low wind speed i.e. <5m/s. Distinct cluster of points in Chandigarh wind direction can be seen. This suggests that the source could be traffic. As traffic has very high density over there. To investigate that hypothesis for source3 we filtered Chandigarh wind direction. We are providing the diel-box and whiskers plot for that direction only.

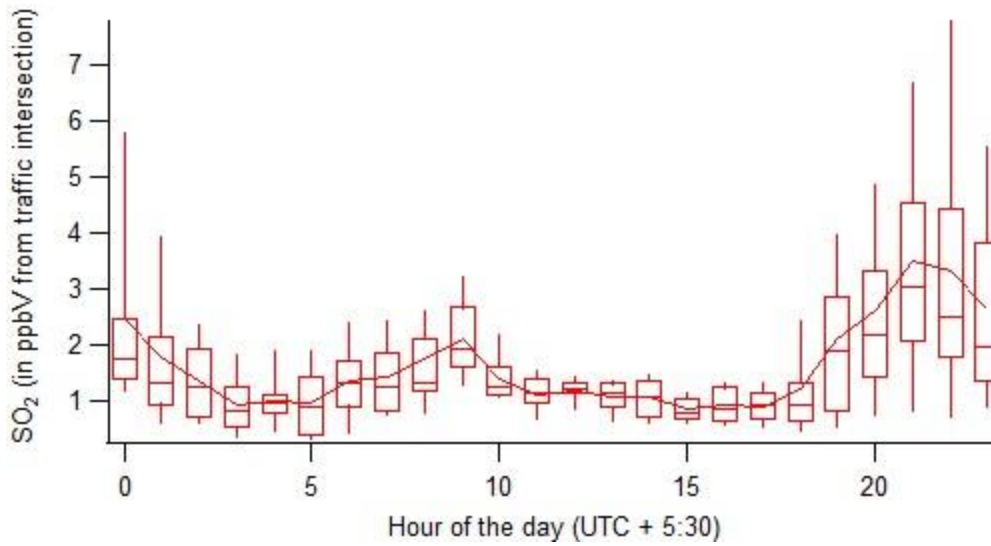


Figure24. Diel-box and whisker plot for Chandigarh wind direction

We see that there is peak only in the evening hours which suggests that it is indeed traffic.

Chapter 4

Summary and Conclusions

Sulfur dioxide was analyzed from period march to June 2013 which represents the typical summer time conditions of Indo-Gangetic plain.

So, average value and standard deviation of sulfur dioxide is found to be 4.8 and 5.4 respectively. In diel cycle we observed the high values are in the morning time. And in wind-rose plot we observed the highest concentration of sulfur dioxide from north and south-east direction due to major power plants lies in that region. First we identified two potential sources of SO₂ affecting our site in summer one of them is regional crop residue burning the other source are power plants. But after further investigation we have been able to identify three sources separately.

1. First could be biomass combustion both from domestic biofuel and crop residue burning.
2. Second could be power plants. Here very interesting thing is that as we are down wind so it seems emission characteristics agree with those values ascribed to industrial coal in the emission inventory but differ strongly from those ascribed to power plant coal. We do not see extremely high SO₂ that describes Indian power plant emission inventory. So emission of power plant could be overestimated in the current emission inventory.
3. Third seems to be traffic. And m42 is also coming out of it but not in larger amount and it could be diesel.

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