SOURCE APPORTIONMENT AND CHEMICAL CHARACTERIZATION OF TRACE ELEMENTS IN SUSPENDED PARTICULATE MATTER AT KOLHAPUR CITY

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION

I, **Mr. Atul Balwant Ayare** hereby ***declare*** that the Research Thesis entitled **“Source Apportionment and Chemical Characterization of Trace Elements in Suspended Particulate Matter at Kolhapur City”** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Chemical Engineering** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or institution for the award of any degree.

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CERTIFICATE

This is to *certify* that the Research Thesis entitled **“Source Apportionment and Chemical Characterization of Trace Elements in Suspended Particulate Matter at Kolhapur City”** submitted by **Atul Balwant Ayare** (Register No. **CH07P01**) as the record of the research work carried out by him, is, *accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of degree of **Doctor of Philosophy**.

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My Father

and

Smt. Lobha Balwant Ayare

My Mother

ABSTRACT

Ambient air pollution in an increasingly urbanized world directly threatens the health of a large fraction of the world's population. There is a growing recognition that air-borne emissions from major urban and industrial areas influence both air quality and climate change on scales ranging from regional up to continental and global. Deteriorating urban air quality affects the viability of important natural and agricultural ecosystems in regions surrounding highly urbanized areas, and significantly influences regional atmospheric chemistry and global climate change. This challenge is particularly acute in the developing world where the rapid growth of megacities (cities having population equal to or more than 10 million) is producing atmospheric pollution of unprecedented severity and extent. For example, the deterioration of air quality is a problem that is directly experienced by a majority of the 300 million urban Indians, about 30% of India's population. In developing countries, migration from the countryside to the megacities has brought as a consequence greater emissions into the atmosphere. This is mainly produced by the increase of vehicular traffic; a problem exacerbated by the tendency in these countries to have a stock of old and badly maintained vehicles and badly maintained roads. At the same time, the number of vehicles in circulation has increased as well. These factors have produced far-reaching changes in air quality in urban contexts, especially in the 1990s, when the majority of clean air plans were tightened up. The urban area has expanded with a result that urban population is now closer to Industrial establishments. Airborne particles which result from chemical and allied industries are nothing but heavy metals and aerosols contains reactive, corrosive and carcinogenic chemical molecules.

Trace elements are released into the atmosphere by human activities, such as combustion of fossil fuels and wood, high temperature industrial activities and waste incineration. The combustion of fossil fuels constitutes the principal anthropogenic source of Ba, V, Co, Ni, Se, Mo, Sn, Sb, and Hg, and particularly of Cr, Mn, Cu, Zn, and As. High percentages of Ni, Cu, Zn, As, and Cd are emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Ni, Cu, Zn, Cd, and Pb. Several trace elements are emitted through the abrasion of tires (Cu, Zn, Cd) and brake pads (Sb, Cu), corrosion (V, Fe, Ni, Cu, Zn, Cd) lubricating oils (V, Cu, Zn,

Mo, Cd) or fuel additives (V, Zn, Cd, Pb). The platinum group elements, Rh, Pd and Pt, represent a relatively new category of traffic related trace elements in the environment, especially urban one, due to their application in automobile catalytic converters since the beginning of the 1980s. Studies of the transport and mobilization of trace elements up to now have attracted attention of many researchers. Trace elements are persistent and widely dispersed in the environment and interacting with different natural components result in toxic effects on the biosphere. Air pollution is a major health risk that may worsen with increasing industrial activity. At present, urban outdoor air pollution causes 1.3 million estimated deaths per year worldwide, according to the World Health Organization. The researchers studied the impact of human-made emissions on air quality, assuming past emission trends continue and no additional climate change and air pollution reduction measures (beyond what is in place since 2005) are implemented. Air pollution would also increase in Europe and North America, but to a much lesser extent than in Asia, due to the effect of mitigation policies that have been in place for over two decades. The results show that in 2025 and 2050, under the business-as-usual scenario studied, East Asia will be exposed to high levels of pollutants, such as nitrogen dioxide, sulphur dioxide and fine particulate matter ($PM_{2.5}$). Northern India and the Arabian Gulf region, on the other hand, will suffer a marked increase in ozone levels. The analysis now published is the first to include all five major air pollutants know to negatively impact human health: $PM_{2.5}$, nitrogen dioxide, sulphur dioxide, ozone, and carbon monoxide. The scientists considered pollutants released through human activity, as well as those occurring naturally such as desert dust, sea spray, or volcanic emissions. Taking all pollutants into account, eastern China, northern India, the Middle East, and North Africa are projected to have the world's poorest air quality in the future. In the latter locations this is due to a combination of natural desert dust and man-induced ozone. The effect of anthropogenic pollution emissions are predicted to be most harmful in East and South Asia, where air pollution is projected to triple compared to current levels.

Increasingly, source apportionment analyses are being used as a relatively accurate, rapid, and cost-effective means of identifying and targeting sources and their relative contributions to the total pollution load. This scientific information helps air quality modellers as well as policy- and decision-makers. The data obtained from source apportionment studies provides policy- and decision-makers with practical tools to identify and quantify different sources of air pollution, increasing their ability to put in place effective policy and regulatory measures and control strategies to reduce air pollution to acceptable levels. Additionally, co-benefits can be realized – for example, source apportionment studies targeting specific air pollutants can also be used to assess climatic impacts, identify clean energy measures and greenhouse gas emission reduction strategies. Successful application of source apportionment (receptor modeling) methods and support to effective policy- and decision-making depends on the accuracy and relevance of the air quality measurements and the interpretations made by the scientist and air quality manager. Environment Canada's air quality experts have included source apportionment studies and the improvement of source apportionment techniques and analyses as an integral component of their science and research, constantly seeking the highest quality of data and information.

In India, Source Apportionment Studies have already been carried out in the cities of Bangalore, Chennai, Delhi, Kanpur, Mumbai and Pune. The primary focus of the study was on particulate matter, although it also deals with other pollutants like NOx, SO_2, Ozone (O^3), $PM_{2.5}$, etc. Central Pollution Control Board, New Delhi has signed Memorandum of Contracts (MoCs) for source apportionment studies for the cities of Mumbai, Chennai and Kanpur with NEERI, IIT- Mumbai and IIT- Kanpur respectively and for source profiling for sources other than vehicles with IIT Mumbai. The Automotive Research Association of India (ARAI), Pune has conducted studies on emission factors for vehicles required as inputs in the studies.

Based on the extensive literature survey on chemical characterization of trace elements and source apportionment studies abroad and in India, methodology adopted in Source factorizations, it was seen that PMF and CMB models were used to predict the quantification of trace elements in particulate matter from the different sources. In India, it was observed that the Source apportionments studies carried out by CPCB, New Delhi were carried out with the help of Chemical Mass Balance (CMB) model which need huge dataset of the sources.

Both CMB and PMF provide quantitative estimates of the source contributions. In the CMB analysis, source profiles are provided whereas in PMF, the source profiles are estimated. If it is some of the source profiles are known, they can be used in PMF to constrain the extracted source profiles and thereby reduce the rotational indeterminacy. Both CMB and PMF are employing least squares fitting, but there are some important differences in how the underlying error structures are modelled and how many unknowns are being estimated. With PMF it is not possible to precisely assign errors to the source profiles and contributions. In a CMB analysis, it is possible to assign define error estimates to each source contribution value. However, there are no diagnostics provided in the CMB model that would alert the user to misspecification of the source profiles. Also since the CMB analysis is done on a sample-by-sample basis, there can be errors in the estimated source contributions because of the variations that can occur in the source profiles. PMF uses all of the data and thus, estimates the average source profile over the time interval during which samples were acquired. Thus, there are some similarities in the process and the outcome, but there are also some important differences in what is being estimated, the input data that is required, and the estimates of the uncertainties in the calculated values.

Metropolitan cities selected for such studies had Source data available with CPCB. It is observed that Metropolitan Cities worldwide as well as India have adopted Source Apportionment Studies routinely and results are promising for better Air Quality Management in such cities. But II tier cities are, yet, to adopt such studies due to lack of source information and other necessary data to carry out Source Apportionment Studies.

With the recent initiation of the Indian economic and the Investment policies, there is an increased growth in all the sectors in India along with an economic growth. The main areas of the property investments are the metro related areas and the tier I cities. For quite some time, most of the investors have been investing in these tier I cities and the metro related areas which has eventually saturated the areas. Both residential and the commercial investments have burgeoned these areas. Various large scale investments have made the realty sector quite fast along with an array of challenging projects. Apparently the unplanned development has resulted in the congestion of the city and is filled with residential and commercial properties.

However, since all these main areas are congested, the government of these cities is forced to concentrate on alternative smaller cities like the Tier II cities. Few of the areas like Indore, Jaipur, Kochi, Ludhiana, Nasik, Nagpur and Chandigarh are in demand. The Indian real estate is now completely focusing in these areas and is extending new avenues for its development. The realtors are introducing an array of constructions, services and solutions for the development and the benefit of investors. Also the current situation and demand of the residential real estate market in the Tier I and the metro areas has forced the property investors to move on to the Tier II cities. As most of these cities are on the verge of development with wider infrastructure and open space unlike other metro related areas, most of the buyers prefer these areas.

Apart from just the spread of residential projects in the Tier II cities, there is also an equivalent demand for the commercial property in these areas. As witnessed the retail real estate in India is on an upsurge and there is an array of retail markets and shops which are coming up in these areas on a fast pace. Also there is an increased change in the lifestyle of people and they have adopted the mall culture. Owning to all these aspects the developers find these cities more lucrative and also have various options for construction with better returns. Also the developers are witnessing greater investments in these areas when compared to metro cities. Most of the investors prefer investing in these areas because of the lesser time each project takes for construction and they also get better returns. The labour is cheap with safer markets along with a higher yield.

Kolhapur in Maharashtra is fast growing II tier city in terms of Industrial Development, Co-operative movements, growing number of Agro based industries, leather industries and of course, tourism for which the city is all known. Hence, the present study was carried out in Kolhapur city to estimate and analyze chemically trace metals in SPM at Kolhapur City, which constitutes a long term threat to the health of general population. The results of source apportionment will be taken to appropriate dispersion model for accurate forecasting. The modelling and simulation will help urban planners and air quality planners for zoning policy decision making.

The objectives of the present study were to to identify the locations for assessment of air quality based on wind direction/dispersion, to generate the required site specific data on topography/elevation, development activities etc. in selected locations for dispersion study, to measure Meteorological data i.e. Wind Speed, Wind Direction, Ambient Temperature etc. at selected locations for the study, to measure the concentration of Suspended Particulate Matter (SPM) at selected locations for the study, to characterize and quantify the presence of trace metals in SPM i.e. Cu, Pb, Ni, Zn, Cd, Mn, Fe, to identify the sources (Source Apportionment) of SPM by using United States Environmental Protection Agency (US EPA) Positive Matrix Factorization (PMF) Receptor model, to identify contribution of trace elements from various identified sources, to validate the results of modelling with characterization of trace elements in soil samples at selected locations by mass balance and to suggest methods and procedures for minimization of trace elements at selected locations

The methodology as per standard protocol and laboratory practices was adopted to carry out experimental work as well as calculations of results to arrive at conclusions. Selection of three locations viz. Urban area like Shahu Blood Bank Corner on downwind direction of the city, Industrial area like Shiroli MIDC and Gokul Shirgaon MIDC, both on upwind direction of the city was done and collected wind data at these locations to build Wind rose to know the predominant wind direction and wind speed to be used for dispersion studies. High Volume Sampler and measured the concentration of SPM for 24 hours during July 2008 to July 2009 at all three locations mentioned above. Simultaneously, the soil samples were collected from each sampling locations. Acid digestion was carried out to extract trace elements from SPM collected from air as well as soil for determination and chemical characterization of trace elements i.e. Cu, Pb, Ni, Zn, Cd, Mn, and Fe using Atomic Absorption Spectrophotometer. The observed concentrations of trace elements were given as input to United States Environmental Protection Agency (US EPA) Positive Matrix Factorization (PMF) Receptor model predict the concentrations of trace elements on three locations. The US EPA PMF model was run under standard conditions mentioned and documented by US EPA and sources of each trace element were found out. Source Apportionment, which includes quantitative estimation of each source, was determined and percentage contribution of each source was calculated. The validation was done on the basis of the results of PMF model with characterization of trace elements in soil samples at locations. The trace element/s with higher concentration at all locations was found out and detailed analysis was carried out to justify the cause of higher concentrations.

The present study has been undertaken for identifying the sources of air pollution and their contributions to atmospheric pollutants in the form of particulate matter and the trace metal concentration in SPM in Kolhapur and its industrial at suburbs. The SPM samples were collected during July 2008 to July 2009 at three different sampling locations in the Kolhapur city (Maharashtra, India) namely Shahu Blood Bank Corner (SBBC) in the city, Gokul Shirgaon MIDC (GS) Area which is on South East of the city and Shiroli MIDC (SS) area which is on East of the city. Seven trace elements were analyzed using AAS. The first and most important pre-requisite in trace element analysis of atmospheric SPM is the precautions in processing and analysis of samples, to avoid contamination at each and every stage of sample collection and handling. The chemical composition data in particulate matter were analyzed using the US EPA PMF 3.0 receptor model to estimate the contributions from possible emission sources.

Among all the criteria air pollutants, particulate matter (SPM and RSPM) have emerged as the most critical one in almost all urban areas of India. High SPM concentrations are primarily irritants but do not have much relevance for direct health consequences as compared to effects of its respirable fractions (PM_{10} and $PM_{2.5}$). Due to this reason, the worldwide focus of monitoring is now increasingly being shifted to measurement of finer particles (PM_{10} and $PM_{2.5}$), which can penetrate the human respiratory systems. Since 2010 the focus on suspended particulate monitoring has shifted to PM_{10} in India as well. Being a critical pollutant, PM_{10} has also been included in National Ambient Air Quality Standards. The present study was initiated in 2008 and monitoring was completed by 2010. The attempt was to characterize trace elements in SPM and quantification of contribution of each trace element to respective source.

Source Apportionment study, first time is carried out for tier II city like Kolhapur, Maharashtra, India. US EPA PMF model is used since extensive source profiling based data not available. Model validation is done through measurement of emissions from

foundries and traffic, which are major sources and also soil metal analysis. General suggestions for zoning of industries, traffic management and cause consequence study for health impact are suggested.

Keywords: Source Apportionment, Suspended Particulate Matter, Chemical Characterization, Trace Elements, Positive Matrix Factorization, Kolhapur City, Tier II

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ABBREVIATIONS

ABCs	Atmospheric brown clouds
ACCENT	Atmospheric Composition Change: European Network of Excellence
AOGCM	Atmosphere-ocean general circulation model
AQ	Air quality
AQEG	Air Quality Expert Group
ATC	Annual tropospheric column
AURN	Automatic Urban and Rural Network (air quality monitoring)
AZM	Annual zonal mean
BAU	Business as usual
BC	Black carbon
BS	Black smoke
BTL	Biomass to liquid
ºC	Degrees Celsius
C	Carbon
CAFE	Clean Air For Europe
CAP	Common Agricultural Policy
CC	Climate change
CCGT	Combined cycle gas turbines
CCN	Cloud condensation nuclei
CCM	Chemistry climate model
CCZ	Congestion charging zone
C/N	Ratio of carbon to nitrogen
CDNC	Cloud droplet number concentration
CEPA	California Environmental Protection Agency
CERC	Cambridge Environmental Research Consultants
CFC	Chlorofluorocarbon
CH_3SH	methanethiol
CH_3SCH_3	dimethyl sulphide (DMS)
CH_3SSCH_3	Dimethyldisulphide (DMDS)
CH_4	Methane
CHP	Combined heat and power
CLE	The current legislation scenario for emissions by IIASA

CLRTAP	Convention on Long-Range Transport of Air Pollution
CO	Carbon monoxide
CO_2	Carbon dioxide
COP	Conference of Parties
COS	Carbonyl sulphide
CS_2	Carbon disulphide
CSM	Climate systems model
CTM	Chemical transport model
Defra	Department for Environment, Food and Rural Affairs
DfT	Department for Transport
DMDS	Dimethyldisulphide (CH_3SSCH_3)
DMS	Dimethyl sulphide (CH_3SCH_3)
DPF	Diesel particulate filter
DTI	Department for Trade and Industry
DU	Dobson unit, 1DU= 2.68 x 10^{16}molecule per cm
EA	Environment Agency
ECCP	European Climate Change Programme
EEA	European Environmental Agency
EGR	Exhaust gas recirculation
EMEP	European Monitoring and Evaluation Programme - a Cooperative Programme under CLRTAP
EU	European Union
EU25	The 25 countries that were members of the European Union before Romania and Bulgaria joined on 1 January 2007
EU ETS	EU Emission Trading
FACE	Free air carbon dioxide enrichment
FGD	Flue gas desulphurisation
GAINS	Greenhouse gas air pollution interactions and synergies, an IIASA model
GCM	General circulation model
GHG	Greenhouse gas
GHGI	Greenhouse gas inventory
GISS	Goddard Institute for Space Studies (USA)
g km^{-1}	Grams per kilometre
GOME	Global Ozone Monitoring Experiment
g passenger-km^{-1}	Grams per passenger kilometre
GVW	Gross vehicle weight
GWP	Global warming potential

H_2	Hydrogen
HadAM3	Hadley Centre Global Atmosphere Climate Model
HadCM3	Hadley Centre Coupled Ocean Atmosphere Global Climate Model
HadRM3	Hadley Centre Regional Climate Model
HCFC	Hydrochloroflurocarbon
HCHO	Formaldehyde
HDV	Heavy duty vehicles – road vehicles greater than 3.5 tonnes weight (GVW)
HFC	Hydroflurocarbon
HGV	Heavy goods vehicles – road vehicle greater 7.5 tonnes (GVW), where GVW is the gross vehicle weight i.e. the combined weight of the vehicle and the goods
hr^{-1}	Per hour
HNO_3	Nitric acid
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
H_2O_2	Hydrogen peroxide
HO_2	Hydroperoxy radical
IGCC	Integrated gasification combined cycle
IIASA	International Institute for Applied Systems Analysis
IPCC	Intergovernmental Panel on Climate Change
K	Kelvin (thermodynamic temperature)
KPa	Kilopascal (unit of pressure)
kt	Kilotonne
ktC	Kilotonne Carbon
LCA	Life Cycle Analysis
LDV	Light Duty Vehicles – road vehicles less than 3.5 tonnes weight
LEV	Low emission vehicles
LEZ	Low emission zone
LGV	Light goods vehicles – goods vehicles less than 3.5 tonnes in weight
LNT	Lean NO_X traps
LOSU	Level of scientific understanding
LPG	Liquefied petroleum gas
LRTAP	Long–Range Transboundary Air Pollution
LWC	Liquid water content (of cloud)

MATCH	Multiscale Atmospheric Transport and Chemistry Model
MBT	Mechanical biological treatment
MFR	The maximum feasible reduction scenario for emissions by IIASA
MODIS	Moderate resolution imaging spectroradiometer
MOZART	Model of ozone and related chemical tracers version 2
ms^{-1}	Metres per second
$\mu g\ m^{-3}$	Micrograms per cubic metre of air
MSW	Municipal solid waste
N	Nitrogen (element)
N_2	Nitrogen (gas)
NAEI	National Atmospheric Emissions Inventory
NASA	National Aeronautics and Space Administration (USA)
NCAR	National Centre for Atmospheric Research
NCEP	National Centres for Environmental Prediction
NECD	National Emissions Ceilings Directive
NEGTAP	The National Expert Group on Transboundary Air Pollution
NERC	Natural Environment Research Council
netcen	National environmental technology centre, part of AEA Technology plc – now AEA Energy & Environment
NH_3	Ammonia
NH_4	Ammonium
NMVOC	Non-methane volatile organic compound
NO	Nitrogen monoxide, also termed nitric oxide
NO_2	Nitrogen dioxide
NO_3	Nitrate
NO_X	Nitrogen oxides (NO + NO_2)
NO_y	Total reactive nitrogen oxides
N_2O	Nitrous oxide
N_2O_5	Nitrogen pentoxide
O_3	Ozone
OC	Organic carbon
OH	Hydroxyl radical
PAH	Polycyclic aromatic hydrocarbon
PAN	Peroxyacetyl nitrate
PCB	Polychlorinated biphenyl
PFC	Perfluorocarbons

Pg	Petagrams (10^{15}g)
POCP	Ozone forming potential
POP	Persistent organic pollutants
PORG	Photochemical Oxidant Review Group
PM	Particulate matter
PM_{10}	Airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter and which transmits particles of below this size
$PM_{2.5}$	Airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 2.5 µm aerodynamic diameter and which transmits particles of below this size
PM_1	Airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 1 µm aerodynamic diameter and which transmits particles of below this size
$PM_{0.1}$	Airborne particulate matter passing a sampling inlet with a 50% efficiency cut-off at 0.1 µm aerodynamic diameter and which transmits particles of below this size
PM_{coarse}	Fraction of the measured particle mass concentration determined from PM_{10} minus $PM_{2.5}$
ppb	Parts per billion (1,000,000,000)
ppm	Parts per million (1,000,000)
ppt	Parts per trillion (1,000,000,000,000)
PRUDENCE	Prediction of Regional scenarios and Uncertainties for defining European Climate Change Risks and Effects
PTM	Photochemical trajectory model
QBO	Quasi biennial oscillation
RAINS	Regional Air Pollution and Simulation, model used by IIASA
RFI	Radiative forcing index
RO_2	Organic peroxy radical
RCA	Rossby centre regional atmosphere climate model
RCEP	The Royal Commission on Environmental Pollution
RCM	Regional climate model
ROG	Reactive organic gases
RVP	Reid vapour pressure
S	Sulphur
SCR	Selective catalytic reduction
SDSM	Statistical downscaling model
SF_6	Sulphur hexafluoride

SH	Southern hemisphere
SIA	Secondary inorganic aerosol
SMMT	Society of Motor Manufacturers and Traders Limited
SO_2	Sulphur dioxide
SO_4	Sulphate
SO_x	Oxides of sulphur
SOA	Secondary organic aerosol
SPM	Suspended Particulate Matter
SRES	Special Report on Emissions Scenarios
SSF	Solid smokeless fuel
STE	Stratosphere-troposphere exchange
STOCHEM	Three dimensional Lagrangian model of tropospheric chemistry
Tg	Teragrams (10^{12} g)
TORCH	Tropospheric organic chemistry experiment
TWh	TeraWatt hours
UKCIP	UK Climate Impacts Programme
UKMO	United Kingdom Meteorological Office
UNFCCC	United Nations Framework Convention on Climate Change
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
USA	United States of America
UTLS	Upper Troposphere Lower Stratosphere
VCA	The Vehicle Certification Agency
VED	Vehicle excise duty
VOC	Volatile organic compound
WBCSD	World Business Council for Sustainable Development
WDE	Water-diesel emulsion
WMO	World Meteorological Organisation
W	Watt (unit of power)
W m^{-2}	Watts per square metre
Yr	Year

Chapter 1

INTRODUCTION

Environmental effects due to urbanization have been observed since early in the 18th century. Until the middle of the 20th century, urbanization levels were too low and the numbers of large cities were too small for there to be any significant effects other than local climatic and hydrological impacts. As late as 1900, there were barely 43 cities in the world exceeding 5,00,000 populations, of which only 16 exceeded 10,00,000. Since 1950 the number of large cities have increased very rapidly (about 400 exceed 10,00,000) as per UNEP/WHO (1993) report. Metropolitan areas have grown to form even larger agglomerations and some very large urban areas with populations in the tens of millions have emerged. For example, by the year 2,000, Calcutta, Bombay, Cairo, Jakarta and Seoul are expected to be in the 15-20 million people range. The environment in large urban areas has deteriorated and resulted in an increased incidence of diseases and ailments. The effects of urban development can be defined by many factors. The most important of these factors relate to air quality, the availability of safe water supplies, and provisions for sanitation and waste management. Smog hanging over cities is the most familiar and obvious form of air pollution. But there are different kinds of pollution—some visible, some invisible—that contribute to global warming. Generally any substance that people introduce into the atmosphere that has damaging effects on living things and the environment is considered as air pollution.

1.1 AIR POLLUTION

Ambient air pollution in an increasingly urbanized world directly threatens the health of a large fraction of the world’s population. There is a growing recognition that air-borne emissions from major urban and industrial areas influence both air quality and climate change on scales ranging from regional up to continental and global. Deteriorating urban air quality affects the viability of important natural and agricultural ecosystems in regions surrounding highly urbanized areas, and significantly influences regional atmospheric chemistry and global climate change. This challenge is particularly acute in the developing world where the rapid growth of megacities (cities having population equal to or more than 10 million) is producing atmospheric pollution of unprecedented severity and extent. For example, the deterioration of air quality is a problem that is directly experienced by a majority of the 300 million urban Indians, about 30% of India's population (Economic Survey of Delhi, 2003). In developing countries, migration from the countryside to the megacities has brought as a consequence greater emissions into the atmosphere. This is mainly produced by the increase of vehicular traffic; a problem exacerbated by the tendency in these countries to have a stock of old and badly maintained vehicles. At the same time, the number of vehicles in circulation has increased as well. These factors have produced far-reaching changes in air quality in urban contexts, especially in the 1990s, when the majority of clean air plans were tightened up.

Air pollution is a major health risk that may worsen with increasing industrial activity. At present, urban outdoor air pollution causes 1.3 million estimated deaths per year worldwide, according to the World Health Organization. The researchers studied the impact of human-made emissions on air quality, assuming past emission trends continue and no additional climate change and air pollution reduction measures (beyond what is in place since 2005) are implemented. They point out that, while pessimistic, the global emissions trends indicate such continuation.

Air pollution would also increase in Europe and North America, but to a much lesser extent than in Asia, due to the effect of mitigation policies that have been in place for over two decades.

The results show that in 2025 and 2050, under the business-as-usual scenario studied, East Asia will be exposed to high levels of pollutants, such as nitrogen dioxide, sulphur dioxide and fine particulate matter (PM2.5). Northern India and the Arabian Gulf region, on the other hand, will suffer a marked increase in ozone levels.

The analysis now published is the first to include all five major air pollutants know to negatively impact human health: $PM_{2.5}$, nitrogen dioxide, sulphur dioxide, ozone, and carbon monoxide. The scientists considered pollutants released through human activity, as well as those occurring naturally such as desert dust, sea spray, or volcanic emissions.

Taking all pollutants into account, eastern China, northern India, the Middle East, and North Africa are projected to have the world's poorest air quality in the future. In the latter locations this is due to a combination of natural desert dust and man-induced ozone. The effect of anthropogenic pollution emissions are predicted to be most harmful in East and South Asia, where air pollution is projected to triple compared to current levels.

1.2 SOURCES OF AIR POLLUTION

Air pollution in urban area comes from a wide variety of sources. The single most important source for the classical pollutants viz. sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs), and particulate matter (PM) is generally the combustion of fossil fuels. Of particular importance is the burning of fuels for road transport and electricity generation. There are three major sources of air pollution in urban areas, namely mobile sources, stationary sources, and open burning sources that can be categorized into the source groups motor traffic, industry, power plants, trade, and domestic fuel. The investigation published in 1996 by Mage et al. indicates that motor traffic is a major source of air pollution in megacities.

1.3 AIR POLLUTION AND HEALTH EFFECTS

Air pollution is recognized as a major threat to human health. The United Nations Environment Programme has estimated that globally 1.1 billion people breathe unhealthy air (UNEP, 2002). Epidemiological studies have shown that concentrations of ambient air particles are associated with a wide range of effects on human health, especially on the cardio-respiratory system (Baldasano, J.M., Valera, E., Jimenez, P. et al. 2003). A growing body of evidence indicates that particulate pollution increases daily deaths and hospital admissions throughout the world (Pope et al., 1995; Zanobetti et al., 2001). Gaseous co-pollutants, seasonal patterns or weather did not confound the association between particulate pollution and cardiopulmonary mortality (Schwartz, 1994; Samet et al., 1998, 2000). Similarly, it was not modified significantly by race, sex and socioeconomic status (Zanobetti and Schwartz, 2000c). Thus, the association between particulate air pollution exposures and cardio-pulmonary mortality appeared causal.

The World Health Organization (WHO) has estimated that urban air pollution is responsible for approximately 800,000 deaths and 4.6 million lost life-years each year around the globe (WHO, 2002). The burden of ill-health is not equally distributed as approximately two-thirds of the deaths and lost life-years occur in developing countries of Asia. The estimated health impact of urban air pollution is based largely on the results of epidemiological studies conducted in industrialized countries of Europe and North America that had been extrapolated to other countries of the world. Admittedly, the constituents of air pollution in different parts of the world are largely similar, but the magnitude of exposure, general health status of the people, nutritional and other disparities and the level of health care facilities are different across the globe. These inherent differences make extrapolation of findings from developed to developing countries questionable.

Epidemiological studies have established the link between air pollutants and health effects. There are possible short-term and long-term health effects of exposure to air pollution. In the short term, high levels of air pollution can lead to an acute respiratory distress. In addition, blockage of sunlight may promote the spread of harmful bacteria and viruses that would otherwise be killed by ultraviolet B. The possible long-term health effects of exposure to air pollution are unknown and difficult to detect. Components of smoke haze, including Polycyclic Aromatic Hydrocarbons (PAH), are known carcinogens, the effects of which may not be apparent for years. The consequences may be more severe for children, for whom the particulates inhaled are high relative to body size. Continued pollution levels above ambient air quality standards are likely to create a number of adverse health consequences and a subsequent economic impact. High levels of particulate matter (e.g., PM_{10} or TSP), for example, have been linked to a number of significant health problems, ranging from decreased lung function to increased respiratory and cardiac hospital admissions to premature death. NO_2, in recent epidemiological studies, has been increasingly associated with a number of respiratory and cardiovascular conditions, including worsening bronchitis, emphysema, heart disease, and even premature cardiovascular mortality.

1.4 AIR POLLUTION AND PARTICULATE MATTER

Airborne suspended particulate matter (SPM) is a serious worldwide concern especially since it is linked with adverse health effects. Several epidemiological studies have been made across the world revealing the association of SPM in air with acute and chronic respiratory disorders, lung cancer, morbidity and mortality. Odds ratio estimated by several studies of the dose–response relationship for particulate matter (PM)-associated respiratory sickness and premature mortality, increased with rise in PM levels. Associations have been found with cardiovascular deaths, with myocardial infarctions and ventricular fibrillation. PM is also associated with autonomic function of the heart, including increased heart-rate, decreased heart-rate variability and increased cardiac arrhythmias. Such health disorders are widely seen in urban areas worldwide that suffer from serious air-quality problems due to increasing population, combined with change in land use and vehicular traffic. In India, haphazard urbanization, unprecedented vehicular emissions and inadequate infrastructure development are supplementary factors for the fall in air-quality. Challenge for the future generation in India lies in grappling the menace of air pollution-induced diseases, where already the public health is in a worrying state with a variety of diseases (Song, X.H, Polissar, A.V. and Hopke, P.K. et al. 2001).

There is a increasing concern about the possible adverse effects of ambient Suspended Particulate Matters (SPM) on human health and the specific role of traffic exhaust emissions like diesel exhaust (DE). Clean air legislation and the various abatement measures have resulted in the decline of the concentrations of the classic air pollutants. However, epidemiology data show adverse health effects at SPM concentrations below national ambient air quality standards and health based guidelines. An important source of air pollution is traffic, the volume of which, has increased substantially, and, despite improvements in engine technology, so has the amount of emissions from automobile engines. This change in the pattern of air pollution has been paralleled by a progressive increase in the proportion of children and adults suffering with the asthma and other allergic diseases. It is seen that living close to major highways is associated with the development of allergies, and also that the adjuvant effect of Diesel particulates on the development of specific airborne allergens. Furthermore, epidemiological studies have demonstrated a clear association between cardiovascular morbidity, decreased lung function, increased emergency room admissions and airborne concentrations of PM. Human exposure chamber studies have shown that exposure to diesel exhaust has an acute inflammatory effect on normal human airways (Utell, M. et al. 1997).

Uncertainties about health effect-relevant PM characteristics and components and their respective sources seriously complicate the process of PM health risk assessment and standard setting and the application of cost-effective emission and risk control measures. Of eminent importance, both from the scientific and regulatory point of view, is whether the mass concentration of ambient PM and/or its composition is related to the biological activity and toxicity. From this perspective, the new EU PM Daughter Directive will also be based on the consideration of controlling the fine fraction of PM_{10} (i.e. $PM_{2.5}$) or to relate to a source related PM fraction like traffic and motor vehicle exhaust emissions (Utell, M. et al. 1997)..

The pan-European research initiative Health effects of particles from motor engine exhaust and ambient pollution (HEPMEAP) focuses on the inflammatory and toxicological potential of ambient PM related with traffic. More detailed description of scope and overall objectives of the HEPMEAP study are published elsewhere (http://www.hepmeap.org). As part of this project ambient PM was collected at various sites in European countries as well as directly from diesel and petrol fuelled car engine exhaust and was characterized physically and chemically. The characterization is aimed at describing the PM in terms of elemental composition, acid aerosol related ions and a selection of organic compounds enabling largely the explanation of the found mass as well as in contributions of main sources (Utell, M. et al. 1997)..

Northeast Asia is known to emit a large amount of dust particles and anthropogenic pollutants due to its high population density and increasingly high rate of energy consumption. This region has recently attracted significant attention in terms of 25 atmospheric chemistry and has been the focus of international measurement activities, such as the Asia-Pacific Regional Aerosol Characterization Experiment (ACE-Asia) (Huebert et al., 2003), East Asia/North Pacific Regional

Experiment (APARE), Transport and Chemical Evolution over Pacific (TRACEP) Pacific Exploratory Mission-West (PEM-WEST), being a subproject of the International Global Atmospheric Chemistry (IGAC) Program, and the Atmospheric Brown Cloud (ABC) program (Ramanathan et al., 2001) supported by UNEP. Moreover, as the Korean peninsula is located in the middle of the westerly wind latitude region of northeast Asia, many studies on the influence of long range transport (LRT) have been performed in this region.

1.5 TRACE ELEMENTS IN PARTICULATE MATTER

Direct effects of air pollutants on plants, animals and soil can influence the structure and function of ecosystems, including their self-regulation abilities, thus affecting the quality of life. Trace elements are released into the atmosphere by human activities, such as combustion of fossil fuels and wood, high temperature industrial activities and waste incineration. The combustion of fossil fuels constitutes the principal anthropogenic source of Ba, V, Co, Ni, Se, Mo, Sn, Sb, and Hg, and particularly of Cr, Mn, Cu, Zn, and As. High percentages of Ni, Cu, Zn, As, and Cd are emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Ni, Cu, Zn, Cd, and Pb. Several trace elements are emitted through the abrasion of tires (Cu, Zn, Cd) and brake pads (Sb, Cu), corrosion (V, Fe, Ni, Cu, Zn, Cd) lubricating oils (V, Cu, Zn, Mo, Cd) or fuel additives (V, Zn, Cd, Pb). The platinum group elements, Rh, Pd and Pt, represent a relatively new category of traffic related trace elements in the environment, especially urban one, due to their application in automobile catalytic converters since the beginning of the 1980s. Studies of the transport and mobilization of trace elements up to now have attracted attention of many researchers. Trace elements are persistent and widely dispersed in the environment and interacting with different natural components result in toxic effects on the biosphere. The extensively employed direct collection of atmospheric deposition using bulk sampling devices offer a practical approach for monitoring of atmospheric trace elements deposition (Rizzo, M. J., Scheff, P. A., et al., 2007). Identifying air pollution sources that contribute to downstream receptor locations is important for policy making and air-quality management. Between the emission sources and the receptors are the transport, transformation and removal processes of the pollutants. Occasional sources like fireworks and lightning also impact air quality (Rizzo, M. J., Scheff, P. A., et al., 2007). All these sources are distributed widely in different areas and the pollutants are released at different heights. When these pollutants mix in the air, chemical reactions take place and transformation occur. The source-receptor models allow establishing relationships between a receptor and the likely sources through the association of concentration values at the receptor point with the corresponding atmospheric variables and processes.

1.6 ROLE OF CENTRAL POLLUTION CONTROL BOARD (CPCB) IN NATIONAL AIR MONITORING PROGRAMME (NAMP)

Ambient air quality monitoring is being carried out in various cities & towns in India under the National Air Monitoring Programme (NAMP). Air quality data generated over the years reveal that particulate matter concentrations are exceeding the standard permissible limits at many places, particularly in urban areas. Based on these data, Central Pollution Control Board (CPCB) identified more than 50 non-attainment cities and towns including 16 major cities, which recorded significantly higher levels of SPM & RSPM (PM_{10}). These cities have problems due to multiplicity and complexity of air polluting sources (e.g. industries, automobiles, generator sets, fuel burning, construction activities, etc.) and even the background contribution of natural dust (crustal origin) cannot be ruled out, particularly, in the cities developed on alluvial plains having loose topsoil. Due to multiplicity and complexity of air polluting sources, apportionment of these sources indicating their contribution to ambient air pollution is vital for planning cost-effective control strategies (CPCB Report, 2005).

1.7 ACTION PLANS SET BY CPCB

Air quality scenario demands formulation of comprehensive action plans for improvement in the non-attainment cities and towns. These Action Plans need to be realistic, technically feasible & economically viable to deliver the intended benefits. The steps & activities required for formulating a sound action plan necessarily include the following: (i) appropriate air quality monitoring networks & data generation; (ii) identification of emission sources; (iii) estimation of pollution load; (iv) assessment of contribution of these sources on ambient air concentrations and prioritization of the prominent sources that need to be tackled; (v) techno-economic evaluation of the control options & intervention analysis; and (vi) selection/introduction of the best practical mitigation measures for short and long term city-specific Action Plans (CPCB Report, 2005).

1.8 ROLE OF MAHARASHTRA POLLUTION CONTROL BOARD (MPCB) IN NAMP

Maharashtra Pollution Control Board (MPCB) is operating air quality monitoring at 45 stations of Maharashtra spread in 10 districts covering 15 towns. This is being done as part of National Air Monitoring program (NAMP), through independent institutes who directly report to CPCB. It is observed of-late that the air quality information from these stations is not readily available to MPCB. MPCB, as the regulatory agency in the state, require the information of air quality levels at different locations for planning the pollution control strategy, for dissemination of information, and other related matters. MPCB is making the Ambient Air Quality Management (AAQM) data available for public information through electronic and print media and also, through MPCB website on a daily basis.

Table 1.1 presents the details of the locations dor air quality monitoring in Maharashtra. It can be seen that the present network of AAQM of 45 stations is not adequate to represent entire Maharashtra. Considering the various aspects, it had proposed to CPCB that all these already approved NAMP stations will be managed by MPCB, by augmenting the entire Air quality monitoring network. In the augmentation and strengthening process, some stations will be added at cities covered under NAMP and some new cities/ industrial areas will be monitored.

Central Pollution Control Board has 45 sanctioned NAMP stations in the state of Maharashtra. The present scenario of the NAMP in Maharashtra is presented in the following table. Recently, MPCB has already made three stations at Aurangabad and two stations at Dombivali-Ambernath operational.

Table 1.1 Air Quality Monitoring Stations in Kolhapur

Sr. No.	Name of City	No. of stations	Operated by	Remarks
1.	Mumbai	3	NEERI	Managed by CPCB
2.	Thane	3	Thane Municipal Corporation	In Operation since July,2005
3.	Pune	3	University of Pune	In Operation since July,2005
4	Nagpur	3	Vishveshrayya National Institute of Technology	In Operation since July,2005
		3	NEERI	
5.	Chandrapur	3	MPCB	In Operation since July,2005
6.	Aurangabad	3	Saraswati Bhuvan College, Aurangabad	In Operation since July,2005
7.	Dombivali - Ambarnath	2	MPCB	Operational since Oct. 2004
8.	Nashik	3	K T H M College, Nashik.	In Operation since July,2005
9.	Solapur	2	Walchand Institute of Technology.	In Operation since July,2005
10.	**Kolhapur**	**3**	**Shivaji University, Kolhapur**	**In operation since December 2005**
11.	Tarapur MIDC	3	MPCB	In operation since Jan - 2006
12.	Lote MIDC	2	MPCB	In operation since March – 2006
13.	Taloja MIDC	3	K.B.P.College, Vashi	In operation since April – 2006

14.	Navi Mumbai (TTC)	3	K.B.P.College, Vashi	In operation since April – 2006
15.	Amaravati	3	Govt. Engg. College, Amaravati	In operation since Nov. – 2006
	Total	45		

(Source: Maharashtra State Pollution Control Board)

1.9 SOURCE APPORTIONMENT STUDIES IN INDIA

With the above background, source apportionment studies have been initiated in six cities viz. Delhi, Bangalore, Pune, Kanpur, Mumbai and Chennai. The study would focus on apportionment of respirable particulate matter [PM_{10} and $PM_{2.5}$ (limited)], being most critical. In addition, three studies viz. (i) development of emission factors for vehicular sources; (ii) development of source profiles for vehicular sources; and (iii) development of source profiles for non-vehicular sources have also been initiated. Outcome of these studies would be required as input to source apportionment studies in six cities (CPCB Report, 2005). Based on the Source Apportionment Studies carried out in six cities in India, the following broad conclusions emerge, which provide guidance, with adequate scientific evidence, to plan strategies for improving air quality in urban areas:

1. Levels of PM_{10} and $PM_{2.5}$ in the ambient air are significantly high irrespective of the type of locations. Even background locations indicate presence of considerable levels of particulates, which could be occurring naturally and/or due to transport of finer dust from other settlements surrounding the cities. The concentrations of these pollutants are relatively higher at kerbside/roadside locations. While vehicles contribute significantly at all the locations, their contributions at kerbside locations are comparatively higher.

2. Winter and post monsoon seasons had been found most critical when standard exceedence rates are higher than in the summer months.

3. PM pollution problem is severe and NO_2 is the emerging pollutant. These two pollutants require immediate attention to control their emissions.

4. O^3 concentrations in all cities did not exceed the proposed hourly standard of 180 $\mu g/m^3$ at any of the locations, where sampling was done.

However, in case of Mumbai and Pune, the peak hourly concentration observed is very close to 180 $\mu g/m^3$ (90 ppb). Although higher ozone concentrations are expected around 1 – 3 pm, but it appears that good dilution and high speed winds (in afternoon) bring the required reduction in ambient concentration. As such, Ozone does not seem to be of much concern. Similarly, CO levels may exceed marginally the hourly standard of 4000 $\mu g/m^3$ in at a few kerbside locations. In all cities, there are morning and evening peaks in CO levels corresponding to vehicular movement.

5. With regard to air toxics, Benzene levels are higher in Bangalore, Pune and Kanpur. The values of formaldehyde are also matter of concern in Mumbai, Pune and Bangalore.

6. High Elemental Carbon (EC) to Organic Carbon (OC) ratio (EC/OC) represents freshly contributed diesel/coal combustion particles biomass and garbage burning. Many cities have shown this ratio to be high at kerbside and industrial locations. EC and OC contribution to $PM_{2.5}$ is even more than what it is to PM_{10}; and have high (25 – 75%) values in all the cities. It signifies an important point that $PM_{2.5}$ has much higher component of toxic EC and OC that mostly come from combustion sources like vehicles and others.

7. Higher fraction of $PM_{2.5}$ in PM_{10}, and higher values of EC and OC (which have more severe health impacts) at kerbside locations indicate that control of vehicular exhaust would be an important element of any strategy or action plan for improving air quality and minimizing adverse effects on the health of people.

8. Elemental and ion analysis show abundance of soil constituents (e.g. Si, Fe, Ca, Na). This clearly suggests that there could be significant sources of particulate pollution from soil, and road dust. The soil related fraction drops down drastically (about 5% against 15 – 60% in PM_{10}) in $PM_{2.5}$. The re-suspension of road dust due to

vehicular movements on paved/unpaved roads and construction activities, emerging as prominent sources, would largely be contributing to coarser fraction of PM_{10} and combustion sources including vehicles, DG sets, refuse burning, etc. would emit particles in the finer size (< $PM_{2.5}$). Hence, strategies for reduction of PM_{10} and $PM_{2.5}$ would involve different categories of sources.

9. There are significant quantities of SO_4– and NO_3–, (10-15% in most cities and 20-30% in Kanpur) in PM_{10} indicating an important contribution of secondary particles. These contributions are even high at the background upwind direction in all cities. It signifies long-range transport of particles in the city as well as formation of secondary particles in the city. Any control strategy for reduction of particulate will have to consider control of SO_2, NO_2 and NH_3.

10. The presence of molecular markers like hopanes and steranes in much higher quantities compared to background location indicates that effect of vehicles is prevalent. Higher concentration of levoglucosan confirms contribution from biomass burning.

11. Within the transport sector, the PM10 contribution in terms of emission load is mainly from heavy duty diesel vehicles (40 – 59%) in almost all the cities. With regard to NOx emissions, again heavy duty vehicles are major contributors (43 – 75%).

12. Though, there are city-specific variations among the dominance of sources, re-suspension of road dust and combustion sources including vehicles, refuse burning & DG sets; emerge as prominent sources in all the cities for PM.

13. Several epidemiological studies have linked PM_{10} and especially $PM_{2.5}$ with significant health problems. $PM_{2.5}$ is of specific concern because it contains a high proportion of toxins, and aerodynamically it can penetrate deeper into the lungs. Therefore, while planning control strategies greater emphasis is to be given on reduction of $PM_{2.5}$ and toxic constitutes of particulates.

14. An effective control strategy would require combination of engineering as well as non-engineering solutions. Prioritization of these solutions, in addition to their

effectiveness, should also be driven by the comparative account of short and long term implementation dilemma. Low cost with high effectiveness and low cost with shorter implementation period shall be a better option, when compared with high effectiveness with high costs or long implementation period.

Among all the criteria air pollutants, particulate matter (SPM and RSPM) have emerged as the most critical one in almost all urban areas of India. High SPM concentrations are primarily irritants but do not have much relevance for direct health consequences as compared to effects of its respirable fractions (PM_{10} and $PM_{2.5}$). Due to this reason, the worldwide focus of monitoring is now increasingly being shifted to measurement of finer particles ($PM_{2.5}$ and even PM_1), which can penetrate the human respiratory systems. Since 2000, the focus on suspended particulate monitoring has shifted to PM10 in India as well. Being a critical pollutant, PM10 has also been included in National Ambient Air Quality Standards. In view of this, the main focus of this study is on characterization and apportionment of PM10. Limited exercise on characterization and apportionment of $PM_{2.5}$ has also been included in order to have a better understanding and correlation between these two fractions at source and receptors.

1.10 RECEPTOR MODELS FOR SOURCE APPORTIONMENT STUDY

Ambient air quality data analysis and receptor techniques are an increasingly important component of effective air quality management. Identifying the types of emission sources, whether they are anthropogenic or the result of naturally occurring events such as forest fires, and their relative contributions to measured air pollution helps identify and quantify the sources that would be most effective to control.

Receptor models provide the theoretical and mathematical framework for quantifying source contributions at that receptor. There are two basic types of receptor models:

1. Sources are known (e.g. Chemical Mass Balance); or
2. Sources are unknown (e.g. Factor Analysis and Positive Matrix Factorization).

In the first type, a regression technique is used to match chemical profiles or “fingerprints” in the measured ambient particulate matter to those in the emissions from potential sources. Chemical Mass Balance (CMB) requires a priori knowledge of major sources and their emission characteristics in the study area. CMB modeling provides a means by which to estimate the percentage contribution of each source to the measured pollutant concentration. These statistical techniques are used for identifying and quantifying the contribution of important emission sources.

The second type i.e. Positive Matrix Factorization (PMF) requires only ambient measurement data to perform source apportionment. These models rely on the internal variability of the data to determine factor profiles and their contributions to each sample. These factor profiles are related back to specific sources, such as burning or diesel emissions. At a minimum, a hundred or more samples from many locations and/or one location over a long time period are needed for this type of receptor modelling.

The fundamental principle of receptor models is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne particulate matter in the atmosphere. This methodology has generally been referred to within the air pollution research community as receptor modelling (Hopke P. K.; 1985; Hopke P. K. ed.; 1991). The approach to obtaining a data set for receptor modelling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples.

The receptor model includes Chemical Mass Balance (CMB), Factor Analysis (FA), time series and regression analyses. The CMB model requires knowledge about source profiles/source signatures. Therefore, the FA approach is suitable. The FA approach includes the traditional Principal Component Analysis (PCA) and a new variant of FA, Positive Matrix Factorization (PMF), which is better suited to environmental applications than PCA (Paatero and Tapper, 1994). Unlike PCA, PMF utilizes the known (or estimated) errors of the data matrix and imposes non-negativity constraints on the resulting factors.

Receptor modelling approaches such as positive matrix factorization (PMF) are effective tools in source identification for aerosols on urban to regional scales (Bhanuprasad et al., 2008; Pekney et al., 2006). PMF studies typically analyze large data sets of several hundred samples spanning a few years of measurements containing 25–30 chemical species to resolve emission source categories on temporal scales of weeks to seasons. As such large data sets are not available yet in the Indian region, recently, PMF was used to resolve a smaller number (six) of source categories using a relatively small data set, e.g. 23 species in 27 samples (Bhanuprasad et al., 2008). The uncertainty in PMF predictions of factor contributions (based on the relative standard deviation of species with high signal to noise ratio) was satisfactory (5–6%), giving confidence in the application of PMF to smaller data sets towards an understanding of regional scale source–receptor relationships in India.

Positive Matrix Factorization (PMF) is a development in the class of data analysis techniques called Factor Analysis (Paatero and Tapper, 1993, 1994), where the fundamental problem is to resolve the identities and contributions of components in an unknown mixture (Malinowski, 2002). PMF has been used as a source apportionment tool in many air quality studies (Kim and Hopke, 2004a, b; Kim et al., 2004a, b, 2007; Lee and Hopke, 2006; Hwang and Hopke, 2007; Lanz et al., 2007; Sunder Raman and Hopke, 2007; Ulbrich et al., 2009; Vianna et al., 2008). PMF results have been coupled with surface wind direction data to provide identification of the locations of local emission sources affecting a receptor site (Lee et al., 2006; Pekney et al., 2006).

Source apportionment (receptor modelling) studies involve the ambient sampling and measurement of atmospheric particles or gases, followed by laboratory analyses to separate and identify the constituents of the samples collected, by their chemical composition. Chemical speciation monitoring helps scientists understand the properties of the airborne pollutants at the receptor site(s) and to identify the emissions sources, including potential sources which are not readily identified in preliminary emissions inventories, such as cooking fires and airborne particles transported over long distances. Additionally, the analyses help quantify the contribution of known emissions sources and can help validate and improve the emissions inventory itself.

Objectives of source apportionment studies can include:

- To quantitatively relate emissions to the characteristics of targeted SPM at a specific receptor site.
- To evaluate the effectiveness of control strategies over time.
- To improve and validate emission inventories by determining major sources of air pollutants such as particulate matter and other contaminants.
- Strengthening environmental management, particularly at regional and local levels.
- Enhance the linkages between specific emissions sources and ambient air quality.
- Guiding the application of source models.
- Evaluating and improving source model results.
- Providing data to support the reduction of emissions through integrated strategies.

1.11 SOURCE APPORTIONMENT STUDY FOR DECISION MAKING IN EFFECTIVE URBAN AIR QUALITY MANAGEMENT PROGRAM

Increasingly, source apportionment analyses are being used as a relatively accurate, rapid, and cost-effective means of identifying and targeting sources and their relative contributions to the total pollution load. This scientific information helps air quality modellers as well as policy- and decision-makers. The data obtained from source apportionment studies provides policy- and decision-makers with practical tools to identify and quantify different sources of air pollution, increasing their ability to put in place effective policy and regulatory measures and control strategies to reduce air pollution to acceptable levels. Additionally, co-benefits can be realized –

for example, source apportionment studies targeting specific air pollutants can also be used to assess climatic impacts, identify clean energy measures and greenhouse gas emission reduction strategies. Successful application of source apportionment (receptor modeling) methods and support to effective policy- and decision-making depends on the accuracy and relevance of the air quality measurements and the interpretations made by the scientist and air quality manager. Environment Canada's air quality experts have included source apportionment studies and the improvement of source apportionment techniques and analyses as an integral component of their science and research, constantly seeking the highest quality of data and information. Table 1.2 shows source apportionment studies undertaken by various Government, Non Government, Research Centres, organizations, Institutes worldwide.

Table 1.2 Source Apportionment Studies Worldwide

Country	Institute	Sampling Period
Shanghai (China)	Shanghai Academy of Environmental Science (SAES), Shanghai, China.	One-month continuous monitoring in October, January, April and June during 2000 -2001, representing $PM_{2.5}$ pollution
Beijing (China)	Department of Environmental Sciences, Peking University, Beijing, China.	In January, April, July, and October 2000, $PM_{2.5}$ samples were collected in Beijing.
Bangkok (Thailand)	Asian Institute of Technology (AIT), Bangkok, Thailand.	Samples were collected from Feb. 2002 to the end of 2003 and covered both dry and wet seasons.
Hanoi (Vietnam)	Vietnam Atomic Energy Commission, Hanoi, Vietnam.	1999–2001
Cairo (Egypt)	Desert Research Institute, Reno, Nevada U.S.A.	Intensive monitoring studies were carried out during the periods of February/March and October/ November 1999 and June 2002.
Qalabotjha (South	Desert Research Institute, Reno, Nevada, U.S.A.	Samples collected every day for 24 hours. Samples taken during midwinter in July,

Africa)		1997. Samplers on roof-tops of buildings.
Addis Ababa (Ethiopia)	Desert Research Institute, Reno, Nevada, U.S.A.	Twenty-one samples were collected during the dry season (26 January–28 February 2004) at 12 sites in and around Addis Ababa for PM_{10}
Dhaka and Rajshahi, Bangladesh	Bangladesh Atomic Energy Center, Dhaka, Bangladesh.	The samples for this study were collected during June 2001 to June 2002 in Dhaka and August 2001– May 2002 in Rajshahi.
Sao Paulo (Brazil)	University of Sao Paulo (USP), Brazil	Two sampling campaigns were carried out continuously during the wintertime of 1997 (June 10th until September 10th) and summertime of 1998 (January 16th until March 6th).
Santiago (Chile)	University of Sao Paulo (USP), Brazil.	Aerosol sampling was performed during wintertime 2000, with a 12-hour sampling time from July 4 to August 31, 2000.

(Source: Tools for Improving Air Quality Management, March 2011)

In India, Source Apportionment Studies have already been carried out in the cities of Bangalore, Chennai, Delhi, Kanpur, Mumbai and Pune. The primary focus of the study was on particulate matter, although it also deals with other pollutants like NOx, SO_2, Ozone (O^3), $PM_{2.5}$, etc. Table 1.3 presents source apportionment studies being conducted at India

Table 1.3 Source Apportionment Studies in India

City	Institute	Year
Bangalore	The Energy and Resources Institute (TERI)	2010
Chennai	Indian Institute of Technology Madras	2010

Delhi	National Environmental Engineering Research Institute (NEERI), Nagpur	2010
Kanpur	Indian Institute of Technology (IIT), Kanpur	2010
Mumbai	National Environmental Engineering Research Institute	2010
Pune	The Automotive Research Association of India, Pune	2010

(Source: Central Pollution Control Board (CPCB) website: http://www.cpcb.nic.in)

Central Pollution Control Board, New Delhi has signed Memorandum of Contracts (MoCs) for source apportionment studies for the cities of Mumbai, Chennai and Kanpur with NEERI, IIT- Mumbai and IIT- Kanpur respectively and for source profiling for sources other than vehicles with IIT Mumbai. The Automotive Research Association of India (ARAI), Pune has conducted studies on emission factors for vehicles required as inputs in the studies.

From the earlier paragraphs, it is observed that Metropolitan Cities worldwide as well as in India have adopted Source Apportionment Studies routinely and results are promising for better Air Quality Management in such cities. But II tier cities are, yet, to adopt such studies due to lack of source information and other necessary data to carry out Source Apportionment Studies. Kolhapur in Maharashtra is a fast growing II tier city in terms of Industrial Development, Co-operative movements, growing number of Agro based industries, leather industries and of course, tourism for which city is all known. Hence, Kolhapur is selected for the present study.

1.12 KOLHAPUR CITY, MAHARASHTRA

Kolhapur city in Maharashtra is divided into different zones: Administrative, Diplomatic Enclave, Residential Areas, and Industrial Areas, Educational sectors, rural and green areas. Extreme meteorological variations have been recorded in the past year. This year the maximum highest temperature ever has been recorded as 42ºC in the month of April. Moreover the wind speed which is required for the flushing of the pollutants is in the range of 2.5 – 3.5 m/sec. In dry, and low windy days, natural dust and anthropogenic pollutants, when generated in excess, take longer time to disperse off. The rainfall has declined in recent years, following the changes observed in many parts of the country.

1.13 IMPORTANCE OF SOURCE APPORTIONMENT STUDY AT KOLHAPUR

The air pollution has emerged as a serious issue in urban Kolhapur in terms of degradation of ambient air quality. The monitoring carried out by MPCB showed that most of the parameters have either crossed the given standards or have just reached the threshold values. The local air quality in the city is mainly degraded due to the presence of SPM, the major sources of which are vehicle, industry, roadside burning of solid waste, construction activities, improper roads, brick kilns and natural and road dust. The number of vehicles has also increased because of the passion for new vehicle. The number is more in case of two stroke engines. According to World Bank study the major cause of SPM in South-East Asian Countries was two stroke vehicles using straight mineral oil as an engine lubricant up to 12% instead of 2% for motor cycles and 3% for three wheelers. The numbers of diesel trucks and buses have also increased due to upcoming IT Park. These diesel engines are the major source for increasing SPM level. Another serious issue related to vehicular pollution is that of the presence of Lead (Pb).

In the industrial Areas in Kolhapur, Iron and Steel Industries, Textile Mills, Foundries etc. are great threat to the local atmosphere due to large emission levels of huge bulk of SPM and trace metals. There is a need to replace the old methodology by recent environmentally friendly technologies in these industries and foundries, for e.g. there is no regular stack monitoring carried out by the Industries and Foundries. Foundry industry which is the major source of SPM because the ‘green sand’ used in production still use cupola furnace rather than using electric Induction Furnace which is relatively pollution free. Owing to the increasing exploitation of the resources, sometimes with obsolete and polluting plants and without suitable emission controls, environmental levels of heavy metals are on increase in the urban atmosphere of Kolhapur. The local habitants are particularly on risk.

It is seen that no such study on source apportionment of particulate matters has been conducted in Kolhapur City. Also no such emission inventory has been built for air quality decision making. No single literature is available or published anywhere on emission scenario of Kolhapur. Few papers were presented on the topic of concentrations of pollutants in city but source identification of trace metals and PM have not been done yet. It is seen that there is growing concentration of Particulate matter in the city. Also MPCB is launching new monitoring stations for determination of concentrations of air pollutants for its policy making. Due to the presence of 5 Star MIDC nearer to Kolhapur, there shall be a threat of alarming concentration levels of particulate matter due to the presence of Multi Product and large scale production nature of companies and its businesses. Poor urban planning and unorganized industrial structure has possible future impact on residents of city with high emissions from automobiles and industries.

In this study, an attempt is made to estimate and analyze chemically trace metals in Atmospheric Aerosols at Kolhapur City which constitutes a long term threat to the health of general population. The results of source apportionment will be taken to appropriate dispersion model for accurate forecasting. The modeling and simulation will help urban planners and air quality planners for zoning policy decision making. The study is aimed at studying the levels and variations of trace metals in Atmospheric Aerosols which will be collected during July 2008 to July 2009 i.e. three seasons like Monsoon, winter and summer.

1.14 OBJECTIVES OF THE STUDY AT KOLHAPUR CITY

The following are the broad objectives of the study.

1. To identify the locations for assessment of air quality based on wind direction/dispersion
2. To generate the required site specific topography/elevation, development activities etc. data in selected locations for dispersion study
3. To measure Meteorological data i.e. Wind Speed, Wind Direction, Ambient Temperature etc. at selected locations for the study

4. To measure the concentration of Suspended Particulate Matter (SPM) at selected locations for the study
5. To characterize and quantify the presence of trace metals in SPM i.e. Cu, Pb, Ni, Zn, Cd, Mn, Fe etc.
6. To identify the sources (Source Apportionment) of SPM by using United States Environmental Protection Agency (US EPA) Positive Matrix Factorization (PMF) Receptor model
7. To identify contribution of trace elements from various identified sources
8. To validate the results of modelling with characterization of trace elements in soil samples at selected locations by mass balance
9. To suggest methods and procedures for minimization of trace elements at selected locations

1.15 ORGANIZATION OF THE THESIS

Chapter 1 presents the Introduction, justification and objectives of the present study while Literature review on Air Pollution, its sources, effects on human being, types of SPM and Aerosols, various trace elements in ambient air as well as soil, their effects on human being and source apportionment of aerosols and its receptor modelling are presented in Chapter 2. The methodologies and protocols followed for the generation of required air quality data and source Apportionment methodology, the method used for validation of the US EPA Model and necessary methods adopted to arrive at results of Source Apportionment is described in Chapter 3. Chapter no. 4 provides US EPA PMF Modelling approach and its application in the present study along with the results of investigations carried out. The conclusions drawn based on the results of the study are presented in Chapter 5.

Chapter 2

LITERATURE REVIEW

This chapter deals with review of Air pollution disasters, health impacts, cause effect relationship, air pollutants, regulations, trace elements and their sources, source apportionment studies, different dispersion models and reason behind conducting Source apportionment study at Kolhapur city.

2.1 AIR POLLUTION DISASTERS

From centuries, urban air pollution has posed a problem for city dwellers. The earlier manifestation of pollution was the smoke produced by burning poor quality coal in relatively cold climates in Northern Europe. This caused high sulphur dioxide (SO_2) and particle exposure, sometimes with serious health impacts. The Industrial Revolution introduced point sources of larger emissions from various processes. The most important of these was the burning of coal for energy production, resulting in the release of SO_2 and combustion particles (smoke) (Carter J. Brandon, et al., 1997).

Coal burning in small and large sources was allowed to continue without required abatement well into the 20th century. Elevated stacks were the only mode of pollution abatement. Large emissions of SO_2 and smoke particles overloaded the atmosphere during temperature inversions in stable high-pressure situations with stagnant air, leading to notorious air pollution episodes. The 1952 London episode was the worst, resulting in an estimated 4,000 deaths in five days (Climate Change report, National Geographic, 2010).

Mr. Sunil Choukiker, Associate Director (Environment Advisory Group) with VisionRI Connexion Services Private Limited, New Delhi, India in his report titled ‘Major Air Pollution Episodes: Environmental Distortions that Kill, 2010’ stated that although the components of air pollution have changed over the years with the emergence of industrial sources releasing toxic gases like Methyl Isocyanide (CH3CN) in the case of Bhopal disaster in 1984; coal still remains an important source of air pollution,. In addition, vehicular pollution sources have expanded rapidly in the last three decades. Traffic activity in urban areas of industrialized western nations has witnessed a four to five fold increase over the decades. In developing nations, this increase has been ten-fold to more. Prime examples of urban air pollution are the smog in London and photochemical smog in Los Angeles and Mexico City. A brief description of these major pollution episodes and its effects are presented.

2.1.1 London Episodes, 1873-1963

The industrial revolution in the 19th century saw the set in of air pollution in Europe on a large scale. The industries and the households relied heavily on coal for heating and cooking. Due to burning of coal for heat during the winter months, emissions of smoke and sulphur dioxide were much greater in winters than they were during the summer months. Smoke particles trapped in the fog gave it a yellow/black colour and this smog often settled over cities for many days (UNEP/WHO (1993).

The effects of smog on human health were evident, particularly when smog persisted for several days. Many people suffered respiratory problems and increased deaths were recorded, notably those relating to bronchial causes. The smog-related deaths were first recorded in London in 1873, when it killed 500 people. In 1880, the toll was more than 1000 (UNEP/WHO (1993). London had one of its worst experiences of smog in December 1892. It lasted for three days and resulted in about 1000 deaths. Despite gradual improvements in air quality during the 20th century, eight air pollution episodes occurred in London between 1948 and 1962. The December 1952 episode is the major episode in the history of air pollution (UNEP/WHO (1993).

The “Killer Smog” began on Thursday, Dec. 4, 1952 as a high-pressure air mass created a subsidence temperature inversion over southern England. With the particulate and SO_2 levels going up due to extensive use of coal as fuel for space heating and electric production, the fog turned black. At the same time the high-pressure area stalled and became stationary. The build up of pollutants combined with the fog resulted in essentially zero visibility. Within a matter of three days, the pollutants were concentrated enough to cause deaths. The old and respiratory affected died first, but younger people exposed to the outside atmosphere were also affected. The maximum daily SO_2 concentration recorded at that time was 1.34 ppm (about 4000 µg/m^3, standard SO_2 conc. in clean dry atmosphere is 0.0002 ppm) and smoke levels were 4.46 mg/m^3. The Great London Smog lasted for five days and lifted on 9th Dec, resulting in about 4000 deaths (UNEP/WHO (1993).

2.1.2 Meuse Valley, 1930

An episode occurred in the first week of December 1930, when a thick mist lay over large parts of Belgium. On December 3rd, 4th and 5th, several thousand cases of acute pulmonary attacks occurred in the densely populated valley of the Meuse, east of Liege, resulting in 60 deaths. Post episode investigations led to the conclusion that the cause was poisonous products in the waste gas of the many factories in the valley, in conjunction with unusual climatic conditions. During that time, the day temperature was a little above freezing point while at night it measured up to 10^{o}C below, while the wind speed was only 1-3km/hr. It was impossible to indicate any definite substance or chemical compound as the cause, but the investigators were of the opinion that the disaster in all probability had been brought about by sulphur dioxide (SO_2) or oxidation products of that compound, of which quantities were found in the factory smoke. The investigation also looked into the question of fluorine intoxication, however its role is doubtful (UNEP/WHO (1993).

The cases of illness were reported after the mist had lasted about 2 days. It was estimated that the total number of cases was several thousands. In three days, there were 60 deaths, of which fifty-six were in the eastern half of the valley and only four deaths were reported from the west of Engis. The area around Engis was the worst affected (UNEP/WHO (1993).

2.1.3 Donora Fog, 1948

Horror visited the US Steel company town of Donora on the Halloween night of 1948, when a temperature inversion descended on the town. Fluoride emissions from the Donora Zinc Works smelting operation and other sources containing sulphur, carbon monoxide and heavy metal dusts were trapped by weather conditions, causing 20 deaths within 14 hours (Fenger, J. et al, 1999).

Cold ground and high-pressure conditions intensified the elevated inversion of the anticyclone that arrived in the region. The situation was aggravated by local conditions of meteorology, industrial pollutant emissions and peculiar terrain of the area. The meteorological conditions and the geographical characteristics of the area produced a strong temperature inversion with a temperature gradient as high as 33^{o}C/km. The fog was held close to the ground by the stability of the elevated inversion layer. During the third and fourth days of the episode, as ambient levels of pollutants escalated, almost half of the population of 14,000 people became ill. Almost 43 % of the population in Donora and Webster, PA experienced the effects of the smog. Most of the affected were above the age group of 60 years and above (29% of this group were seriously affected). The health effects were mainly symptoms affecting the lung, and in particular, upper respiratory symptoms such as nasal discharge, constriction of the throat, or sore throat were experienced (Gros, V., Sciare , J., Yu , T. et al., 2007).

2.1.4 Mexico, Poza Rica, 1950

A catastrophic exposure episode involving the release of large quantities of hydrogen sulfide occurred in Poza Rica, Mexico in November 1950 (GB Steventon et al., 2002). Poza Rica, a city of 22,000 people located about 210 km northeast of Mexico City, was then the centre of Mexicos leading oil-producing district and the site of several oil field installations, including a sulphur-recovery plant. An early morning malfunction of the waste gas flare resulted in the release of large quantities of unburned hydrogen sulfide into the atmosphere. The unburned gas, aided by a low-level temperature inversion and light early morning breezes, was carried to the residential area adjacent to the plant area. Residents of the area succumbed while attempting to leave the area and assisting stricken neighbors. Within a matter of 3 hours, 320 persons were hospitalized and 22 were killed (GB Steventon et al., 2002).

2.1.5 Cincinnati, Ohio. 1968

A similar accident with a fortunately less tragic ending occurred on August 25, 1968, in Cincinnati. About 2,500 pounds of SO_2 escaped into the air from a burst pipe at a chemical plant located in the northern industrial part of Cincinnati (JR McNeill et al., 2009). The release of SO_2 started at mid night and lasted for about 8 hours. People who are staying at about 200 meters to the east of the plant were affected. People were awakened by a rotten-egg smell and difficulty in breathing. Fortunately nobody was killed.

2.1.6 New York, 1953, 1962-1963, 1966

New York City also experienced air pollution disasters. in 1953, 1962-1963 and 1966 causing excess deaths. New York with the nation's highest SO_2 concentrations often avoids air pollution disasters because of its excellent ventilation (JR McNeill et al., 2000). In December 1962, adverse weather conditions such as low wind speeds and occurrence of shallow inversions, then the SO_2 and smoke concentrations which reached peak values were the major reasons. Total deaths increased to 269, which was in excess of even three standard deviations above the expected mortality for that week (JR McNeill et al., 2009).

2.1.7 Bhopal Disaster, 1984

In the mid night of 2nd - 3rd December 1984, in a densely populated area of Bhopal, Central India, a poisonous vapor burst from the tall stacks of the Union Carbide pesticide plant. About forty tons of toxic gases had leaked from the Carbides Bhopal plant and spread throughout the city. The cause was the contamination of Methyl Isocyanate (MIC) storage tank with water carrying catalytic material (Sriramachari S., (2004).

Residents of the city awoke to clouds of suffocating gas, unaware of the magnitude of the devastation, which had engulfed them. The city of Bhopal was immediately turned into a city of dead bodies, and the whole place smelled of burning chilli peppers. Of the million people living in Bhopal at that time, more than 2,000 died immediately (one fourth of actual figures) and as many as 300,000 were injured. In addition, about 7,000 animals were affected, of which about 1000 were killed (Sriramachari S., (2004). The precise number of deaths still remains a mystery till date. The degree of injury was so high that about 30% of the injured were unable to return to their jobs. Among the survivors, most of them still suffer agonizing pain from the disastrous effects of the massive poisoning while there are still apprehensions of the future generations being affected. The Bhopal Disaster was the worst episode in the history of industrial air pollution.

2.2 HEALTH IMPACTS OF AIR POLLUTION

Exposure to air pollution is associated with numerous effects on human health, including pulmonary, cardiac, vascular, and neurological impairments. The health effects vary greatly from person to person. High-risk groups such as the elderly, infants, pregnant women, and sufferers from chronic heart and lung diseases are more susceptible to air pollution. Children are at greater risk because they are generally more active outdoors and their lungs are still developing. Exposure to air pollution can cause both acute (short-term) and chronic (long-term) health effects. Acute effects are usually immediate and often reversible when exposure to the pollutant ends. Some acute health effects include eye irritation, headaches, and nausea. Chronic effects are usually not immediate and tend not to be reversible when exposure to the pollutant ends. Some chronic health effects include decreased lung capacity and lung cancer resulting from long-term exposure to toxic air pollutants. The scientific techniques for assessing health impacts of air pollution include air pollutant monitoring, exposure assessment, dosimetry, toxicology, and epidemiology (Conner Teri, L., Gary, A.N., Mathew, S.L. and Ronald, W., et al., 2001).

Although in humans, pollutants can affect the skin, eyes and other body systems, they affect primarily the respiratory system. Air is breathed in through the nose, which acts as the primary filtering system of the body. The small hairs and the warm, humid conditions in the nose effectively remove the larger pollutant particles.

The air then passes through the pharynx, esophagus, and larynx before reaching the top of the trachea. The trachea divides into two parts, the left and the right bronchi. Each bronchus subdivides into increasingly smaller compartments. The smallest compartments of the bronchi are called bronchioles, which contain millions of air sacs called alveoli. Both gaseous and particulate air pollutants can have negative effects on the lungs. Solid particles can settle on the walls of the trachea, bronchi, and bronchioles. Most of these particles are removed from the lungs through the cleansing (sweeping) action of "cilia", small hair like outgrowths of cells, located on the walls of the lungs. This is what occurs when you cough or sneeze (Conner Teri, L., Gary, A.N., Mathew, S.L. and Ronald, W., et al., 2001).

A cough or sneeze transports the particles to the mouth. The particles are removed subsequently from the body when they are swallowed or expelled. However, extremely small particles may reach the alveoli, where it takes weeks, months, or even years for the body to remove the particles. Gaseous air pollutants may also affect the function of the lungs by slowing the action of the cilia. Continuous breathing of polluted air can slow the normal cleansing action of the lungs and result in more particles reaching the lower portions of the lung (Milford, J. B. and Davidson, C.I. et al., 1985).

The lungs are the organs responsible for absorbing oxygen from the air and removing carbon dioxide from the blood-stream. Damage to the lungs from air pollution can inhibit this process and contribute to the occurrence of respiratory diseases such as bronchitis, emphysema, and cancer. This can also put an additional burden on the heart and circulatory system (Milford, J. B. and Davidson, C.I. et al., 1985).

Table 2.1 summarizes the major pollutants and their sources and effects. Hazardous air pollutants may cause other less common but potentially hazardous health effects, including cancer and damage to the immune system, and neurological, reproductive and developmental problems. Acute exposure to some hazardous air pollutants can cause immediate death.

Human health effects associated with indoor air pollution are: headaches, tiredness, dizziness, nausea, and throat irritation. More serious effects include cancer and exacerbation of chronic respiratory diseases, such as asthma. Radon is estimated to be the second leading cause of lung cancer in the U.S. Environmental tobacco smoke causes eye, nose and throat irritation, and is a carcinogen. Asthma, particularly in children, is associated with poor indoor air quality.

Table 2.1 Pollutants and their Sources and effects

Pollutant	Sources	Effects
Ozone. A gas that can be found in two places. Near the ground (the troposphere), it is a major part of smog. The harmful ozone in the lower atmosphere should not be confused with the protective layer of ozone in the upper atmosphere (stratosphere), which screens out harmful ultraviolet rays.	Ozone is not created directly, but is formed when nitrogen oxides and volatile organic compounds mix in sunlight. That is why ozone is mostly found in the summer. Nitrogen oxides come from burning gasoline, coal, or other fossil fuels. There are many types of volatile organic compounds, and they come from sources ranging from factories to trees.	Ozone near the ground can cause a number of health problems. Ozone can lead to more frequent asthma attacks in people who have asthma and can cause sore throats, coughs, and breathing difficulty. It may even lead to premature death. Ozone can also hurt plants and crops.
Carbon monoxide. A gas that comes from the burning of fossil fuels, mostly in cars. It cannot be seen or smelled.	Carbon monoxide is released when engines burn fossil fuels. Emissions are higher when engines are not tuned properly, and when fuel is not completely burned. Cars emit a lot of the carbon monoxide found outdoors. Furnaces and heaters in the home	Carbon monoxide makes it hard for body parts to get the oxygen they need to run correctly. Exposure to carbon monoxide makes people feel dizzy and tired and gives them headaches. In high concentrations it is fatal. Elderly people with

	can emit high concentrations of carbon monoxide, too, if they are not properly maintained.	heart disease are hospitalized more often when they are exposed to higher amounts of carbon monoxide.
Nitrogen dioxide. A reddish-brown gas that comes from the burning of fossil fuels. It has a strong smell at high levels.	Nitrogen dioxide mostly comes from power plants and cars. Nitrogen dioxide is formed in two ways—when nitrogen in the fuel is burned, or when nitrogen in the air reacts with oxygen at very high temperatures. Nitrogen dioxide can also react in the atmosphere to form ozone, acid rain, and particles.	High levels of nitrogen dioxide exposure can give people coughs and can make them feel short of breath. People who are exposed to nitrogen dioxide for a long time have a higher chance of getting respiratory infections. Nitrogen dioxide reacts in the atmosphere to form acid rain, which can harm plants and animals.
Particulate matter. Solid or liquid matter that is suspended in the air. To remain in the air, particles usually must be less than 0.1-mm wide and can be as small as 0.00005 mm.	Particulate matter can be divided into two types—coarse particles and fine particles. Coarse particles are formed from sources like road dust, sea spray, and construction. Fine particles are formed when fuel is burned in	Particulate matter that is small enough can enter the lungs and cause health problems. Some of these problems include more frequent asthma attacks, respiratory problems, and premature death.

	automobiles and power plants.	
Sulfur dioxide. A corrosive gas that cannot be seen or smelled at low levels but can have a “rotten egg” smell at high levels.	Sulfur dioxide mostly comes from the burning of coal or oil in power plants. It also comes from factories that make chemicals, paper, or fuel. Like nitrogen dioxide, sulfur dioxide reacts in the atmosphere to form acid rain and particles.	Sulfur dioxide exposure can affect people who have asthma or emphysema by making it more difficult for them to breathe. It can also irritate people's eyes, noses, and throats. Sulfur dioxide can harm trees and crops, damage buildings, and make it harder for people to see long distances.
Lead. A blue-gray metal that is very toxic and is found in a number of forms and locations.	Outside, lead comes from cars in areas where unleaded gasoline is not used. Lead can also come from power plants and other industrial sources. Inside, lead paint is an important source of lead, especially in houses where paint is peeling. Lead in old pipes can also be a source of lead in drinking water.	High amounts of lead can be dangerous for small children and can lead to lower IQs and kidney problems. For adults, exposure to lead can increase the chance of having heart attacks or strokes.

Toxic air pollutants. A large number of chemicals that are known or suspected to cause cancer. Some important pollutants in this category include arsenic, asbestos, benzene, and dioxin.	Each toxic air pollutant comes from a slightly different source, but many are created in chemical plants or are emitted when fossil fuels are burned. Some toxic air pollutants, like asbestos and formaldehyde, can be found in building materials and can lead to indoor air problems. Many toxic air pollutants can also enter the food and water supplies.	Toxic air pollutants can cause cancer. Some toxic air pollutants can also cause birth defects. Other effects depend on the pollutant, but can include skin and eye irritation and breathing problems.
Stratospheric ozone depletes. Chemicals that can destroy the ozone in the stratosphere. These chemicals include chlorofluorocarbons (CFCs), halons, and other compounds that include chlorine or bromine.	CFCs are used in air conditioners and refrigerators, since they work well as coolants. They can also be found in aerosol cans and fire extinguishers. Other stratospheric ozone depleters are used as solvents in industry.	If the ozone in the stratosphere is destroyed, people are exposed to more radiation from the sun (ultraviolet radiation). This can lead to skin cancer and eye problems. Higher ultraviolet radiation can also harm plants and animals.
Greenhouse gases. Gases that stay in the air for a long	Carbon dioxide is the most important	The greenhouse effect can lead to changes in

time and warm up the planet by trapping sunlight. This is called the "greenhouse effect" because the gases act like the glass in a greenhouse. Some of the important greenhouse gases are carbon dioxide, methane, and nitrous oxide.	greenhouse gas. It comes from the burning of fossil fuels in cars, power plants, houses, and industry. Methane is released during the processing of fossil fuels, and also comes from natural sources like cows and rice paddies. Nitrous oxide comes from industrial sources and decaying plants.	the climate of the planet. Some of these changes might include more temperature extremes, higher sea levels, changes in forest composition, and damage to land near the coast. Human health might be affected by diseases that are related to temperature or by damage to land and water.

(Source: Environmental Protection Agency)

Long before pollutant effects become manifest in human health, they are first seen in the environment. Air pollution impacts in the ecosystem form and function are also a serious concern. Damage to ecosystems from air pollution can exact a significant economic as well as an environmental cost. There are many harmful environmental effects of air pollution: acid rain, the greenhouse effect, depletion of stratospheric ozone, smog, and decreased visibility.

2.3 CAUSE EFFECT RELATIONSHIP OF AIR POLLUTION

Smog hanging over cities is the most familiar and obvious form of air pollution. But there are different kinds of pollution—some visible, some invisible—that contribute to global warming. Generally any substance that people introduce into the atmosphere that has damaging effects on living things and the environment is considered air pollution (Watson J. G. et al., 2002).

Carbon dioxide, a greenhouse gas, is the main pollutant that is warming Earth. Though living things emit carbon dioxide when they breathe, carbon dioxide is widely considered to be a pollutant when associated with cars, planes, power plants, and other human activities that involve the burning of fossil fuels such as gasoline and natural gas. In the past 150 years, such activities have pumped enough carbon dioxide into the atmosphere to raise its levels higher than they have been for hundreds of thousands of years (Watson J. G. et al., 2002).

Other greenhouse gases include methane—which comes from such sources as swamps and gas emitted by livestock—and chlorofluorocarbons (CFCs), which were used in refrigerants and aerosol propellants until they were banned because of their deteriorating effect on Earth's ozone layer.

Another pollutant associated with climate change is sulfur dioxide, a component of smog. Sulfur dioxide and closely related chemicals are known primarily as a cause of acid rain. But they also reflect light when released in the atmosphere, which keeps sunlight out and causes Earth to cool. Volcanic eruptions can spew massive amounts of sulfur dioxide into the atmosphere, sometimes causing cooling that lasts for years. In fact, volcanoes used to be the main source of atmospheric sulfur dioxide; today people are.

Industrialized countries have worked to reduce levels of sulfur dioxide, smog, and smoke in order to improve people's health. But a result, not predicted until recently, is that the lower sulfur dioxide levels may actually make global warming worse. Just as sulfur dioxide from volcanoes can cool the planet by blocking sunlight, cutting the amount of the compound in the atmosphere lets more sunlight through, warming the Earth. This effect is exaggerated when elevated levels of other greenhouse gases in the atmosphere trap the additional heat (Zhuang, G. S., Guo, J. H., Yuan, H., Zhao, C. Y., et al., 2003).

Most people agree that to curb global warming, a variety of measures need to be taken. On a personal level, driving and flying less, recycling, and conservation reduces a person’s "carbon footprint"—the amount of carbon dioxide a person is responsible for putting into the atmosphere (Gros, V., Sciare , J., Yu , T., et al., 2007).

On a larger scale, governments are taking measures to limit emissions of carbon dioxide and other greenhouse gases. One way is through the Kyoto Protocol, an agreement between countries that they will cut back on carbon dioxide emissions. Another method is to put taxes on carbon emissions or higher taxes on gasoline, so that people and companies will have greater incentives to conserve energy and pollute less.

2.4 CRITERIA AIR POLLUTANTS

The Clean Air Act requires EPA to set National Ambient Air Quality Standards for six common air pollutants. These commonly found air pollutants (also known as "criteria pollutants") are found all over the United States. They are particle pollution (often referred to as particulate matter), ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead. These pollutants can harm your health and the environment, and cause property damage (U.S.EPA, 2007). Of the six pollutants, particle pollution and ground-level ozone are the most widespread health threats. EPA calls these pollutants "criteria" air pollutants because it regulates them by developing human health-based and/or environmentally-based criteria (science-based guidelines) for setting permissible levels. The set of limits based on human health is called primary standards. Another set of limits intended to prevent environmental and property damage is called secondary standards. EPA, USA listed below the pollutants for information on sources of the pollutant, why the pollutant is of concern, health and environmental effects, efforts underway to help reduce the pollutant, and other helpful resources (U.S.EPA, 2007).

1. Ozone
2. Particulate Matter
3. Carbon Monoxide
4. Nitrogen Oxides
5. Sulfur Dioxide
6. Lead

2.4.1 Ozone

Ozone is found in two regions of the Earth's atmosphere – at ground level and in the upper regions of the atmosphere. Both types of ozone have the same chemical composition (O3). While upper atmospheric ozone protects the earth from the sun's harmful rays, ground level ozone is the main component of smog (U.S.EPA, 2007).

Troposheric, or ground level ozone, is not emitted directly into the air, but is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC). Ozone is likely to reach unhealthy levels on hot sunny days in urban environments. Ozone can also be transported long distances by wind. For this reason, even rural areas can experience high ozone levels.

High ozone concentrations have also been observed in cold months, where a few high elevation areas in the Western U.S. with high levels of local VOC and NOx emissions have formed ozone when snow is on the ground and temperatures are near or below freezing. Ozone contributes to what we typically experience as "smog" or haze, which still occurs most frequently in the summertime, but can occur throughout the year in some southern and mountain regions.

Ground level ozone- what we breathe- can harm our health. Even relatively low levels of ozone can cause health effects. People with lung disease, children, older adults, and people who are active outdoors may be particularly sensitive to ozone. Children are at greatest risk from exposure to ozone because their lungs are still developing and they are more likely to be active outdoors when ozone levels are high, which increases their exposure. Children are also more likely than adults to have asthma (U.S.EPA, 2007).

Ozone also affects sensitive vegetation and ecosystems, including forests, parks, wildlife refuges and wilderness areas. In particular, ozone harms sensitive vegetation, including trees and plants during the growing season.

Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapors, and chemical solvents are some of the major sources of NOx and VOC.

Under the Clean Air Act, EPA has established health and environmentally protective standards for ozone in the air we breathe. EPA and others have instituted a variety of multi-faceted programs to meet these standards. Learn more about EPA's ozone standards and regulatory actions (U.S.EPA, 2007).

2.4.2 Particulate Matter

"Particulate matter," also known as particle pollution or PM, is a complex mixture of extremely small particles and liquid droplets. Particle pollution is made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles.

The size of particles is directly linked to their potential for causing health problems. EPA is concerned about particles that are 10 micrometers in diameter or smaller because those are the particles that generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs and cause serious health effects. EPA groups particle pollution into two categories:

- "Inhalable coarse particles," such as those found near roadways and dusty industries, are larger than 2.5 micrometers and smaller than 10 micrometers in diameter.
- "Fine particles," such as those found in smoke and haze, are 2.5 micrometers in diameter and smaller. These particles can be directly emitted from sources such as forest fires, or they can form when gases emitted from power plants, industries and automobiles react in the air.

2.4.3 Carbon Monoxide

Carbon monoxide (CO) is a colorless, odorless gas emitted from combustion processes. Nationally and, particularly in urban areas, the majority of CO emissions to ambient air come from mobile sources. CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. At extremely high levels, CO can cause death. EPA first set air quality standards for CO in 1971. For protection of both public health and welfare, EPA set a 8-hour primary standard at 9 parts per million (ppm) and a 1-hour primary standard at 35 ppm.

In a review of the standards completed in 1985, EPA revoked the secondary standards (for public welfare) due to a lack of evidence of adverse effects on public welfare at or near ambient concentrations. The last review of the CO NAAQS was completed in 1994 and the Agency chose not to revise the standards at that time.

2.4.4 Nitrogen Oxides

Nitrogen dioxide (NO2) is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NOx)." Other nitrogen oxides include nitrous acid and nitric acid. While EPA's National Ambient Air Quality Standard covers this entire group of NOx, NO_2 is the component of greatest interest and the indicator for the larger group of nitrogen oxides. NO_2 forms quickly from emissions from cars, trucks and buses, power plants, and off-road equipment. In addition to contributing to the formation of ground-level ozone, and fine particle pollution, NO_2 is linked with a number of adverse effects on the respiratory system (Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B., Nguyen, Q.T., Meyer, E.L. and Pace, T.G. et al., 1990).

EPA first set standards for NO_2 in 1971, setting both a primary standard (to protect health) and a secondary standard (to protect the public welfare) at 0.053 parts per million (53 ppb), averaged annually. The Agency has reviewed the standards twice since that time, but chose not to revise the annual standards at the conclusion of each review. In January 2010, EPA established an additional primary standard at 100 ppb, averaged over one hour. Together the primary standards protect public health, including the health of sensitive populations - people with asthma, children, and the elderly. No area of the country has been found to be out of compliance with the current NO_2 standards.

2.4.5 Sulphur Dioxide

Sulfur dioxide (SO_2) is one of a group of highly reactive gasses known as "oxides of sulfur." The largest sources of SO_2 emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of SO_2 emissions include industrial processes such as extracting metal from ore, and the burning of high sulfur containing fuels by locomotives, large ships, and non-road equipment. SO_2 is linked with a number of adverse effects on the respiratory system (Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B., Nguyen, Q.T., Meyer, E.L. and Pace, T.G. et al., 1990).

EPA first set standards for SO_2 in 1971. EPA set a 24-hour primary standard at 140 ppb and an annual average standard at 30 ppb (to protect health). EPA also set a 3-hour average secondary standard at 500 ppb (to protect the public welfare). In 1996, EPA reviewed the SO_2 NAAQS and chose not to revise the standards.

In 2010, EPA revised the primary SO_2 NAAQS by establishing a new 1-hour standard at a level of 75 parts per billion (ppb). EPA revoked the two existing primary standards because they would not provide additional public health protection given a 1-hour standard at 75 ppb.

2.4.6 Lead

Lead (Pb) is a metal found naturally in the environment as well as in manufactured products. The major sources of lead emissions have historically been from fuels in on-road motor vehicles (such as cars and trucks) and industrial sources. As a result of EPA's regulatory efforts to remove lead from on-road motor vehicle gasoline, emissions of lead from the transportation sector dramatically declined by 95 percent between 1980 and 1999, and levels of lead in the air decreased by 94 percent between 1980 and 1999. Today, the highest levels of lead in air are usually found near lead smelters. The major sources of lead emissions to the air today are ore and metals processing and piston-engine aircraft operating on leaded aviation gasoline (U.S.EPA, 2007).

2.5 AIR QUALITY STANDARDS

2.5.1 National Ambient Air Quality Standards (NAAQS), US EPA

The National Ambient Air Quality Standards (NAAQS) are standards established by the United States Environmental Protection Agency under authority of the Clean Air Act (42 U.S.C. 7401 et seq.) that apply for outdoor air throughout the country. Primary standards are designed to protect human health, with an adequate margin of safety, including sensitive populations such as children, the elderly, and individuals suffering from respiratory diseases. Secondary standards are designed to protect public welfare from any known or anticipated adverse effects of a pollutant (National Air Quality and Emissions Trends Report, 1999; EPA).

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. Primary standards provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. They are listed below. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air (µg/m^3) (EPA, USA, 2011). Annexure IA present the standards listed in Title 40 of the Code of Federal Regulations Part 50 National Air Quality and Emissions Trends Report, 1999; EPA(National Air Quality and Emissions Trends Report, 1999; EPA).

2.5.2 National Ambient Air Quality Standards by CPCB, New Delhi

The Central Pollution Control Board had adopted first ambient air quality standards on November 11, 1982 as per section 16 (2) (h) of the Air (Prevention and Control of Pollution) Act, 1981. The air quality standards have been revised by the

Central Pollution Control Board on April 11, 1994 and were notified in Gazette of India, Extraordinary Part-II Section 3, sub section (ii), dated May 20, 1994. The revised National Ambient Air Quality Standards are depicted in Annexure IB. These standards are based on the land use and other factors of the area (CPCB, 2010).

CPCB, New Delhi, 2010 states that the ambient air quality objectives/standards are pre-requisite for developing programme for effective management of ambient air quality and to reduce the damaging effects of air pollution. The objectives of air quality standards are: -

1. To indicate the levels of air quality necessary with an adequate margin of safety to protect the public health, vegetation and property.
2. To assist in establishing priorities for abatement and control of pollutant level;
3. To provide uniform yardstick for assessing air quality at national level; and
4. To indicate the need and extent of monitoring programme.

2.6 PARTICULATE MATTER

Particle pollution (also called particulate matter or PM) is the term for a mixture of solid particles and liquid droplets found in the air. Some particles, such as dust, dirt, soot, or smoke, are large or dark enough to be seen with the naked eye. Others are so small they can only be detected using an electron microscope.

Particle pollution includes "inhalable coarse particles," with diameters larger than 2.5 micrometers and smaller than 10 micrometers and "fine particles," with diameters that are 2.5 micrometers and smaller (US EPA, 2007). The average human hair is about 70 micrometers in diameter – making it 30 times larger than the largest fine particle. PM represents a broad class of chemically and physically diverse substances. Particles can be described by size, formation mechanism, origin, chemical composition, atmospheric behavior and method of measurement. The concentration of particles in the air varies across space and time, and is related to the source of the particles and the transformations that occur in the atmosphere. PM can be principally characterized as discrete particles spanning several orders of magnitude in size, with inhalable particles falling into the following general size fractions:

- PM_{10} (generally defined as all particles equal to and less than 10 microns in aerodynamic diameter; particles larger than this are not generally deposited in the lung);
- $PM_{2.5}$, also known as fine fraction particles (generally defined as those particles with an aerodynamic diameter of 2.5 microns or less)
- $PM_{10-2.5}$, also known as coarse fraction particles (generally defined as those particles with an aerodynamic diameter greater than 2.5 microns, but equal to or less than a nominal 10 microns); and
- Ultrafine particles generally defined as those less than 0.1 microns.

Sharma et al., (2004) mentioned that fine and coarse particles are distinct in terms of the emission sources, formation processes, chemical composition, atmospheric residence times, transport distances and other parameters. Fine particles are directly emitted from combustion sources and are also formed secondarily from gaseous precursors such as sulfur dioxide, nitrogen oxides, or organic compounds. Fine particles are generally composed of sulfate, nitrate, chloride and ammonium compounds, organic and elemental carbon, and metals. Combustion of coal, oil, diesel, gasoline, and wood, as well as high temperature process sources such as smelters and steel mills, produce emissions that contribute to fine particle formation. Fine particles can remain in the atmosphere for days to weeks and travel through the atmosphere hundreds to thousands of kilometers, while most coarse particles typically deposit to the earth within minutes to hours and within tens of kilometers from the emission source. Some scientists have postulated that ultrafine particles, by virtue of their small size and large surface area to mass ratio may be especially toxic. There are studies which suggest that these particles may leave the lung and travel through the blood to other organs, including the heart. Coarse particles are typically mechanically generated by crushing or grinding and are often dominated by resuspended dusts and crustal material from paved or unpaved roads or from construction, farming, and mining activities.

Singh et al., (1985) states that Environmental pollution is a common problem in both developing and developed countries. Every year large quantities of toxic wastes are discharged into the environment from the ever increasing production of goods and from the burning of fossil fuels to generate the energy needed to sustain industrial and domestic activities. Sulphur dioxide, nitrogen dioxide and suspended particulate matter (SPM) are regarded as major air pollutants in India.

The developing countries, air quality crisis in cities is attributed to vehicular emission which contributes to 40-80% of total air pollution. The urban population is mainly exposed to high levels of air pollution including metals because of motor vehicle emissions, which is also the main source of fine and ultrafine particles, which influence the air quality. These particles can penetrate deep into the respiratory system, and studies indicate that the smaller the particle, more severe the health impacts as stated by Pope et al., (2000).

Maenhaut, W. et al., (2005) stated that the impact of vehicular pollution on human health in urban areas is at peak level as vehicle emissions are near the ground level where people live and work. Atmospheric pollutants exist in both gaseous and pollutants forms. Diesel exhaust, in addition to generating pollutants like hydrocarbons, oxides of nitrogen and carbon is a major contributor to particulate matter in most places of the world. Symptoms like chronic cough, wheezing and breathlessness have been reported on exposure to these pollutants.

2.7 PARTICULATE MATTER AND ITS SIGNIFICANCE RELATED TO HEALTH

Sengupta et al., (2005) reported that India has 23 major cities of over 1 million people and ambient air pollution exceeds the WHO Standards in many of them. Suspended particulate matter in ambient air is a complex, multiphase system consisting of particle sizes ranging from <0.01Cm to >100Cm reports that nanoparticles (Particles <0.1 Cm) in mass median aerodynamic diameter have been postulated to affect cardiopulmonary system Urban areas exhibit both the highest level of pollution and largest target of impact on human health.). Diesel and Petroleum exhaust contain various substances, which are harmful to human beings as mentioned by Gurjar et al., (2004).

Particulate matter refers to the solid and liquid particles that are dispersed into ambient air. These particles can be classified in several ways. Firstly, they can be classified into primary and secondary particles based on the mechanism of their formation. Primary particles are emitted directly as particles, whereas secondary particles are formed from precursor gases in the atmosphere via gas-to-particle conversion. Both types of particles are subject to growth and transformations since there can be formation of secondary material on the surface of existing particles. Secondly, particles can be classified by their physical size; the size is from a few nanometers (nm) to tens of micrometers (μm) in diameter. Size is the single most important determinant of the properties of particles and it has implications on formation, physical and chemical properties, transformation, transport, and removal of particles from the atmosphere (Fang et al. 2000).

Wilson et al., (2002) found that ambient particulate mass typically has a modal size distribution, meaning that the total mass of particulate matter tends to concentrate around one or more distinguishable points on the particle size scale. The modal character of the particle mass size distribution results from continuous processes leading to particle formation on one hand, and processes leading to removal of particles from the atmosphere on the other hand. Thus, the number of observable modes in particle size distribution varies depending on age of the aerosol and the vicinity of active sources of particles of different sizes. The definition of fine and coarse particles is anoperational one based on a bimodal size distribution. Due to the overlap between fine- and coarse-mode particles in the intermodal region (1-3 _m), measurement of $PM_{2.5}$ is only an 16 approximation of fine-mode particles and measurement of $PM_{2.5-10}$ is only an approximation of coarse-mode particles.

Fang et al. (2000) stated that the balance of the factors that lead to pollutant accumulation and the factors that lead to pollutant dispersion controls temporal and spatial variations in concentrations of pollutants. Firstly, the concentration and other characteristics of suspended particulate matter are determined by the presence and activity of sources. Once formed, particles change their size and composition by condensation or evaporation, by coagulating with other particles or by chemical reactions as stated by Seinfeld and Pandis et al., (1998).

Pohjola et al. (2000) stated that meteorological factors such as wind speed and direction, temperature, amount of precipitation, and the height of the atmospheric boundary layer, are most important in governing the concentration variations of particulate matter. The highest PM concentrations are often reported during stable meteorological conditions such as inversion with low wind speeds as mentioned also by Pohjola et al. (2000). Also the physical and chemical processes affecting the particles are regulated to a great extent by meteorological factors.

2.8 TRACE ELEMENTS IN PARTICULATE MATTER

H. J. M. Bowen, *Trace Elements in Biochemistry*. Academic Press, (1966) has mentioned that the term trace element is a bit hard to define. For igneous and metamorphic systems (and sedimentary rocks for that matter), an operational definition might be as follows: trace elements are those elements that are not stoichiometric constituents of phases in the system of interest. Clearly this definition is a bit fuzzy: a trace element in one system is not one in another. For example, potassium (K) never forms its own phase in mid-ocean ridge basalts (MORB), its concentration rarely exceeding 1500 ppm; but K is certainly not a trace element in granites. For most silicate rocks, O, Si, Al, Na, Mg, Ca, and Fe are ‘major elements’. H, C, S, K, P, Ti, Cr, and Mn are sometimes ‘major elements’ in the sense that they can be stoichiometric constituents of phases. These are often referred to as ‘minor elements’. All the remaining elements are always trace elements, with the exception of a few rare, but important, circumstances such as pegmatites and ore deposits.

In analytical chemistry, a trace element is an element in a sample that has an average concentration of less than 100 parts per million measured in atomic count, or less than 100 micrograms per gram. In biochemistry, a trace element is a dietary mineral that is needed in very minute quantities for the proper growth, development, and physiology of the organism as stated also by H. J. M. Bowen, *Trace Elements in Biochemistry*. Academic Press, (1966).

Further he stated that in geochemistry, a trace element is a chemical element whose concentration is less than 1000 ppm or 0.1% of a rock's composition. The term is used mainly in igneous petrology. Trace elements will either prefer liquid or solid phase. If compatible with a mineral, it will prefer a solid phase. If it is incompatible with an element it will prefer a liquid phase. The measurement of this ratio is known as the partition coefficient. Trace elements can be substituted for network-forming cations in mineral structures. Minerals do not have to contain trace elements, i.e. they do not have to appear in in the mineral's chemical formula.

Mertz. W., et al., (1987) mentioned in his research findings that essential trace elements are required by man in amounts ranging from 50 micrograms to 18 milligrams per day. Acting as catalytic or structural components of larger molecules, they have specific functions and are indispensable for life. Research during the past quarter of a century has identified as essential six trace elements whose functions were previously unknown. In addition to the long-known deficiencies of iron and iodine, signs of deficiency for chromium, copper, zinc, and selenium have been identified in free-living populations. Four trace elements were proved to be essential for two or more animal species during the past decade alone. Mertz. W., et al., (1987) also mentioned that marginal or severe trace element imbalances can be considered risk factors for several diseases of public health importance, but proof of cause and effect relationships will depend on a more complete understanding of basic mechanisms of action and on better analytical procedures and functional tests to determine marginal trace element status in man.

2.8.1 Marker Elements

Table 2.2 present a large number of **Marker Elements** which are regulated in USA under the Clean Air Act and in Europe under the Air Framework Directive (Guttikunda et al., 2009). A variety of persistent organic pollutants, which can attach to particulate matter are listed below.

Table 2.2 Marker Elements Associated with Various Emission Sources

Sr. No.	Emission Source	Marker Elements
1	Soil	Al, Si, Sc, Ti, Fe, Sm, Ca
2	Road dust	Ca, Al, Sc, Si, Ti, Fe, Sm
3	Sea salt	Na, Cl, Na^+, Cl^-, Br, I, Mg, Mg^{2+}
4	Oil burning	V, Ni, Mn, Fe, Cr, As, S, SO_4^{2-}
5	Coal burning	Al, Sc, Se, Co, As, Ti, Th, S
6	Iron and steel industries	Mn, Cr, Fe, Zn, W, Rb
7	Non- Ferrous metal industries	Zn, Cu, As, Sb, Pb, Al
8	Glass industry	Sb, As, Pb
9	Cement industry	Ca
10	Refuse incineration	K, Zn, Pb, Sb
11	Biomass burning	K, EC, OC Br
12	Automobile gasoline	EC, Br, Ce, La, Pt, SO_4^{2-}, NO_3^-
13	Automobile diesel	OC, EC, S, SO_4^{2-}, NO_3^-

(Source: Urban Particulate Pollution Source Apportionment - Part 1. Definition, Methodology, and Resources; Dr. Sarath Guttikunda, January, 2009)

2.9 EFFECTS OF SOME TRACE METALS ON HUMANS

Trace metals are generally classified as those essential to life (essential elements) and those not known to be essential to life processes (non essential elements) (e.g. Cu & Zn) are beneficial to human health, but they also become toxic when taken in excess (Copius Peereboom, et al., 1985). The biological effect is a function of the elements concentration in the organism, very low concentration of an essential element is incompatible with life. With increasing concentration specific functions increase to reach a pleatu that can be maintained through a range of elements concentration levels. Beyond this range further increasing concentrations results in deleterious effects, chronic or acute toxicity and death depending on the actual concentration level to which the exposure occurs. For non essential elements (e.g. Pb & Cd), the transition level at which an effect can be considered as adverse is very difficult to judge. The situation continually changes, as the sensitivity of measurements increase, and very small effects are recognized.

Copius Peereboom, et al., (1985) concluded that the toxic effect of an element are measured by its dose-response relationship where the response is the magnitude of an adverse effect Doses are either acute or chronic. An acute dose is a large amount of toxic materials which produces a rapid onset of effects, often intense and can result in death. He showed that A chronic dose is usually a lesser amount but continued over a long period of time. Therefore the toxic material has a chance to build up in the body and its adverse effects are seen as a gradual onset of symptoms. At times the symptoms of acute and chronic exposures are different, and the effects may also differ. Another feature which affects the response to a toxic metal is that some people specially children are more sensitive, and therefore more at risk than others.

2.10 ESSENTIAL TRACE METALS

Feinendegan and Kasperek, et al., (1979) observed that the essential elements have four major functions in the human body, namely as stabilizers, as elements of structures, as essential elements for hormonal functions and as a co-factor in enzymes. Lack of essential trace elements will influence physiological state of health. In fact, health depends largely on a normal supply and concentration of essential trace elements in tissues. Changes in trace elements concentration may lead to severe reactions.

2.10.1 Copper

Copper is a chemical element with the symbol **Cu** and atomic number 29. It is a ductile metal, with very high thermal and electrical conductivity. Pure copper is rather soft and malleable, and a freshly exposed surface has a reddish-orange color. It is used as a thermal conductor, an electrical conductor, a building material, and a constituent of various metal alloys.

Copper just above its melting point keeps its pink luster color when enough light outshines the orange incandescence color. Copper have high ductility and electrical conductivity, which makes copper suitable for electrical work. The metal is usually supplied in a fine-grained polycrystalline form. Pure copper is pink; copper exposed to air has a reddish tarnish. Together with osmium (bluish), caesium (yellow) and gold (yellow), it is one of only four elemental metals with a natural color other than gray or silver. Copper's characteristic color results from its electron configuration. Copper has the second highest electrical and thermal conductivity after silver at a conductivity of 59.6×10^{6} S/m (Fergussion, J.E. and Kim, N.D. et al., 1991). The purity of copper in electronics is expressed in nines, with a digit specifying the number of nines in the percentage of purity, followed by an N. The higher the digit, the purer the copper is. Copper forms a rich variety of compounds with oxidation states +1 and +2. It does not react with water, but it slowly reacts with atmospheric oxygen forming a layer of brown-black copper oxide. Hydrogen sulfides and sulfides react with copper to form various copper sulfides on the surface.

The adult human body contains only about 50-120 mg of copper, very little compared to other trace elements such as iron and Zinc. Many fundamentally important copper metalloenzymes are known with multiple biochemical functions.copper metallp proteins exist in liver, red cells and other tissues (Fergussion, J.E. and Kim, N.D. et al., 1991). The incorporations of iron into hemoglobin require the copper enzyme, ferroxidase. In contrast to Zn, clinical signs of Cu deficiency appear fairly late and are preceded by biochemical changes. Cu efficiency is accompanied by hypocupremia and low ceruloplasmic (cu-protein) levels (where levels fall to 30% of normal and below). Usual features of Cu deficiency are anemia, arthritis, arterial disease, loss of pigmentation, myocardial disease and neurologic effects (Turnlund et al., 1998). Excessive copper produces epigastric pain, nausea, vomiting and diarrhea which usually prevent the more serious manifestations of copper toxicity. Serious manifestation includes coma, hepatic necrosis, vaccular collapse and death. Wilson's disease, a genetic disorder, and certain liver and biliary diseases are associated with the accumulation of toxic levels of Cu in the liver and other tissues without excessive intake (Fergussion, J.E. and Kim, N.D. et al., 1991).

2.10.2 Zinc

Zinc which is known as spelter, is a metallic chemical element; it has the symbol Zn and atomic number 30. It is the first element in group 12 of the periodic table. Zinc is, in some respects, chemically similar to magnesium, because its ion is of similar size and its only common oxidation state is +2. Zinc is the 24th most abundant element in the Earth's crust and has five stable isotopes. The most exploited zinc ore is sphalerite, a zinc sulfide.

Zinc is an essential mineral of "exceptional biologic and public health importance" Consumption of excess zinc can cause ataxia, lethargy and copper deficiency. Zinc, also referred to in nonscientific contexts as spelter is a bluish-white, lustrous, diamagnetic metal, and has a hexagonal crystal structure. The metal is hard and brittle at most temperatures but becomes malleable between 100 and 150 °C. Above 210 °C, the metal becomes brittle again and can be pulverized by beating. Zinc is a fair conductor of electricity. For a metal, zinc has relatively low melting (419.5 °C, 787.1 F) and boiling points (907 °C). Zinc is known to be an essential co-factor in atleat 100 enzymes, regulating the synthesis of proteins and nucleic acid. The important among those are carbonic anhydrase, alcohol dehydrase, DNA and RNA polymerases. A deficiency of Zn develops in a manner, different from that of most nutrients (King & Keen, 1999). Thus in the case of most nutrients, an insufficient dietary intake causes first a mobilization of stores or functional reserves. Therefore tissue concentration of nutrient decline, and eventually, one or more specific functions or metabolic pathways dependent on the nutrient deteriorate.

Thus, reduction in the growth is late manifestation of deficiency. Zn toxicity occurs very rarely. Typical signs of acute Zn toxicity include epigastric pain, diarrhea, nausea and vomiting. Metal fume fever has been reported to occur following the inhalation of Zn oxides fumes. Signs develop within eight hours and include profuse sweating and general weakness. Signs of toxicity disappear 12 to 24 hours after the individual is removed from zinc contaminated environment. The major consequences of the long term ingestion of excessive Zn supplements is the induction of the secondary copper deficiency caused by the competitive interaction between these elements with regard to intestinal absorption (King & Keen, 1999).

2.10.3 Chromium

Chromium is a chemical element which has the symbol **Cr** and atomic number 24, first element in Group 6. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable.

Chromium is remarkable for its magnetic properties: it is the only elemental solid which shows antiferromagnetic ordering at room temperature (and below). Above 38 °C, it transforms into a paramagnetic state

Chromium is a member of the transition metals, in group 6. Chromium has an electronic configuration of $4s^1 3d^5$, owing to the lower energy of the high spin configuration. Chromium exhibits a wide range of possible oxidation states, where the +3 state is most stable energetically; the +3 and +6 states are most commonly observed in chromium compounds, whereas the +1, +4 and +5 states are rare (Vincent, John B. et al. 2010). The exposure to airborne chromium compounds and chromic acid mists, particularly the hexavalent chromates has been observed to produce irritation of the skin and respiratory tract, dermatitis, ulcers, and cancers of the respiratory tract. Two effects that appear to be particularly important in relation to air pollution are hypersensitive to chromium compounds and induction of cancers in the respiratory tract. Chromium metal is thought to be nontoxic. Hexavalent compounds appear to be much more harmful then trivalent compounds (Vincent, John B. et al. 2010).

2.10.4 Manganese

Manganese is a chemical element, designated by the symbol **Mn**. It has the atomic number 25. It is found as a free element in nature (often in combination with iron), and in many minerals. As a free element, manganese is a metal with important industrial metal alloy uses, particularly in stainless steels.

Manganese phosphate is used as a treatment for rust and corrosion prevention on steel. Depending on their oxidation state, manganese ions have various colors and are used industrially as pigments. Manganese (II) ions function as cofactors for a number of enzymes in higher organisms, where they are essential in detoxification of superoxide free radicals. The element is a required trace mineral for all known living organisms. In larger amounts, and apparently with far greater activity by inhalation, manganese can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible. Manganese is a silvery-gray metal resembling iron. It is hard and very brittle, difficult to fuse, but easy to oxidize. Manganese metal and its common ions are paramagnetic. The most common oxidation states of manganese are +2, +3, +4, +6 and +7, though oxidation states from −3 to +7 are observed (Takeda, A. et al. 2003). Mn^{2+} often competes with Mg^{2+} in biological systems. Manganese compounds where manganese is in oxidation state +7, which are restricted to the unstable oxide Mn_2O_7 and compounds of the intensely purple permanganate anion MnO_4^-, are powerful oxidizing agents. The most stable oxidation state for manganese is +2, which has a pale **pink** color, and many Manganese (II) compounds are known, such as Manganese (II) sulfate ($MnSO_4$) and manganese (II) chloride ($MnCl_2$).

The human body contains about 10 mg of manganese, which is stored mainly in the liver and kidneys. In the human brain the manganese is bound to manganese metalloproteins most notably glutamine synthetase in astrocytes. Manganese is also important in photosynthetic oxygen evolution in chloroplasts in plants. Inhalation of manganese oxide may cause chronic manganese poisoning or managic pneumonia. Chronisc manganese poisoining is a disease affecting the central nervous system resulting in otal or partial disability. Manganic pneumonia is a croupous disease often resulting in death. Manganese compounds are known to be catalyzing the oxidation of other pollutants such as sulphur dioxide to more undesirable pollutants. Manganese intoxification has acute effects on lungs, liver, central nervous system of the body. The disease known as manganism is generally considered to result more from inhalation of Mn then ingestion, and its development is dependent on atmospheric manganese concentration, duration of exposure and the size of the suspended Mn particles (Takeda, A. et al., 2003).

2.10.5 Iron

Iron is a chemical element with the symbol **Fe,** and atomic number 26. It is a metal in the first transition series. It is the most common element in the whole planet Earth, forming much of Earth's outer and inner core, and it is the fourth most common element in the Earth's crust.

Elemental iron occurs in meteoroids and other low oxygen environments, but is reactive to oxygen and water. Fresh iron surfaces appear lustrous silvery-gray, but oxidize in normal air to give iron oxides, also known as rust Pure iron is soft (softer than aluminium), but is unobtainable by smelting. Iron chemical compounds, which include ferrous and ferric compounds, have many uses. Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron(II) compounds are called ferrous, and iron(III) compounds ferric. Iron also occurs in higher oxidation states, an example being the purple potassium ferrate (K_2FeO_4) which contains iron in its +6 oxidation state. Iron (IV) is a common intermediate in many in biochemical oxidation reactions. Numerous organometallic compounds contain formal oxidation states of +1, 0, −1, or even −2 (Bramfitt, B. L.; Benscoter, Arlan O. et al., 2002). Iron plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Iron is also the metal used at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals. Although an essential element the inhalation of iron oxides produce a benign siderosis. In addition to the benign condition there may be very serious synergistic effects as well as other undesirable effects, such as chronic bronchitis. In the laboratory the iron oxides act as a vehicle to transport the carcinogens in high local concentrations to the target tissue, similarly sulphur dioxide is transported in high local concentration deep into the lungs by iron oxide particles.

Large amounts of ingested iron can cause excessive levels of iron in the blood. High blood levels of free ferrous iron react with peroxides to produce free radicals, which are highly reactive and can damage DNA, proteins, lipids, and other cellular components (Bramfitt, B. L.; Benscoter, Arlan O. et al., 2002). Damage to the cells of the gastrointestinal tract can also prevent them from regulating iron absorption leading to further increases in blood levels. Iron typically damages cells in the heart, liver and elsewhere, which can cause significant adverse effects, including coma, metabolic acidosis, shock, liver failure, coagulopathy, adult respiratory distress syndrome, long-term organ damage, and even death. Humans experience iron toxicity above 20 milligrams of iron for every kilogram of mass, and 60 milligrams per kilogram is considered a lethal dose. Overconsumption of iron, often the result of children eating large quantities of ferrous sulfate tablets intended for adult consumption, is one of the most common toxicological causes of death in children under six (Bramfitt, B. L.; Benscoter, Arlan O. et al., 2002).

2.11 NON ESSENTIAL TRACE ELEMENTS

Bellinger et al., (1992) observed that among the non essential elements, exposure to lead and cadmium are of particular importance. Although a certain fraction of amount absorbed is excreted, lead and cadmium tend to accumulate in important organs by body. There is only a narrow tolerable region of these metals. Hence once accumulated, these metals disturb the well being of human body. Since the mid 1970’s attention has been focused on the possible health implications of long term environmental exposure to trace metals, particularly lead. Lead and its organic compound are toxic. They are cumulative toxins which can enter the body by inhalation of dust fumes and vapor or by ingestion as observed by Folinsbee, et al.,(1988).

2.11.1 Lead

Lead is a main-group element with the symbol Pb, and atomic number 82. Lead is a soft, malleable poor metal. It is also counted as one of the heavy metals. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid. Lead is a poisonous substance to animals. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. Like the element mercury, another heavy metal, lead is a potent neurotoxin that accumulates both in soft tissues and the bones (Pauling, Linus et al.,1947).

Lead is bright and silvery when freshly cut but the surface rapidly tarnishes in air to produce the commonly observed dull luster normally associated with lead. It is a dense, ductile, very soft, highly malleable, bluish-white metal that has poor electrical conductivity when compared to most other metals. This metal is highly resistant to corrosion.

Various oxidized forms of lead are easily reduced to the metal. An example is heating PbO with mild organic reducing agents such as glucose. A mixture of the oxide and the sulfide heated together will also form the metal (Pauling, Linus et. Al., 1947).

$$2\ PbO + PbS \rightarrow 3\ Pb + SO_2$$

Metallic lead is attacked (oxidized) only superficially by air, forming a thin layer of lead oxide that protects it from further oxidation. The metal is not attacked by sulfuric or hydrochloric acids. It dissolves in nitric acid with the evolution of nitric oxide gas to form dissolved $Pb\ (NO_3)_2$.

$$3\ Pb + 8\ H^+ + 8\ NO{-}3 \rightarrow 3\ Pb^{2+} + 6\ NO{-}3 + 2\ NO + 4\ H_2O$$

When heated with nitrates of alkali metals, metallic lead oxidizes to form PbO (also known as litharge), leaving the corresponding alkali nitrite. PbO is representative of lead's +2 oxidation state. It is soluble in nitric and acetic acids, from which solutions it is possible to precipitate halide, sulfate, chromate, carbonate ($PbCO_3$), and basic carbonate ($Pb_3(OH)_2(CO_3)_2$) salts of lead (Pauling, Linus et al., 1947). The sulfide can also be precipitated from acetate solutions. These salts are all poorly soluble in water. Among the halides, the iodide is less soluble than the bromide, which, in turn, is less soluble than the chloride.

Goyer et al., (1993) observed that Lead causes neurological and biochemical changes in the body. The first signs of low level lead exposure are effects on the biosynthesis of haeme (the iron prohyrin component of hemoglobin) observed by Boeckx, (1986). Schuhmacher et al., (1992) studied that Lead is known to anhibit alpha- aminolovulinic acid dehydratase (ALAD) activity (causing a decrease in haeme synthesis.

Alpha-aminolevulinic acis synthesis (ALAD) is a rate controlling enzyme in the haeme biosynthetic pathway and is subject to negative feed back regulation. Therefore, the decrease in haeme synthesis as a result of ALAD inhibition results and increase in the blood and urine concentration of alpha-Aminolevulinic acid(ALA) (Goyer et al., 1993).

Lead interacts or competes for gastro intestinal absorption, tissue deposition and as a co-factor in metal-enzymes with essential trace metals, particularly calcium, iron, and zinc. Deficiencies of calcium and iron clearly inhance lead absorption. Laed competes with zinc as a co-factor with haeme enzymes , particularly aminolevulinic acid dehydratase and ferochelates. Lead increases copper deficiency (Goyer et al., 1993).

2.11.2 Cadmium

Cadmium is a chemical element with the symbol **Cd** and atomic number 48. The soft, bluish-white metal is chemically similar to the two other metals in group 12, zinc and mercury. Similar to zinc it prefers oxidation state +2 in most of its compounds and similar to mercury it shows a low melting point compared to transition metals. Cadmium and its congeners are not considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states. Average concentration in the earth's crust is between 0.1 and 0.5 parts per million (ppm).

Cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. Cadmium was used for a long time as a pigment and for corrosion resistant plating on steel. Cadmium compounds were used to stabilize plastic. With the exception of its use in nickel-cadmium batteries and cadmium telluride solar panels, the use of cadmium is generally decreasing in its other applications. These declines have been due to competing technologies, cadmium's toxicity in certain forms and concentration and resulting regulations. Although cadmium is toxic, one enzyme, a carbonic anhydrase with cadmium as reactive center has been discovered. Cadmium is a soft, malleable, ductile, bluish-white bivalent metal. It is similar in many respects to zinc but forms complex compounds. The most common oxidation state of cadmium is +2, though rare examples of +1 can be found (Scoullos, M. J. et al., 2001). Cadmium burns in air to form brown amorphous cadmium oxide (CdO). The crystalline form of the same compound is dark red and changes color when heated, similar to zinc oxide. Hydrochloric acid, sulfuric acid and nitric acid dissolve cadmium by forming cadmium chloride ($CdCl_2$) cadmium sulfate ($CdSO_4$) or cadmium nitrate ($Cd(NO_3)_2$). The oxidation state +1 can be reached by dissolving cadmium in a mixture of cadmium chloride and aluminium chloride, forming the Cd22+ cation, which is similar to the Hg22+ cation in mercury(I) chloride (Scoullos, M. J. et al., 2001).

$$Cd + CdCl_2 + 2\ AlCl_3 \rightarrow Cd_2\ [AlCl_4]_2$$

The most dangerous form of occupational exposure to cadmium is inhalation of fine dust and fumes, or ingestion of highly soluble cadmium compounds. Inhalation of cadmium-containing fumes can result initially in metal fume fever but may progress to chemical pneumonitis, pulmonary edema, and death. Cadmium is also an environmental hazard. Human exposures to environmental cadmium are primarily the result of fossil fuel combustion, phosphate fertilizers, natural sources, iron and steel production, cement production and related activities, nonferrous metals production, and municipal solid waste incineration. Tobacco smoking is the most important single source of cadmium exposure in the general population. It has been estimated that about 10% of the cadmium content of a cigarette is inhaled through smoking (Scoullos, M. J. et al., 2001). The absorption of cadmium from the lungs is much more effective than that from the gut, and as much as 50% of the cadmium inhaled via cigarette smoke may be absorbed. On average, smokers have 4-5 times higher blood cadmium concentrations and 2-3 times higher kidney cadmium concentrations than non-smokers. Despite the high cadmium content in cigarette smoke, there seems to be little exposure to cadmium from passive smoking. No significant effect on blood cadmium concentrations could be detected in children exposed to environmental tobacco smoke (Scoullos, M. J. et al., 2001).

2.12 SOURCES OF TRACE METALS IN ATMOSPHERE

Emissions to the atmosphere are normally considered the most important one, as the atmosphere is probably the main avenue for the transport of heavy elements. Trace metals are contributed to the atmosphere from wide variety of natural and anthropogenic sources. Major emission source categories for WHO Criteria Air Pollutants are given in Table 2.3.

Table 2.3 Major Emission Source Categories for WHO Criteria Air Pollutants

Major Pollutants	Major Emission Sources
Arsenic	Non-ferrous metal industry
	Stationary combustion sources
	Use as catalyst and reagent in inorganic chemical Industry
	Pesticide use
Cadmium	Metal production ,especially zinc processing
	Electroplating
	Production of plastics, pigments and batteries

	Waste incineration
	Fertilizer processing and application
	Natural sources ,especially volcanoes
Chromium	Production of chromium compounds
	Chromium production from chromite
Lead	Road traffic mainly gasoline powered vehicles
	Non-ferrous metal industry
	Iron and steel industry
	Production of lead-acid batteries
Manganese	Use as additive in metallurgical processes
	Production of dry-cell batteries
	Chemical industry
	Glass, leather and textile industries
	Fertilizer use
Mercury	Coal combustion in stationary sources
	Electrical apparatus Electrolytic production of caustic soda and chlorine
	Pharmaceutical industry
	Production and use of antifouling paints
Nickel	Burning of residual and fuel oils
	Nickel mining and refining
	Municipal waste incineration
Vanadium	Natural source, especially weathering and volcanoes
	Metallurgical processes

2.12.1 Natural sources of trace metals

Natural sources include dust raised by winds, volcanic activity, forest fires, vegetation and sea salt sprays. As per Table 2.4, the summary of annual fluxes from natural sources clearly implicates biogenic processes as the principal contributor of trace metals to the atmosphere.

Ross Mosher and Duce, (1987) concluded that volatile and particulate material of biogenic origin account 30-50% of the As, Cd, Cu, Mn, Pb, and Zn and for over 50% of Se and Mo emitted annually from natural sources .This very important source has either been ignored or badly estimated in most of the previously published estimates of natural trace metal flux. It should however, be noted that high biogenic outputs have been recognized in recently published models of the global atmospheric cycles of selenium and mercury.

It is estimated that volcanoes and fumaroles account from about 50% of the Cd and Hg and for 20-40% of the As, Cr, Cu, Ni, Pb and Sb released naturally (Table no 4).Volcanic eruptions are episodic in nature and the values listed are believed to be the average source strengths.

According to Jaworowski et al; (1981), a number of previous models have regarded windblown dusts as the major natural sources of atmospheric metals .The data in table no 4 in fact show that, except for Cr,the soil derived dust accounts for only 20-30% of Cu,Mo,Ni,Pb,Sb and Zn for less than 10% of the Hg and Se released from natural sources. Forest fires and sea salt arrays represent minor sources of the airborne trace metals, each source generally contributing less than 10% of the baseline flux natural sources of atmospheric metals. The data in table no 4 in fact show that, except for Cr,the soil derived dust accounts for only 20-30% of Cu, Mo, Ni, Pb, Sb and Zn for less than 10% of the Hg and Se released from natural sources. Forest fires and sea salt arrays represent minor sources of the airborne trace metals, each source generally contributing less than 10% of the baseline flux.

2.12.2 Anthropogenic sources of trace metals

Pacyna et al., (1988) discussed about anthropogenic sources of trace metals. The emission from anthropogenic sources now exceeds the flux from natural sources, implying that mankind has become the key element in the regional and global cycle of most of the trace metals. The anthropogenic sources can be divided into 6 groups namely, stationary fuel combustion, internal combustion engines ,non-ferrous metal manufacturing, iron, steel and ferro alloy plants and foundaries, waste incineration and cement production. Most industrial processes release one trace metal or another to the atmosphere. The principal contributors to worldwide trace metal pollution are shown in table

The smelting of base metals accounts for over 50% of the As, Cd, Cu and Zn, for about 40% of the Sb and Se, and for 10% or less of the other elements released by industrial plants.(Table no 2.5). As, Cd , Pb and Se are recovered as byproducts from beneficiation of base metal ores. The burning of fuel oil is generally recognized as the dominant source of atmospheric vanadium. Oil combustion also accounts for about 50% of the total anthropogenic emissions of Sn and Ni, so that in some regions, the Mn or Sn and Mn or Ni ratios may also be used in finger printing the sources of air pollution. Coal combustion is the largest single source of atmospheric Mo(84%),Hg(58%),Se(47%) and Sb (37%) pollution. It would clearly appear that the Mn/Mo ratio would be most ideal for finger printing any air masses released from coal fired power plants .It should be noted that coal combustion is an important contributor to the air borne Sn (15%) ,Ni(25%),Cr(37%) and Mn(29%) of anthropogenic origin (Pacyna et al., 1988).

Automobile remains the single largest source of airborne lead accounting for about 75% of the total anthropogenic Pb emission. The contribution from this source is declining rapidly however, in response to the phase out of leaded gasoline in Europe and North America. The principal source of pollutant Mn are the secondary non ferrous metal plants while iron and steel mills account for about 50% of the anthropogenic Cr emission. With the exception of Hg (33%), refuse incineration now accounts for less than 10% of the anthropogenic trace metal emissions. Burning of fuel wood is the major source of atmospheric trace metal pollution in many rural and remote areas of the developing countries .Energy generation, vehicular traffic and industrial metal production have brought about a sizeable increase in trace element emissions. These are often highly localized especially in urban and industrial areas. Therefore localized concentrations can become quite high.

2.13 CONCENTRATION LEVELS OF TRACE METALS IN ATMOSPHERE

According to Harrison et al., (2003), the identification of the chemical forms of the trace metals in the aerosols is a difficult problem, because most methods available for solids require relatively higher concentration of species. The instruments employed are the Scanning Electron Microscope (SEM) and X-ray Diffraction. Most work has been done on lead species, because of high levels of lead in the particulate matter. The actual lead compounds in particulate aerosol will depend on other constituents in the atmosphere, and the age of the aerosol. The primary material from the exhaust of motor cars is mainly PbClBR. However, PbO, Pb(OH)X (X= Cl ,Br) and some PbSO4,Pb3(PO4)2,PbO,PbO.PbSO$ and Pb may also occur in larger particulates. In the smaller particles α and β NH4Cl.2PbClBr, 2NH4Cl. Pb ,Cl ,Br are found. When phosphorous is present in petrol , the compound Pb5(PO4)2 (Cl.Br) may form. Some organo lead compounds such as R4Pb and R3PbCl are also emitted. Particulate materials from smelters contain PbS, PbSO4 and PbO-PbSO4.

Nriagy et al., (1980) and Pacyna et al., (1986) discussed about species of Cadmium in aerosols. Much less is known about the species of the other heavy metals in aerosol, mainly because of their low concentration, making it difficult to identify the compound. The Cd species in aerosols are probably Cd, S, Cd O, Cd(OH2) and mixed oxides of copper and zinc.From smelters there is evidence that CdO , ZnO and ZnS occurs in the stack.

According to Hinds et al., (1998) and Seinfeld & Pandis et al., (1998), aerosol particles are ubiquitous in the Earth’s atmosphere. These particles influence climate, cloud formation, weather, visibility, atmospheric chemistry as well as human health. All liquid or solid particles suspended in air are defined as aerosol particles. Soot, pollen, sea salt particles, mineral dust, asbestos fibres, fly ash and many other types of particles are summarized by this definition.

2.14 TEMPORAL AND SEASONAL VARIATIONS IN ATMOSPHERIC CONCENTRATIONS OF METALS

Variations in atmospheric concentrations of trace metals have been observed in urban and rural locations. These changes are determined mainly by variations in source emissions, wind direction and local ventilation systems. Temporal variations in the levels of atmospheric Pb have shown a characteristic annual cyclic pattern with the Pb level reaching a maximum during the winter months and reducing by a factor of 2-3 to a minimum in summer. Many studies have demonstrated that shift in the wind trajectory from polluted to unpolluted sectors can endanger a substantial build up of zinc in the air at given location. Pronounced seasonality in air borne concentrations of metals have been observed at many locations.

The maximum concentrations of anthropogenic elements were observed during the winter months due to increased fuel combustion and local inversions. The deep ground based inversions along with a strong stability condition of the atmosphere leading to poorer dispersion of the pollutants mostly accounts for the winter maxima of pollutants. The seasonal fluctuations in absolute concentrations of elements in air show an increase of 2 to 11 fold in winter concentrations of As , Cr, Pb, Sb ,V and Zn compared to their summer concentrations. This variation was attributed to increased combustion of fossil fuels and persistence of inversion layers in winter.

From the above discussions it is well clear that estimation of trace elements is necessary. There is need to know about the natural and anthropogenic sources as well as the atmospheric levels of these metals. The knowledge of the environmental pathways of these metals to human being is also necessary. Table 2.4 presents the health effects and TLV’s of some trace metals.

Table 2.4 Health effects and TLV's of some trace metals

METALS	EFFECTS	TLV
V	At very high concentrations gastric intestinal disorders, kidney damage and cardiac palpitation have been observed.	0.5µg/m³
As	Its compounds are highly toxic, causes stomach disorders.	120ng/m³
Zn	Exposure to high concentrations of zinc oxide fumes results in fever.	
Hg	Methyl mercury and mercury vapors are poisonous causing hearing impairment and blindness.	0.1mg/m³
Cr	Lung cancer is induced by chromium salts.	0.5µg/m³
Cd	Causes lung damage.	0.1mg/m³
Pb	Damages the nervous system, causes anemia.	10µg/m³

(Source: US EPA www.epa.gov)

2.15 DISPERSION MODELING

Good Practice Guide for Atmospheric Dispersion Modeling prepared by National Institute of Water and Atmospheric Research, Newzealand, 2004 discusses dispersion modeling. Dispersion modeling is the mathematical simulation of how air pollutants disperse in the ambient atmosphere. It is performed with computer programs that solve the mathematical equations and algorithms which simulate the pollutant dispersion. The dispersion models are used to estimate or to predict the downwind concentration of air pollutants or toxins emitted from sources such as industrial plants, vehicular traffic or accidental chemical releases.

Such models are important to governmental agencies tasked with protecting and managing the ambient air quality. The models are typically employed to determine whether existing or proposed new industrial facilities are or will be in compliance with the National Ambient Air Quality Standards (NAAQS) in the United

States and other Nations. The models also serve to assist in the design of effective control strategies to reduce emissions of harmful air pollutants.

As per US EPA, Air dispersion models are also used by public safety responders and emergency management personnel for emergency planning of accidental chemical releases. Models are used to determine the consequences of accidental releases of hazardous or toxic materials, Accidental releases may result fires, spills or explosions that involve hazardous materials, such as chemicals or radionuclides. The results of dispersion modeling, using worst case accidental release source terms and meteorological conditions, can provide an estimate of location impacted areas, ambient concentrations, and be used to determine protective actions appropriate in the event a release occurs. Appropriate protective actions may include evacuation or shelter-in-place for persons in the downwind direction. At industrial facilities, this type of consequence assessment or emergency planning is required under the Clean Air Act (United States) (CAA) codified in part 60 of Title 40 of the Code of Federal Regulations.

The dispersion models vary depending on the mathematics used to develop the model, but all require the input of data that may include:

- Meteorological conditions such as wind speed and direction, the amount of atmospheric turbulence (as characterized by what is called the "stability class"), the ambient air temperature, the height to the bottom of any inversion aloft that may be present, cloud cover and solar radiation.

- Source term (the concentration or quantity of toxins in emission or accidental release source terms) and temperature of the material

- Emissions or release parameters such as source location and height, type of source (i.e., fire, pool or vent stack) and exit velocity, exit temperature and mass flow rate or release rate.

- Terrain elevations at the source location and at the receptor location(s), such as nearby homes, schools, businesses and hospitals.

- The location, height and width of any obstructions (such as buildings or other structures) in the path of the emitted gaseous plume, surface roughness or the use of a more generic parameter “rural” or “city” terrain.

Many of the modern, advanced dispersion modeling programs include a pre-processor module for the input of meteorological and other data, and many also include a post-processor module for graphing the output data and/or plotting the area impacted by the air pollutants on maps. The plots of areas impacted may also include isopleths showing areas of minimal to high concentrations that define areas of the highest health risk. The isopleths plots are useful in determining protective actions for the public and responders (Briggs, G.A., et al., 1968).

The atmospheric dispersion models are also known as atmospheric diffusion models, air dispersion models, air quality models, and air pollution dispersion models. Dispersion modelling uses mathematical equations, describing the atmosphere,dispersion and chemical and physical processes within the plume, to calculate concentrations at various locations. Whilst, there have been various review papers on atmospheric modelling and their approaches to dispersion in street canyons (Vardoulakis, Fisher et al. 2003) and comparisons between different models using test meteorological data (Ellis, McHugh et al. 2001; Sivacoumar and Thanasekaran 2001; Hall, Spanton et al. 2002; Caputo, Gimenez et al. 2003), these have focussed on modelling gaseous dispersion.

Unfortunately, only a few studies have simultaneously measured particle concentration with gases and the differences between the studies may be partially responsible for the differences observed. In open sites several studies have shown varying correlations between the concentrations of gases and particles. Monn, Fuchs et al. (1997) showed a poor correlation between the outdoor PM_{10} concentrations and NO_2 concentrations in an urban environment with a better correlation between $PM_{2.5}$ and NO_2, although only 2 locations were studied in the latter case. In contrast, Clairborn, Mitra et al. (1995) showed a good correlation between SF_6 and PM_{10} although only distances upto 60m from the motorway were measured. Roorda-Knape, Janssen et al. (1998) observed that benzene, $PM_{2.5}$ and PM_{10} showed no significant decrease in concentration upto 300m from a major motorway. This was consistent with the small decrease in the $PM_{2.5}$ concentration observed by Hitchins et al. (2000). In that study the authors observed that particle number concentration decreased faster than NO_2 concentration from a motorway. Zhu et al. (2002); showed that number concentration of particles between 6 and 220nm correlated well with CO concentration from a motorway. All of these studies were made in an open environment where the wind direction was perpendicularly away from the road.

However, differences have been observed between the local dispersion of gases and particles. Simultaneous measurements of CO and particle number concentration by Morawska et al. (2005); showed that CO concentration was not significantly correlated to particle number concentration around the site and examination of between-site comparisons with the two pollutants showed different spatial and temporal trends. In another study of urban sites Harrison and Jones et al., (2005); observed that particle concentrations correlated only weakly with NOx, with the highest correlation observed at a curbside monitoring location, where concentrations are less affected by dispersion. In addition, an examination of many urban studies like Morawska et al., (2005); has shown that the vertical profiles of particle number concentration around buildings differed from that of gases. These studies differ from the previous studies in that they were conducted in a more complex environment where wind flows were heavily affected by turbulence and emissions were not limited to a single line source.

In general the studies show that in open environments the gas and particle concentrations correlate quite well, whilst in a more complex urban environment significant differences are observed between gas and particle dispersion. Van Dingenen et al., (2004); stated that in an urban environment where traffic emissions are the dominant source of particles, particle showed $PM_{2.5}$ and PM_{10} had an R2 value of 0.95 across all sites in the monitoring network. However, the $PM_{10}/PM_{2.5}$ ratio varied too much to propose a single $PM_{10}/PM_{2.5}$ ratio. In the same study they observed no correlation between annual average particle number concentration and either $PM_{2.5}$ or PM_{10} concentrations. This is in contrast to Harrison et al.,(1999); who found that in an urban measurement study hourly particle number concentration more closely correlated with $PM_{2.5}$ than PM_{10} measurements, although both SPM ranges showed good correlation with the hourly particle number concentrations during the 3 month period. Therefore, models that are designed to model the dispersion of passive scalars, such as inert gases should be capable of modelling the $PM_{2.5}$ and PM_{10} concentrations in certain open environments, especially for longer averaging periods and in the larger airshed where short term variations resulting from transient particle formation events are evened out.

The modelling of particle number concentration involves the incorporation of aerosol dynamics modules into dispersion models. Thus the discussion of particle dispersion modelling must involve both a discussion of the limitations of the various dispersion approaches to the treatment of particles and the aerosol dynamic packages used to evaluate particle processes occurring within the plumes. To complicate the situation further, Lohmeyer et al., (2001) observed that concentrations calculated by the different models differed by a factor of four and even when the same model was employed results varied between groups. The agreement with predicted concentrations was seen to depend on the quality of the input data.

2.16 DISPERSION MODELS

2.16.1 Box Models

Box models are based on the conservation of mass. The site is treated as a box into which pollutants are emitted and undergo chemical and physical processes. It requires the input of simple meteorology and emissions and the movement of pollutants in and out of the box is allowed. The inside of the box is not defined and the air mass is treated as if it is well mixed and concentrations uniform throughout. One advantage of the box model is because of the simplified meteorology box models can include more detailed chemical reaction schemes (e.g. Master Chemical Mechanism) and detailed treatment of the aerosol dynamics, that are able to represent the chemistry and physics of particles within the atmosphere better. However, following inputting initial conditions a box model simulates the formation of pollutants within the box without providing any information on the local concentrations of the pollutants. For this reason they are unsuitable to modelling the particle concentrations within a local environment, where concentrations and thus particle dynamics are highly influenced by local changes to the wind field and emissions (Reff, A.; Eberly, S.I.; Bhave, P.V. et al., 2007).

2.16.2 Gaussian Models

Gaussian type models are widely used in atmospheric dispersion modelling, in particular for regulatory purposes, and are often "nested" within Lagrangian and Eulerian models. Gaussian models are based on a Gaussian distribution of the plume in the vertical and horizontal directions under steady state conditions. The normal distribution of the plume is modified at greater distances due to the effects of turbulent reflection from the surface of the earth and at the boundary layer when the mixing height is low. The width of the plume is determined by σy and σz, which are defined either by stability classes or travel time from the source. One severe limitation of plume models with regards to modelling particle dispersion is that since the plume models use steady state approximations they do not take into account the time required for the pollutant to travel to the receptor (Reff, A.; Eberly, S.I.; Bhave, P.V. et al., 2007).

Therefore, aerosol dynamics must be calculated by post processing treatment of the results. In addition, regional modelling generally requires the incorporation of chemical modelling to accurately predict the formation of particles through secondary organic aerosol (SOA) formation. Even NOx and SOx chemistry, which is fundamental to determining particles and ozone concentrations, is often only calculated using a simple exponential decay. More advanced models can simulate some of the chemical transformations using post processing treatment of the chemistry. Although most Gaussian models only consider diffusion and advection of the pollutants more advance Gaussian models have recently been developed that include physical processes such as deposition and fast chemical reactions.

Furthermore, the Gaussian plume equation assumes that there is no interaction between plumes, which can become significant within urban environments. Algorithms have been developed to model the chemistry and physical processes within the plume and dispersion around buildings. The effect of wakes from buildings can be achieved by modifying the dispersion coefficients, σy and σz. However, the Gaussian equation is not able to calculate recirculation effects caused by multiple buildings or at intersections.

Some of the restrictions implicit in the Gaussian Plume models can be overcome by approximating the emission as a series of puffs over time, which allows the wind speed to be varied. In this approach each puff behaves according to the Gaussian dispersion equation and the overall contribution of the source is calculated by integration of the individual puffs with respect to time and summation of the contribution of individual puffs at the receptor position (Reff, A.; Eberly, S.I.; Bhave, P.V. et al., 2007).

In order to calculate the concentration of pollutants over an urban area multiple source plumes are often used. The different equations used are determined by the nature of the source and heights of the source and receptor. Some further limitations of the Gaussian treatment means that Gaussian models are not designed to model the dispersion under low wind conditions or at sites close to the source, *i.e.* distances less than 100m. According to Benson et al., (1984); Sokhi, Fisher et al. (1998); gaussian models have been shown to consistently overpredict concentrations in low wind conditions. Whereas hybrid models, Sharan, Yadav et al. (1996); Thomson and Manning (2001); which use a combination of the Gaussian plume and puff models, include along wind dispersion of the pollutants in order to better estimate concentrations under low wind speed conditions. A further limitation is a result of the simplified treatment of turbulence and meteorology so they are best suited to calculating hourly pollutant concentrations.

Since Gaussian plume equations assume a homogeneous wind field it is not recommended that they are used for far field modelling as the meteorology is expected to change over such large distances. Caputo et al., (2003); observed that four Gaussian models calculated non zero concentrations for the whole downwind domain and so suggested that they should be limited to distances a few tens of kilometres from the source.

2.16.3 Lagrangian Models

Lagrangian models are similar to box models in that they define a region of air as a box containing an initial concentration of pollutants. The Lagrangian model then follows the trajectory of the box as it moves downwind. The concentration is a product of a source term and a probability density function as the pollutant moves from x to x'. Lagrangian models incorporate changes in concentration due to mean fluid velocity, turbulence of the wind components and molecular diffusion (Oettl, Kukkonen et al. 2001; Raza, Avila et al. 2001; Venkatesan, Mathiyarasu et al. 2002; Tsuang et al., 2003).

Lagrangian models work well both for homogeneous and stationary conditions over the flat terrain (Oettl, Kukkonen et al. 2001; Raza, Avila et al. 2001; Venkatesan, Mathiyarasu et al. 2002; Tsuang et al., 2003) and for inhomogeneous and unstable media condition for the complex terrain. It is possible to model the non-linear chemistry using either the superimposition of a concentration grid on the domain, followed by calculation of the concentration in each grid or the particle can be treated as an expanded box and the photochemical module of the model applied to each box.

The meteorological data calculates the variance of the wind velocity fluctuations and Lagrangian autocorrelation function. Since Lagrangian particle models calculate the diffusion characteristics by the generation of semi random numbers they are not confined by stability classes or sigma curves, as is the case with Gaussian dispersion models (Oettl, Kukkonen et al. 2001; Raza, Avila et al. 2001; Venkatesan, Mathiyarasu et al. 2002; Tsuang et al., 2003).

2.16.4 Computational Fluid Dynamic Models

Computational fluid dynamic (CFD) models provide complex analysis of fluid flow based on conservation of mass and momentum by resolving the Navier-Stokes equation using finite difference and finite volume methods in three dimensions (Gidhagen et al., 2004). Turbulence is classically calculated using k-ε closure methods to calculate the isotropic eddy viscosity parameter present in both the momentum and pollution transport equations, which assumes that a pollutant is diluted equally in all directions. This treatment performs well on a flat boundary layer. However, when a stratified boundary layer exists the closure method needs to be modified to include the Coriolis force and reduced wind shear in the upper atmosphere, which results in an overestimation of the eddy viscosity.

2.16.5 Models for dispersion within a street environment

A brief summary of the street models is given here together with a discussion of their applicability to model particle dispersion. Although there are a number of dispersion models used to calculate urban pollutant concentrations in a local environment, some of which also include a complex treatment of wind flow in street canyon environments,

2.16.5.1 Street Canyon

The street canyon, a road and its flanking buildings, forms the basic geometric unit of the built environment. Arnfield et al., (1982); Oke et al., (1987) concluded that the geometry and materials that make up the canyons of a city greatly influence the urban climate. Knowledge of the processes of urban canyons is of great importance, both for understanding the micro-scale climate within the canyon, as well as for understanding the overall urban climate, for example, the coupling between the urban canopy and boundary layers. According to Vardoulakis et al., (2003); within canyon processes are relevant to environmental issues such as energy consumption, ventilation in buildings, dispersion of air pollutants, as well as human comfort and safety. Wind and temperature fields, radiation and energy exchanges, and concentrations of air pollutants in urban street canyons are all topics that have been investigated through field experiments, scaled physical models in wind tunnels, and numerical modelling. Most research has been focused on the complex flow patterns around buildings and within canyons as it is critical for the dispersion of windborne pollutants in the urban environment.

2.17 SOURCE APPORTIONMENT

Quantitatively identifying the relative contributions of different source types to ambient air pollutant concentrations is referred to as source apportionment.

According to Guttikunda S. et al., (2009); when an area experiences high concentrations of PM or ozone, particularly when the concentrations are in exceedance of an air quality standard, analysts seek to identify the contributing emissions sources to assist policy makers in developing control strategies. Source apportionment study, which is primarily based on measurements and tracking down the sources through receptor modeling, helps in identifies the sources & extent of their contribution. The purpose of source apportionment is to give a reasonably clear idea of the total breakdown of emissions from all sources so it can inform the drawing up a targeted action plan. It is not possible to do this with absolute precision, but using modeling, informed by monitoring results, a breakdown of sources affecting a particular receptor or location can be determined in rough percentage terms. Guttikunda S. et al., (2009) stated that there are currently two fundamental approaches to determine and quantify the impacts of air pollution sources.

2.17.1 Top-down or receptor-based source apportionment

The top-down approach begins by sampling air in a given area and inferring the likely pollution sources by matching common chemical and physical characteristics between source and air pollution samples. Top-down methods offer the promise of quantifying the relative contributions of the different sources to ambient air pollution, where rather little may be currently known. Additionally, top-down methods may require few atmospheric measurements and relatively simple analysis; simple of course is a relative term, as demonstrated in the coming sections. Ideally, the two approaches should agree, but this is rarely the case for an initial application and due to the scales of operation. However, proper analysis of the nature of the disagreement can result in improvements to both methods, and acceptable agreement is often achieved after several iterations10. This adds confidence to the selection of air pollution control strategies (Guttikunda S. et al., 2009).

The top-down approach results in

1. Identification of the hot spots with critical pollutant levels in the city or the region
2. Identification of the chemical composition of the particulate pollution, following the
3. chemical analysis of the measured samples
4. Description of the source impact estimates, following receptor modeling based on the
5. source profiles and statistical analysis
6. Differentiation of the primary and secondary pollution at the hot spots
7. Apportionment of the pollution by source

2.17.2 Bottom-up or source-based modeling

Bottom-up approach begins by identifying pollution sources and their emission strengths, which are converted to emissions (via emission factors by category) and then by utilizing meteorological patterns predicting pollution advection (movement) and compositions over time and space. Much is published under this approach to better understand the air pollution at urban, regional, and global levels (Guttikunda S. et al., 2009).

The bottom-up approach results in:

1. Identification of the potential sources - physically and quantitatively (energy and emission strengths) in the city or the region
2. Description of the physical and chemical processes with potential to impact the advection and chemistry of the pollutants, this includes the local topography and meteorological features
3. Documentation of the formation of the secondary pollutants, along with the primary (via emissions) such as sulfates, nitrates, ozone, hydrocarbons, etc.

4. A baseline mapping of the pollution and hot spots for the area of interest
5. Apportionment of the pollution by source

In a regulatory world, the top-down approach is more acceptable, primarily due to the involvement of direct pollution measurements at hot spots, analysis the samples in the lab, and determining (statistically) the contribution of various sources to the pollution at that particular spot. On the downside, the measurement points are few, due to the costs involved in monitoring and chemical analysis, which is (and can be) compensated by a comprehensive bottom-up approach to cover as many hot spots, and a better mapping of the pollution sources in the city.

2.18 SOURCE APPORTIONMENT METHODOLOGY

The flowchart of source apportionment is presented in Figure 2.1.

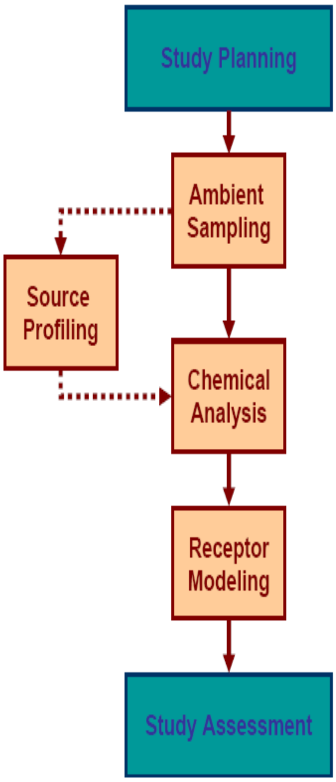


Figure 2.1 Flowchart of Source Apportionment

The four primary steps presented in Figure 2.1 are described below.

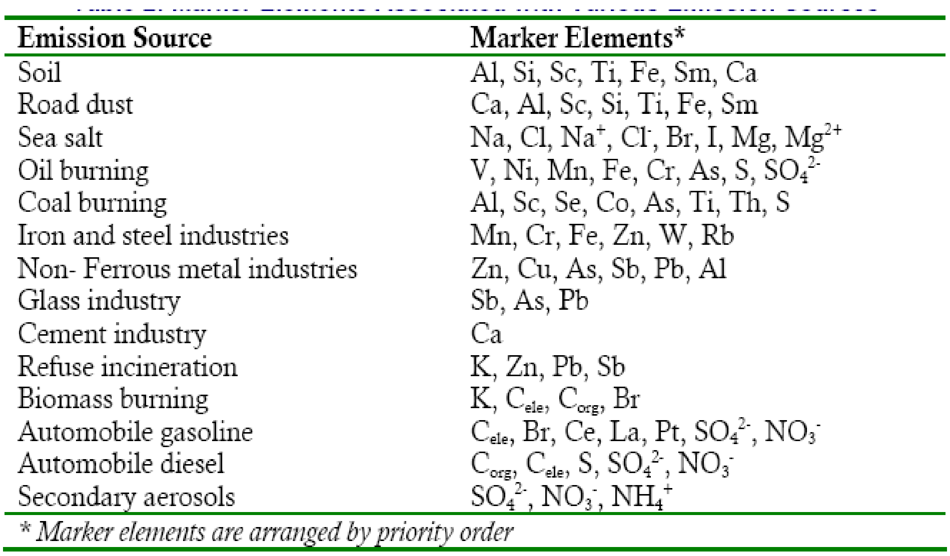
2.18.1 Ambient Sampling

Measurements provide fundamental information for evaluating and managing the impact of aerosols on air quality. Data obtained through measurements form the foundation of all approaches used to define and mitigate PM pollution. To provide the measurement data, variety of instruments have been developed and utilized for various purposes. A full understanding of sampling stations and analysis strategies is required before acceptable measurement techniques and approaches can be specified to meet PM measurements (Guttikunda S. et al., 2009).

2.18.2 Source Profiling

For quantitative purposes, source profiles must contain chemical abundances for a range of components that can be identified appreciably between source and receptor, and that are reasonably constant among different emitters of the same type and operating conditions (Guttikunda S. et al., 2009). Minor chemical components, constituting less than 1 percent of particle mass, are needed for quantitative apportionment as they are more likely to occur with patterns that allow differentiation among sources. Table 2.5 presents marker elements with their emission sources.

Table 2.5 Elements and their sources



Emission Source	Marker Elements*
Soil	Al, Si, Sc, Ti, Fe, Sm, Ca
Road dust	Ca, Al, Sc, Si, Ti, Fe, Sm
Sea salt	Na, Cl, Na^+, Cl^-, Br, I, Mg, Mg^{2+}
Oil burning	V, Ni, Mn, Fe, Cr, As, S, SO_4^{2-}
Coal burning	Al, Sc, Se, Co, As, Ti, Th, S
Iron and steel industries	Mn, Cr, Fe, Zn, W, Rb
Non- Ferrous metal industries	Zn, Cu, As, Sb, Pb, Al
Glass industry	Sb, As, Pb
Cement industry	Ca
Refuse incineration	K, Zn, Pb, Sb
Biomass burning	K, C_{ele}, C_{org}, Br
Automobile gasoline	C_{ele}, Br, Ce, La, Pt, SO_4^{2-}, NO_3^-
Automobile diesel	C_{org}, C_{ele}, S, SO_4^{2-}, NO_3^-
Secondary aerosols	SO_4^{2-}, NO_3^-, NH_4^+

** Marker elements are arranged by priority order*

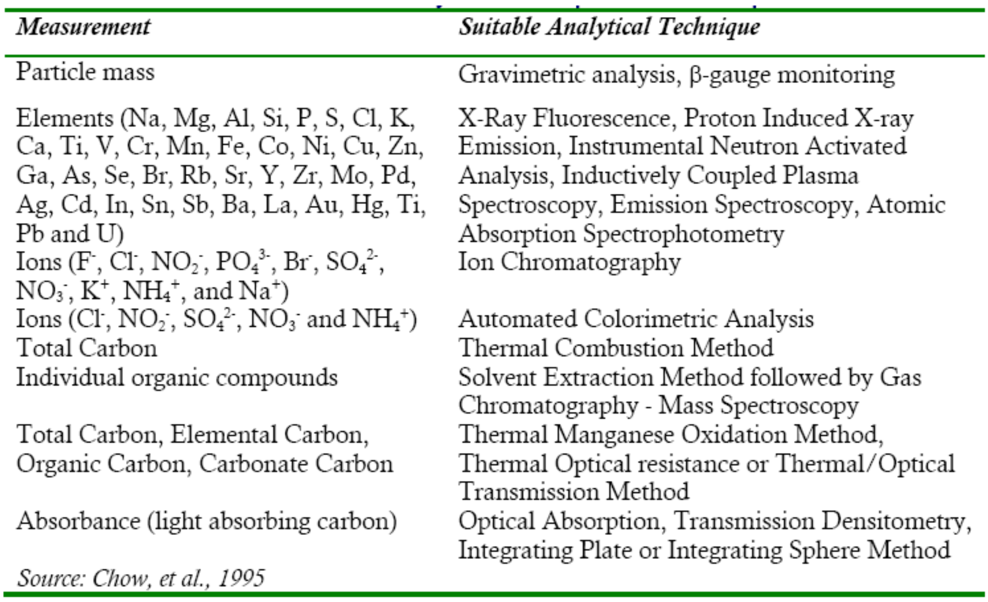
It is important that the source profiles are location specific because of local fuel characteristics and combustion technology. However, because of lack of institutional and financial resources, not all studies include this step of developing local source profiles. In most cases, the source apportionment studies utilize source profiles developed under similar urban characteristics (Guttikunda S. et al., 2009).

2.18.3 Chemical Analysis

The basic method of gravimetric analysis is straightforward - the net PM mass on a filter is determined by weighing the filter before and after sampling with a gravimetric balance in a temperature and relative humidity controlled environment, to remove liquid water while avoiding particle volatilization on the filters (Guttikunda S. et al., 2009).

Atomic Absorption Spectrophotometer is useful for identifying limited elements. The analytical technique is of destructive type, where the samples have to be digested or extracted with acid solutions. Several simple ions, such as sodium, magnesium, potassium, and calcium, are best quantified by this method. Table 2.6 presents analytical techniques useful for Particulate Matter analysis.

Table 2.6 Analytical techniques for PM analysis



Measurement	*Suitable Analytical Technique*
Particle mass	Gravimetric analysis, β-gauge monitoring
Elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Ti, Pb and U)	X-Ray Fluorescence, Proton Induced X-ray Emission, Instrumental Neutron Activated Analysis, Inductively Coupled Plasma Spectroscopy, Emission Spectroscopy, Atomic Absorption Spectrophotometry
Ions (F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, SO_4^{2-}, NO_3^-, K^+, NH_4^+, and Na^+)	Ion Chromatography
Ions (Cl^-, NO_2^-, SO_4^{2-}, NO_3^- and NH_4^+)	Automated Colorimetric Analysis
Total Carbon	Thermal Combustion Method
Individual organic compounds	Solvent Extraction Method followed by Gas Chromatography - Mass Spectroscopy
Total Carbon, Elemental Carbon, Organic Carbon, Carbonate Carbon	Thermal Manganese Oxidation Method, Thermal Optical resistance or Thermal/Optical Transmission Method
Absorbance (light absorbing carbon)	Optical Absorption, Transmission Densitometry, Integrating Plate or Integrating Sphere Method

Source: Chow, et al., 1995

2.18.4 Receptor Modeling

This step involves quantitative assessment of source contributions to the measured ambient samples based on the degree to which source profiles can be combined to reproduce ambient concentrations. The receptor model attributes primary particles to their source types and determines the chemical form of secondary aerosol when the appropriate chemical components have been measured (Reff, A.; Eberly, S.I.; Bhave, P.V. et al. 2007). Figure 2.6 shows general Receptor Modeling approach for source apportionment study. A, B, C, D and E in Figure 2.2 reflects the contribution of each trace elements in the source.

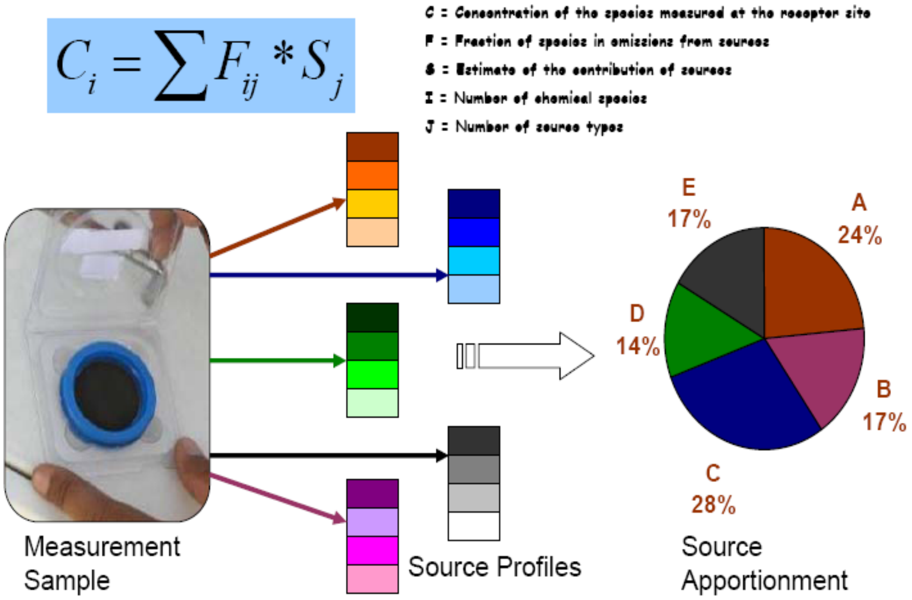


Figure 2.2 General Receptor Modeling

2.19 SOURCE APPORTIONMENT AND RECEPTOR MODELING

Hopke et al., (1985) and (1991); described receptor modeling as an application of multivariate statistical methods to the identification and quantitative apportionment of air pollutants to their sources and to develop a plan of effective air quality management.

Receptor models are focused on the behavior of the ambient environment at the point of impact, as opposed to the source-oriented dispersion models that focus on the transport, dilution and transformations that occur at the source and follow the pollutants to the sampling or receptor site.

The fundamental principle of receptor models is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne particulate matter in the atmosphere. This methodology has generally been referred to within the air pollution research community as receptor modeling (Hopke P. K. et al., 1985; Hopke P. K. et al., 1991). The approach to obtaining a data set for receptor modeling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples.

The receptor model includes Chemical Mass Balance (CMB), Factor Analysis (FA), time series and regression analyses. The CMB model requires knowledge about source profiles/source signatures. Therefore, the FA approach is suitable. Paatero and Tapper et al., (1994); stated that the FA approach includes the traditional Principal Component Analysis (PCA) and a new variant of FA, Positive Matrix Factorization (PMF), which is better suited to environmental applications than PCA. Unlike PCA, PMF utilizes the known (or estimated) errors of the data matrix and imposes non-negativity constraints on the resulting factors.

Receptor modeling approaches such as positive matrix factorization (PMF) are effective tools in source identification for aerosols on urban to regional scales (Bhanuprasad et al., 2008; Pekney et al., 2006). PMF studies typically analyze large data sets of several hundred samples spanning a few years of measurements containing 25–30 chemical species to resolve emission source categories on temporal scales of weeks to seasons. As such large data sets are not available yet in the Indian region, recently, PMF was used to resolve a smaller number (six) of source categories using a relatively small data set in e.g. 23 species in 27 samples. The uncertainty in PMF predictions of factor contributions (based on the relative standard deviation of species with high signal to noise ratio) was satisfactory (5–6%), giving confidence in the application of PMF to smaller data sets towards an understanding of regional scale source–receptor relationships in India.

Positive Matrix Factorization (PMF) is a development in the class of data analysis techniques called Factor Analysis, where the fundamental problem is to resolve the identities and contributions of components in an unknown mixture. PMF has been used as a source apportionment tool in many air quality studies (Kim and Hopke et al., 2004). PMF results have been coupled with surface wind direction data to provide identification of the locations of local emission sources affecting a receptor site (Lee et al., 2006; Pekney et al., 2006).

2.20 US EPA POSITIVE MATRIX FACTORIZATION (PMF) MODEL

Receptor models provide scientific support for current ambient air quality standards and for implementation of those standards by identifying and quantifying contributions for source apportionment. Ambient air quality data sets have been improving greatly due to more species being measured, species being stratified by particle size, and shorter durations of sampling. Receptor model algorithms have also improved greatly to take advantage of these higher quality data sets (Paatero and Tapper et al., 1994)..

To ensure that receptor modeling tools are available for use in the development and implementation of air quality standards, the United States Environmental Protection Agency's Office of Research and Development (ORD) has and continues to develop a suite of receptor modeling tools that are freely distributed to the air quality management community (Paatero and Tapper et al., 1994).

EPA PMF is one of the receptor models that ORD has developed. The user provides a file of sample species concentrations and uncertainties which the model uses to calculate the number of sources types, profiles, relative contributions, and a time series of contributions. The algorithms used in EPA PMF model to compute profiles and contributions have been peer reviewed by leading scientists in the air quality management community and have been certified to be scientifically robust (Paatero and Tapper et al., 1994)..

The PMF 3.0 Fundamentals & User Guide provides details on how PMF is implemented as well as references. EPA PMF software program is a stand-alone product, meaning that it requires no other software and is self-contained. There is no need for a license and the program is available free of charge. The software is menu-driven, using Graphical User Interfaces, and therefore eases inputting of data, generating, evaluating, and exporting of results.

Positive Matrix Factorization (PMF) is a recent type of receptor model, developed by Dr. Pentti Paatero (Department of Physics, University of Helsinki) in the middle of the 1990s, in order to develop a new method for the analysis of multivariate data that resolved some limitations of the PCA.

According to Paatero and Tapper et al., (1994); Paatero et al., (1997), Positive Matrix Factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices—factor contributions and factor profiles—which then need to be interpreted by an analyst as to what source types are represented using measured source profile information, wind direction analysis, and emission inventories. A speciated data set can be viewed as a data matrix X of i by j dimensions, in which i (number of samples) and j (chemical species) were measured. The goal of multivariate receptor modeling is to identify a number of factors p, the species profile f of each source, and the amount of mass g contributed by each factor to each individual sample.

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

Where eij is the residual for each sample/species.

Results are constrained so that no sample can have a negative source contribution. PMF allows each data point to be individually weighed. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. For example, data below detection can be retained for use in the model, with the associated uncertainty adjusted so these data points have less influence on the solution than measurements above the detection limit. The PMF solution minimizes the object function Q based upon these uncertainties (u).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2$$

Variability in the PMF solution can be estimated using a bootstrapping technique, which is a re-sampling method in which “new” data sets are generated that are consistent with the original data. Each data set is decomposed into profile and contribution matrices, and the resulting profile and contribution matrices are compared with the base run. Instead of inspecting point estimates, this method allows the analyst to review the distribution for each species to evaluate the stability of the solution.

2.21 COMPARISON TO OTHER METHODS

Other source apportionment models include Unmix and chemical mass balance (CMB). Although both methods have aims similar to that of PMF, they have different mechanisms. Unmix uses geometrical objects called the “edges” to identify factors (Pekney et al., 2006; Poirot et al., 2001). An edge is identified in the hyperspace of species concentrations where the factor contribution from at least one factor is either zero or present in negligible amounts along the edge. Unmix does not allow individual weighting of data points as does PMF (Pekney et al., 2006; Poirot et al., 2001).

Although major factors resolved by PMF and Unmix are generally the same, Pekney et al., (2006) found out that Unmix does not always resolve as many factors as PMF. With CMB, the user must provide source profiles which the model uses to apportion mass. PMF and CMB have been compared in several studies; Rizzo and Scheff et al., (2007); compared the magnitude of source contributions resolved by each model and examined correlations between PMF and CMB resolved contributions. They found the major factors correlated well and were similar in magnitude; additionally, the PMF-resolved source profiles were generally similar to measured source profiles. In supplementary work, Rizzo and Scheff et al., (2007) used information from CMB PM Source profiles to influence PMF results and used CMB results to help control rotations in PMF. Good correlations were found for most factors, with some biases present in a few of the factors. They also found an additional PMF factor that did not correspond to any CMB factors (Pekney et al., 2006; Poirot et al., 2001).

2.22 USES OF US EPA PMF

PMF has been applied to a wide range of data, including 24-hr speciated $PM_{2.5}$, size-resolved aerosol, deposition, air toxics, and volatile organic compound (VOC) data. A more complete discussion of uses of PMF is available in the "Multivariate Receptor Modeling Workbook" (2007). PMF requires a data set consisting of a suite of parameters measured across multiple samples. For example, PMF is often used on speciated $PM_{2.5}$ data sets with over 100 samples. An uncertainty data set, that assigns an uncertainty value to each species and sample, is also needed.

One of the main positive aspects is the use of know experimental uncertainties as input data which allow individual treatment of matrix elements. This becomes increasingly important with the introduction of the Guide for Expression of Measurements (GUM) and the derived Guide for Quantification of Analytical Measurements (QUAM), which is nowadays commonly accepted references underlying numerous national and international standards.

At the beginning, PMF has been used in air pollution and source apportionment studies (Polissar et al., 2001; Lee et al., 1999) and in precipitation study (Paatero et al., 1994; Anttila et al., 1994). Also recently, applications on air quality and source apportionment (Xie and Berkowitz, 2007; Begum et al., 2006) have been carried out. In addition, in the latest years, PMF has been applied to lakes sediments, wastewater and soils.

As mentioned above, Positive Matrix Factorization differs from the customary factor analysis models such as PCA by the property to take into account standard deviations of observed data values and to introduce the constraint of non negativity of all the factor matrices G and F elements in order to have physically meaningful solutions. It is thus a weighted least square problem in which a certain number of factors have to be determined in order to minimize an ‘object function’. The input data are a multivariate data set containing the measured data and the corresponding uncertainties data matrix.

One of the main features of PMF results is their quantitative nature: it is possible to obtain the composition of the sources determined by the model. In contrast, Paatero et al., (2004) showed the results of PCA are qualitative as they can only distinguish variables that tend to appear together from those ones that do not. Moreover, in contrast to customary factor analysis models, PMF model has been implemented to handle non representative data such as “below detection limit”, missing data and outliers. This is an important property as it prevents the rejection of such values and hence the reduction of the initial data set. These and other positive aspects are detailed described in the following section.

Different approaches to resolve PMF algorithm have been studied, both for usual 2- dimensional matrices and 3-way arrays. The firsts programs developed by Paatero et al., (2004a); Paatero et al., (2004b); are called respectively PMF2 and PMF3 and later on the algorithm has been extended to arbitrary multilinear models by means of the program Multilinear Engine (ME). In the latest years other resolving techniques have been developed, starting from Paatero’s PMF equations, like a new PMF formulation. Moreover, given the importance of receptor models in scientific research, the United States Environmental Protection Agency (US-EPA) has developed a standalone version of PMF, EPA PMF 3.0, freely distributed. EPA PMF 3.0 is based on ME-2 (ME second version; Paatero, 2007).

To have a clear distinction between PMF as a model and the name of the programs, the model is designated as PMF while the programs used to solve the model are designated PMF2, PMF3 and ME-2.

2.23 SOURCE APPORTIONMENT STUDIES

Inhalable particulate measurements from 1984 to 1994 at Edmonton and Calgary reveal similar physical and chemical properties which are comparable to other Canadian prairie cities. Because of geographical and emission-source differences, particulate measurements in these two Alberta cities exhibit characteristics significantly different from those obtained in eastern North American cities. While median PM_{10} concentration is about 25 $\mu g/m^3$, which is approximately 63% of the total suspended particulates (TSP), $PM_{2.5}$ concentration is about 40% of that of PM_{10}. Over the 10 years there was a decreasing trend in both size fractions. $PM_{2.5}$ shows a similar seasonal pattern in Edmonton and Calgary, with a slightly higher concentration in winter; whereas coarse particles are generally higher in spring at Edmonton and in winter at Calgary. Relationships were established from co-located measurements of Dust and Smoke index (in Coefficient of Haze, COH, units) and PM_{10} concentration with a correlation coefficient of 0.51, and TSP and PM_{10} concentrations with a correlation coefficient of 0.93. Sulphate is the highest explainable mass fraction in fine particles, while minerals contribute most to the coarse particles. About 80% of the total sulphur mass is within the fine particle fraction. Seasonal variations within individual chemical components are relatively less than that among chemical components. Particles of different sizes originate from distinct source sectors. Seasonal variations in source contribution are detected, particularly for mineral soil and road salt.

The distribution of air particulate mass and selected particle components (trace elements and polycyclic aromatic hydrocarbons (PAHs)) in the fine and the coarse size fractions was investigated at a traffic-impacted urban site in Thessaloniki, Greece. 76±6% on average of the total ambient aerosol mass was distributed in the line size fraction. A significant seasonal effect was observed for the size distribution of aerosol mass, with a shift to larger fine fractions in winter. Similar seasonal trend was exhibited by PAHs, whereas larger fine fractions in summer were shown by trace elements. The compositional signatures of fine and coarse particle fractions were compared to that of local paved-road dust. A strong correlation was found between coarse particles and road dust suggesting strong contribution of resuspended road dust to the coarse particles. A multivariate receptor model (multiple regression on absolute principal component scores) was applied on separate fine and coarse aerosol data for source identification and apportionment. Results demonstrated that the largest contribution to fine-sized aerosol is traffic (38%) followed by road dust (28%), while road dust clearly dominated the coarse size fraction (57%) (Manoli, E. et al., 2002).

Aerosol samples for $PM_{2.5}$ (particulate matter with aerodynamic diameters less than 2.5 μm), $PM_{2.5–10}$ (particulate matter with aerodynamic diameters between 2.5 and 10 μm) and TSP were collected from June to September 1998 at THU (suburban) and HKIT (rural) sites in central Taiwan. The ratios of $PM_{2.5}/PM_{10}$ averaged 0.70 for the daytime and 0.63 for the nighttime at THU, respectively. At HKIT, the $PM_{2.5}/PM_{10}$ ratios averaged 0.56 for the daytime and 0.72 in the nighttime, respectively. These results indicated that the $PM_{2.5}$ concentrations contribute the majority of the PM_{10} concentration and PM_{10} concentrations contribute the majority of the TSP at both sites. The averaged $PM_{2.5}$ concentrations at THU are higher than those measured at HKIT during the daytime period. However, the average $PM_{2.5–10}$ concentrations in THU are lower than those measured at HKIT during nighttime. The samples collected were also analyzed by atomic absorption spectrophotometry for the elemental analysis of Ca, Fe, Pb, Zn, Cu, Mn and Cr. Meanwhile ion chromatography was used to analyze for the water-soluble ions: sulphate, nitrate and chloride in the Universal samples. The concentrations of heavy metals in PM_{10} during daytime were all higher than nighttime at THU. However, the averaged concentrations of metal elements in PM_{10} during day and night period were distributed irregularly at HKIT. The results indicated that for metal elements collected at HKIT have different emission sources. The concentrations of metal elements during daytime in PM_{10} at THU were generally higher than HKIT. The phenomena owing to the averaged $PM_{2.5}$ particle concentrations at THU (suburban) were higher than those measured at HKIT (rural) and $PM_{2.5}$ occupied the major portions of PM_{10} for both sites during the day period. For anion species, there are no significant differences between day and night period in PM_{10} concentrations at both suburban and rural sites (GC Fang et al., 1999).

Aerosol samples within an industrial region of Bombay were analyzed for elemental concentrations using inductively coupled plasma emission spectroscopy, ultraviolet/visible spectrophotometry and X-ray fluorescence spectroscopy. Nineteen elements were selected as tracers of identified sources of aerosol in the region. The U.S. EPA chemical mass balance model was employed for source apportionment.

Seven major source types were identified and the performance of the model was evaluated at different sampling locations. Model results were unsatisfactory at highly polluted sites in the study regions. It was found that U.S. EPA source profiles are not suitable for such regions in India and site-specific source profiles should be used in the application of chemical mass balance for source apportionment (VK Sharma et al., 1994).

During 2001–2006, $PM_{2.5}$ (particle matter with aerodynamic diameter less than 2.5 microns) and PM_{10} (particle matter with aerodynamic diameter less than 10 microns) were collected at the Beijng Normal University (BNU) site, China, and in 2006, at a background site in Duolun (DL). The long-term monitoring data of elements, ions, and black carbon showed that the major constituents of $PM_{2.5}$ were black carbon (BC) crustal elements, nitrates, ammonium salts, and sulfates. These five major components accounted for 20%–80% of the total $PM_{2.5}$. During this period, levels of Pb and S in PM remained rather high, as compared with the levels in other large cities in the world. Source apportionment results suggest that there were 6 common sources for $PM_{2.5}$ and PM_{10}, i.e., soil dust, vehicular emission, coal combustion, secondary aerosol, industrial emission, and biomass burning. Coal combustion was the largest contributor of $PM_{2.5}$ with a percentage of 16.6%, whereas soil dust played the most important role in PM_{10} with a percentage of 27%. In contrast, only three common types of sources could be resolved at the background DL site, namely, soil dust, biomass combustion, and secondary aerosol from combustion sources (Wang et. al, 2008).

Organic aerosol (OA) dataset were analyzed from an Aerodyne Aerosol Mass Spectrometer (Q-AMS) collected at the Pittsburgh Air Quality Study (PAQS) in September 2002 with Positive Matrix Factorization (PMF). Three components – hydrocarbon-like organic aerosol OA (HOA), a highly-oxygenated OA (OOA-1) that correlates well with sulfate, and a less-oxygenated, semi-volatile OA (OOA-2) that correlates well with nitrate and chloride – are identified and interpreted as primary combustion emissions, aged SOA, and semivolatile, less aged SOA, respectively. The complexityof interpreting the PMF solutions of unit mass resolution(UMR) AMS data is illustrated by a detailed analysis of the solutions as a function of number of components and rotational forcing. A public web-based database of AMS spectra has been created to aid this type of analysis. Realistic synthetic data is also used to characterize the behavior of PMF for choosing the best number of factors, and evaluating the rotations of non-unique solutions. The ambient and synthetic data indicate that the variation of the PMF quality of fit parameter (Q, a normalized chi-squared metric) vs. number of factors in the solution is useful to identify the minimum number of factors, but more detailed analysis and interpretation are needed to choose the best number of factors. The maximum value of the rotational matrix is not useful for determining the best number of factors. In synthetic datasets, factors are “split” into two or more components when solving for more factors than were used in the input. Elements of the “splitting” behavior are observed in solutions of realdatasets with several factors. Significant structure remains in the residual of the real dataset after physically-meaningful factors have been assigned and an unrealistic number of factors would be required to explain the remaining variance. This residual structure appears to be due to variability in the spectra of the components (especially OOA-2 in this case), which is likely to be a key limit of the retrievability of components from AMS datasets using PMF and similar methods that need to assume constant component mass spectra. Methods for characterizing and dealing with this variability are needed. Interpretation of PMF factors must be done carefully. Synthetic data indicate that PMF internal diagnostics and similarity to available source component spectra together are not sufficient for identifying factors. It is critical to use correlations between factor and external measurement time series and other criteria to support factor interpretations.True components with <5% of the mass are unlikely to be retrieved accurately. Results from this study may be useful for interpreting the PMF analysis of data from other aerosol mass spectrometers. Researchers are urged to analyze future datasets carefully, including synthetic analyses, and to evaluate whether the conclusions made here apply to their datasets (Ulbrich I et. al, 2009).

Size- and time-resolved aerosol samples collected using an eight-stage DRUM sampler from 29 March to 29 May in 2002 at Gosan, Jeju Island, Korea, which is one of the representative background sites in East Asia. These samples were analyzed 5 using synchrotron X-ray fluorescence for 3-h average concentrations of 19 elements consisting of S, Si, Al, Fe, Ca, Cl, Cu, Zn, Ti, K, Mn, Pb, Ni, V, Se, As, Rb, Cr, Br. The size-resolved data sets were then analyzed using the positive matrix factorization (PMF) technique in order to identify possible sources and estimate their contribution to particulate matter mass. PMF analysis uses the uncertainty of the measured data 10 to provide an optimal weighting. Fifteen sources were resolved in eight size ranges (0.07–12 μm) and included Chinese aerosol, soil dust, sea salt, biomass burning, coal combustion, oil heating furnace, residual oil-fired boiler, municipal incineration, nonferrous metal source, ferrous metal source, gasoline vehicle, diesel vehicle, copper smelter, and volcano emission. PMF analysis of size-resolved source contributions 15 showed that natural sources represented by soil dust, sea salt and Chinese aerosol contributed about 79% to the predicted primary PM mass in the coarse size range (1.15–12 μm). On the other hand, anthropogenic sources such as coal combustion and biomass burning contributed about 60% in the fine size range (0.56–2.5 μm). The diesel vehicle source contributed the most in the ultra-fine size range (0.07–0.56 μm) 20 and was responsible for about 52% of the primary PM mass (Han J. et. al, 2008).

Secondary organic carbon (SOC) is often a significant portion of organic carbon (OC) in ambient particulate matter (PM). The levels and seasonal patterns of SOC in Hong Kong were examined using more than 2000 PM_{10} measurements made over a 4.5-year period 5 (1998–2002) in a network of ten air quality monitoring stations. The positive matrix factorization (PMF) model was used to analyze this large data set for source identification and apportioning. SOC was subsequently estimated to be the sum of OC present in the secondary sources, i.e., secondary sulfate, secondary nitrate, and secondary organic aerosol. The annual average SOC as estimated by the PMF method 10 was 4.25 μgC/m3 while the summer average was 1.66 μgC/m3 and the winter average was 7.05 μg C/m3. In comparison, the method that uses EC as a tracer for primary carbonaceous aerosol sources to derive SOC overestimated SOC by 70–212% for the summer samples and by 4–43% for the winter samples. The overestimation by the EC tracer method resulted from the inability of obtaining a single OC/EC ratio that 15 represented a mixture of primary sources varying in time and space. They found that SOC and secondary sulfate had synchronous seasonal variation and were correlated in individual seasons, suggesting common factors that control their formation. Considering the well-established fact that both gas phase oxidation and in-cloud processing are important formation pathways for sulfate, the synchronicity of SOC and sulfate suggests that in-cloud pathways are also important for SOC formation. Additionally, the presence of SOC was found to be enhanced more than that of secondary sulfate in the winter. they postulate this to be a combined result of favorable partitioning of semivolatile SOC species in the particle phase and more abundant SOC precursors in the winter (Yuan Z. et. al, 2006).

Source apportionment of total suspended particulate matter (TSPM) and associated heavy metals for the city of Delhi were calculated using the Chemical Mass Balance Model, Version 8 (CMB8), as well as principle component analysis (PCA) of SPSS (Varimax Rotated Factor Matrix method) in coarse- and fine-size mode. Urban particles were collected using a five-stage impactor at six sites in the winter of 2005-06. The impactor segregates the TSPM into five different size ranges (viz. > 10.9, 10.9–5.4, 5.4–1.6, 1.6–0.7 and < 0.7 μm). Four samples were collected from six different sites every 24 hours. Samples were analyzed in five size ranges gravimetrically and chemically for the estimation of SPM and metals. The five different size ranges were divided into two broad categories: coarse (1.6 to > 10.9 μm) and fine (< 1.6 μm). The CMB8 and PCA were executed separately for both coarse and fine size ranges. Results obtained by CMB8 indicate the dominance of vehicular pollutants (62%), followed by crustal dust (35%) in the fine size range; while in the coarse size range crustal dust dominated (64%) over vehicular pollution (29%). Little contribution from paved-road dust and industrial sources was observed. Results of PCA (or factor analysis) reveal two major sources (vehicular and crustal re-suspension) in both coarse and fine size ranges. The correlations of factors (sources) with the metals show that in the coarse size range the dominant source is crustal re-suspension (68%) followed by vehicular pollution (23%). However, this is reversed in the case of the fine size range factor analysis where vehicular pollution (86%) dominated over crustal re-suspension (10%) (Srivastava et al., 2008)

The coarse (2.5-10μm) and fine (< 2.5 μm) fractions of airborne particles were sampled during winter 2000 and 2001 in Auckland and Christchurch, New Zealand.

Sampling was carried out using a versatile air pollution sampler (VAPS) and particle analyses for elemental concentrations utilized proton induced x-ray emission (PIXE) and light reflection/transmission techniques. Emission source identification was by principal component factor analysis (PCFA) with Varimax rotation while the source apportionment used the absolute principal component analysis (APCA) receptor modeling method. The major emission sources identified were classified as sea spray (SS), suspended soil and road dust (SO & RD), domestic emissions (DE), and vehicle emissions (VE, diesel and petrol). In Auckland, source apportionment to SS, SO & RD, DE, and VE emissions averaged 22, 42, 14 and 22 % respectively. The corresponding averages for Christchurch were 23, 29, 25, and 23 %. The colder Christchurch climate corresponded with nearly twice the DE contribution of Auckland. Containing a significant contribution from vehicles, SO & RD made the highest contribution in both cities. In Auckland, as expected, road transport was considered the dominant source of PM_{10}. Contrary to strong local perception, this is the first report to suggest that Christchurch's PM_{10} has a significant contribution from road transport during winter (Senaratne et al., 2005).

Air pollution associated with atmospheric fine particulate matter ($PM_{2.5}$, i.e., particles with an aerodynamic diameter of 2.5 mm or less) were studied in Beijing, China. To provide a better understanding of the sources contributing to $PM_{2.5}$, 24-h samples were collected at 6-day intervals in January, April, July, and October in 2000 at five locations in the Beijing metropolitan area. Both backward trajectory and elemental analyses identified two dust storm events; the distinctly low value of Ca:Si (o0.2) and high Al:Ca (41.7) in Beijing $PM_{2.5}$ appear indicative of contributions from dust storms. Positive matrix factorization (PMF) was used to apportion sources of $PM_{2.5}$, and eight sources were identified: biomass burning (11%), secondary sulfates (17%), secondary nitrates (14%), coal combustion (19%), industry (6%), motor vehicles (6%), road dust (9%), and yellow dust. The lower organic carbon (OC), elemental carbon (EC), SO4 2_, and Ca values of yellow dust enable it to be distinguished from road dust. The PMF method resolved 82% of $PM_{2.5}$ mass concentrations and showed excellent agreement with a previous calculation using organic tracers in a chemical mass balance (CMB) model. The present study is the first reported comparison between a PMF source apportionment model and a molecular marker-based CMB in Beijing (Songa Y. et. al, 2005).

$PM_{2.5}$ samples collected at a centrally located urban monitoring site in Seoul, Korea, every third day from March 2003 to December 2006 and analyzed for their chemical constituents. Sources were identified using positive matrix factorization (PMF). A total of 393 samples were obtained during the sampling period, and 20 chemical species were measured. Nine PM2.5 source categories were identified providing physically realistic profiles and interesting insights into the source contributions to the ambient mass concentrations. The major contributors of PM2.5 were secondary nitrate (20.9%), secondary sulfate (20.5%), gasoline-fueled vehicles (17.2%), and biomass burning (12.1%), with lesser contributions from diesel emissions (8.1%), soil (7.4%), industry (6.7%), road salt and two-stroke vehicles (5.1%), and aged sea salt (2.2%). $PM_{2.5}$ levels in Seoul were influenced by both local urban activities and regional-scale transport. Conditional probability function (CPF) results identified possible source directions of local sources such as motor vehicles (gasoline and diesel), industry, and road salt. Potential source contribution function (PSCF) results showed that possible source areas contributing to the elevated secondary particle concentrations (sulfate and nitrate) in Seoul to be the major industrial areas in China (Heo J. et. al, 2009).

2.24 KOLHAPUR CITY, MAHARASHTRA

Kolhapur city is located in south-western Maharashtra at 16°42′N 74°13′E. It has an average elevation of 545 meters (1788 ft). The geographical area of the district is 7685 Km^2. Kolhapur is situated on the banks of river Panchganga. The population of Kolhapur city was 493,167, as per the 2001 census. According to Environmental Status Report, 2008, the current population of Kolhapur is about 6 Lakh people. The population density of the district is 457 persons per square kilometers. The urban density is 1804 and the rural density is 327 (Sathe et al., 2012).

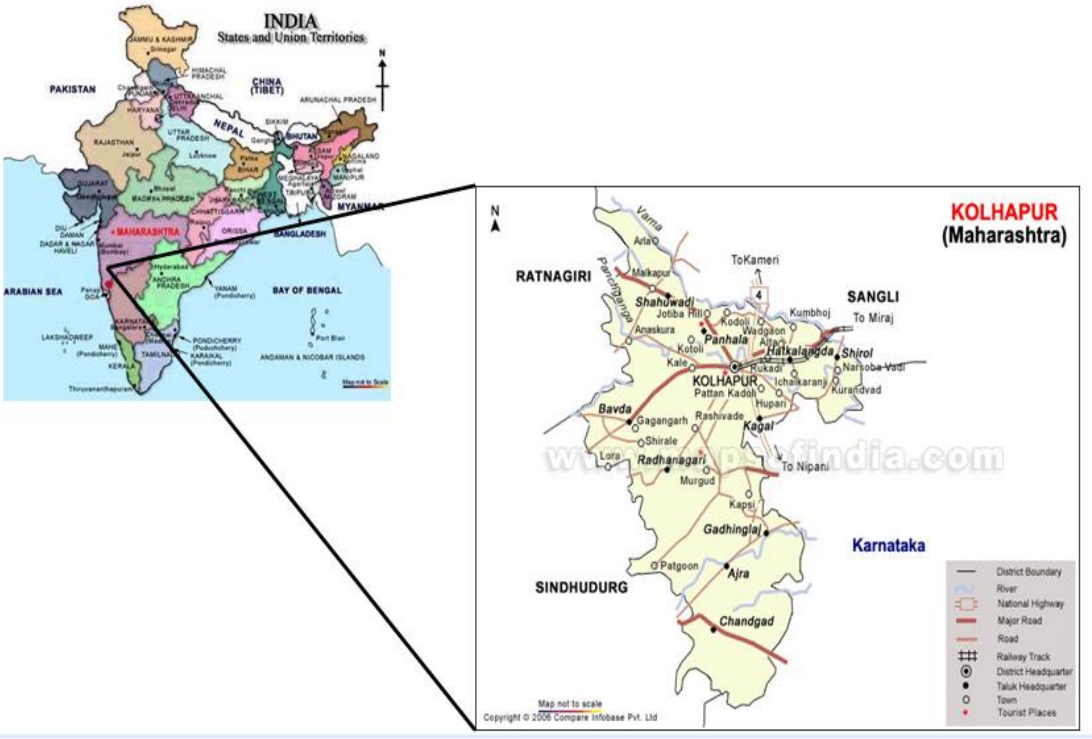


Figure 2.3 Kolhapur City, Maharashtra

Kolhapur is an important city in Maharashtra and is known as Dakshin Kashi from ancient time. It is a famous religious place due to Mahalaxmi & Jotiba temples. It has a great historical importance as many dynasties had Kolhapur as their capital. Due to social developments of Chh. Shahu Maharaja, Kolhapur created an ideal in India. From tourism point of view Kolhapur assumes a special significance as there are many tourist places like Panhala fort, Dajipur sanctuary, Rankala Lake Etc. Every year many devotees and tourists visit Kolhapur. As per KOLHAPUR DISTRICT TOURISM PLAN 2012, Kolhapur is situated on the banks of Panchganga River. It is main city connecting Konkan, Karnataka & Goa with rest of Maharashtra. The land in Kolhapur region is fertile with ample water supply and cash crops like sugar cane & tobacco are grown here. The jaggery, chappal & Kolhapur saj are famous in India .

Kolhapur is known for Art, Education, Industry, Sports specially wrestling. There is Shivaji University in Kolhapur and all colleges from south Maharashtra are affiliated to it. There are two industrial estates at Shiroli & Gokul Shirgaon near Kolhapur and the city is world famous in foundry industry. In the modern development of Kolhapur city many new development projects are under way and Kolhapur Municipal Corporation has provided many facilities & subsidies to IT industry. Hence Kolhapur will attain new peaks of progress in all fields within a short time. Kolhapur has been second highest per capita income city in India, having the maximum amount of sugar factories, Mercedes cars, spinning mills, education centre. Kolhapur is also known for its leather footwear. An International Go carting Track, Resorts/Amusement Park, Multiplexes, recently started mall Big bazaar, starting soon Reliance mall.

Kolhapur city is located on the express highway connected with short travel time of major cities like Pune, Bangalore and Bombay. The Kolhapur airport is being revamped. It now has refueling and night landing facilities, with the expansion plan an increased airstrip for Boeing Air bus.

The city is rising as a new Important IT destination. All major banks have seen the potential growth of Kolhapur; Recently Deustche bank started a Branch in Kolhapur. Kagal 5 star MIDC can proudly posses a investment of 5500 crores with a textile SEZ set up in the adjoining MIDC. The foundry cluster is around the corner. Kolhapur Corporation has been sanctioned over 230 crores for infrastructure by the centre. It will have 50 to 60 kms of 4 lane roads.

Education has always been in the forefront with 2 international schools functioning. National and International big Giants in IT have signed MOU's with Shivaji university and other institutes.

Highlights of Kolhapur city

1. Second highest per capita income in the country is the crown of Kolhapur.
2. Partly edge of agro industry and modern enterprise has made this city very prosperous.
3. Full fledged three industrial estates.
4. Total 19 cooperative sugar mills are functioning very well.

5. Speedy emerging of it industry is new hope for international access.
6. Few hours journey are enough to approach metro places like Goa, Pune and Mumbai.
7. Kolhapur has a great political importance in national level politics. Nurtured artistic and sporty background has garlanded this city with many international awards.
8. Weekend of this city welcomes foreign tourists visiting Kolhapur by Royal Deccan odyssey train.

Thus, Kolhapur is now ready to deal with National as well as International issues in terms of business, social and cultural activities.

2.24.1 Climate in Kolhapur

Kolhapur's climate is a blend of coastal and inland climate of Maharashtra. The temperature has a relatively narrow range between 12°C to 38°C. Summer in Kolhapur is comparatively cooler, but much more humid, compared to neighboring inland cities. Maximum temperatures rarely exceed 40°C and typically range between 33 to 35°C. Lows during summer season are around 24°C to 26°C. Though temperatures are rarely as high as in inland Maharashtra, high humidity often makes the weather muggy and unpleasant.

The city receives abundant rainfall from June to September due to its proximity to the Western Ghats. The heavy rains often lead to severe flooding in these months. Temperatures are low in the rainy season and range between 23°C to 30°C.

Kolhapur experiences winter from November to February. The winter temperatures are significantly higher compared to other cities in Maharashtra such as Pune and Nasik. Lows range from 12°C to 16°C while highs are in the range of 29°C to 32°C. Humidity is low in this season making weather much more pleasant. In 2005 & 2006 there was excessive rainfall in Kolhapur resulting in floods.

2.24.2 Automobiles in Kolhapur

Kolhapur city has a network of 586.59 km roads of different width. Most of the roads are tar roads. Only few roads are WBM type. Few small passages are paved with concrete. After formation of Kolhapur Municipal Corporation, Municipality limit was increased by 66.82 km. However, the developmental activities, such as road broadening, new road construction, widening of narrow roads, alternate ring roads surrounding city for heavy vehicles to eliminate their extra load on city traffic, are long overdue. Major roads like station road, Rankala stand road, Tarabai park road, Mahadwar road, Laxmi puri road, Rajarampuri main lane, Sambhaji nagar road, etc. are the bottle neck points for traffic congestion. Today there are 107 km long roads in the city but all are without side lane or footpath. The pedestrians have to face great difficulties while walking on these roads. The growth of vehicles in Kolhapur city has assumed an extraordinary proportion. The number of two wheelers has increased from 1, 57, 090 numbers in the year 2006 to 1, 81, 600 in the year 2007. There is also a significant increase in the registration of motor cars, suggesting problems of traffic congestion, parking and pollution. Total number of vehicles registered in the year 2008 is 2,37,492 which is a very high number. In addition to the registered vehicles, number of vehicles belonging to floating population adds to the problem. As per Motor Transport Statistics of Maharashtra, 2010 on 31st March 2010, the registred vehicles in RTO, Kolhapur are 6,35,709.

Emission from an individual car, bike or heavy motor vehicle is generally low, but addition of 2,37,492 new vehicles every year increases the intensity of vehicular pollution day by day. Cars, trucks and buses emit significant quantities of carbon monoxide, hydrocarbons, nitrogen oxides, fine particles and lead. The pollutants impair health, destroy vegetation and reduce the general quality of life. Due to tremendous increase of the vehicles in Kolhapur city it is now essential to implement control measures for mitigating the vehicular emissions and their impacts on the environment.

2.24.3 Industries at Kolhapur

The city has become industrialized, due to the proximity of bauxite deposits. There are two main industrial areas, Gokul Shirgaon and Shiroli. These mainly produce such products as aluminum castings, alloys, and bearings. The Shivaji Udyamnagar area is famous for electrical and other metal fabrication workshops which are situated at centre of the city. The Shahu Textile Mill is also located inside the city. The Kagal-Hatkanangale industrial area namely 5-star MIDC is situated 12 km from Kolhapur city and contains lots of very big budget companies.

The industrial area is located 3 km from the National Highway 4 (Mumbai-Bangalore). The other major industrial areas: Shiroli, Udyamnagar in Kolhapur and Gokul-shirgaon are just 12 km and 15 km respectively from Kolhapur City. Kolhapur has three main industrial corporations (MIDC) outside the city namely Shiroli, Gokul Shirgaon and five star MIDC at Kagal. Kolhapur is not only famous as a tourist place but also it is one of the most important places for foundry businesses. Most of the foundries are in the sand casting. Castings manufactured in Kolhapur are recognized globally for their accuracy and finish.Mechanical industries in Kolhapur are the major suppliers to the OEM customers like Tata,Bajaj,Mahindra and Mahindra,General Motors etc. Popular Steels is globally famous for its agricultural equipments. Large scale companies include

1. Kirloskar Oil Engines Ltd
2. Manugraph India Ltd
3. Menon Group of Companies
4. Raymond Textiles

Although there are not many big companies in Kolhapur, it is said that in future this city may be the next destination for the investment by major IT companies after Pune in Maharashtra due to its direct close proximity to the metropolitan cities namely Pune, Mumbai and Bangalore by National Highway 4.

2.24.4 Industrial Areas of MIDC

The Kolhapur industry mainly comprises sugar industries, textile mills, engineering units and foundry units. The industry lacks entrepreneurial capacity. This reflects a need for private initiation and a new entrepreneurial vision. There are nine industrial estates in Kolhapur -- two Maharashtra Industrial Development Cooperation (MIDC) areas and seven cooperative industrial estates. Altogether, 1,207 units function in the two existing MIDC areas. The Kagal 5 star industrial estate comprising 3000 plots, spread over 1100 hectares has been established near Kolhapur. Industries located in around 300 to 400 plots are functioning currently. Besides, a textile zone in an area of 450 acres has also been proposed. Companies like Raymond, Indocomm, Oswal Wardhman and Kirloskar have shown a keen interest in this zone; some of them have already initiated the process of setting up their plants. Also, a silver zone in an area of 80 hectares has been proposed. In the Phase 1 and Phase 2 of the development of the Kagal industrial estate, engineering and foundry industries such as Anshul steel and Menon Casting are proposed.

As far as basic infrastructure of the estate is concerned, water supply is sufficient. MIDC and MSEB are in the process of ensuring power distribution of 100 MW to this estate. The development of roads and storm water drainage is underway. Also, a Common Effluent Treatment Plant (CETP) of 10 MLD will be started in the next six months to treat the industrial effluent. For the infrastructure development of Kagal, MIDC has already spent Rs. 34 crores and plans to spend Rs. 20 crores in the next two years. The Shiroli Industrial estate covers 260 hectares. Of the total 730 plots in this estate, around 650 plots have been sold. 635 industries are currently functioning in this area. MIDC has spent about Rs. 6 crores on providing basic infrastructure in this area. The major industries in this estate are Menon Casting, Manograph Industries, Lokmat, Kolhapur Steel, Saroj Iron Industry, Sriram Foundry, Mahalaxmi Masala Products, Bharat Udyog Ltd. and H.J.Iron. The Gokul Shirgaon industrial estate is spread over 220 hectares. It has 850 plots of which 800 are sold. 750 industries function in this estate, most of them relating to engineering and foundry. The major industries are Gokul, Eurotex, Menon Bearings and Indocount. As far as cooperative industrial estates are concerned, the Government has approved seven estates. 2140 plots have been issued, of which 1,272 are functional; 44,850 workers are engaged in these estates. The Kolhapur industry is a source for OEMs (Original Equipment Manufacturers) outside India. It has the potential to emerge as an engineering component exporter.

2.24.5 Foundries in Kolhapur

The Foundry Industry of Kolhapur has got its own name in Maharashtra. Western Maharashtra is regarded as socio-economically progressive and well developed in Maharashtra. In 1941 Shivaji Udyamnagar Co-operative Society was flourished which is located inside the city. The real architect was J.P. Naik who developed it with the help of Rajaram Maharaj. A special feature of Udyamnagar is that it most of the foundry unit are private and they are run by small entrepreneurs rather than big industrialist. There are around 250 foundry units in Kolhapur, out of this 25 are located inside city also called as “Shivaji Udyamnagar”. These foundries work on Cupola or Induction Furnace.

2.25 AIR QUALITY IN KOLHAPUR CITY

As per Annexure IC, it is seen that though the SOx and NOx levels seem to be within the limit, it has been observed that the Respiratory Suspended Particulate Matter (RSPM) level and Suspended Particulate Matter (SPM) levels are increasing at all the three sites i.e. Dabholkar Corner, Mahadwar Road and Shivaji University campus.

Emission from an individual car, bike or heavy motor vehicle is generally low, but addition of 2,37,492 new vehicles every year increases the intensity of vehicular pollution day by day. Cars, trucks and buses emit significant quantities of carbon monoxide, hydrocarbons, nitrogen oxides, fine particles and lead. The pollutants impair health, destroy vegetation and reduce the general quality of life. Due to tremendous increase of the vehicles in Kolhapur city it is now essential to implement control measures for mitigating the vehicular emissions and their impacts on the environment.

2.26 EMISSIONS FROM FOUNDRIES

In Iron & Steel and other manufacturing industries, foundries and forges produce a lots of pollutants in the environment – both working and ambient environment (NIFFT). In these processes, metals are extracted and produced from ores by various metallurgical processes and processes for moulding, melting and castings etc. are accompanied by evolution of heat, noise, dust fines, fly-ash, oxides of Nitrogen, Sulphur and metals. Particulate matters are generated in large quantities when preparing mould core sands and moulds melting metals, pouring metal, knocking out poured moulds and loading and unloading raw materials. Here metals are given a specific shape by metal castings for various engineering purposes (Dutta et.al. 2008).

Gaseous matters like gases, vapors, fumes and smoke are produced during melting and pouring operations. The major pollutants are emitted from various work areas in Foundry i.e. Pattern shop, Sand preparation, moulding and core making, mould drying and ladle heating, cupola, electric arc furnace, pouring and mould cooling, knockout, fettling, heat treatment etc. In addition, various air pollutants and noise pollutants are produced from forge shops and other manufacturing industrial units. Pollutants are also emitted in sintering, pelletisation, rolling mills, coke-oven plants, refractories etc. in steel making and by-products manufacturing. Coke fired cupolas in Agra, glass making units at Firozabad and more than 200 foundries around Kolkata, Howrah urban metropolitan complex have reported to produce huge amount of particulates and gaseous matter in the atmosphere (Dutta et.al. 2005). These pollutants cause various health hazards in human beings.

SUMMARY

Cities continue to grow, offering employment, better living conditions and basic amenities that are not available in rural areas. The rapid urbanization, however, accompanied by environmental problems such as pollution, waste management, congestion and imbalance in fragile ecosystems. Unless steps are taken, the declining air quality we are witnessing in many developing country cities suggests that as the population continues to grow air quality (and other environmental indicators) will rapidly deteriorate. The impacts will not only be severe in developing country mega cities (cities with a population of more than 10 million) but also in the growing number of secondary and tertiary cities with a population of at least 1 million. The potential for these rapid changes coupled with a growing demand for cleaner air leaves policymakers facing the need to improve their ability to control air pollution. Fortunately, in recent years major advances have been made in techniques utilized to estimate ambient air pollution levels and identify emission sources. These advances offer the opportunity for developing countries to implement sophisticated air quality management programs earlier in their development process than was accomplished by their industrial country counterparts. Being able to identify different air pollution sources accurately is a key element in an effective Air Quality Management System (AQMS). An AQMS brings together the scientific activities of determining air pollution emissions, ambient concentrations by pollution type, and resulting health impacts with political and regulatory aspects to formulate a society’s reaction to air pollution. The present study arises from a concern over the lack of information (quantitatively) on the contributions of different source categories of air pollution in developing countries especially for Particulate Matter (PM), which is the major contributor to the adverse health effects of air pollution. Without reliable and accurate source information, it is difficult for policymakers to formulate rational, effective policies and investments aimed at improving air quality.

It is important to note that the health impacts of urban air pollution are not entirely dependent on the particulate pollution. The health impacts observed or estimated are also dependent on other pollutants, such as ozone, hydrocarbons, acidity in the air due to sulfur and nitrogen compounds, carbon monoxide, etc. However, in the developing countries, the particulate matter forms the major contributor and hence the pressure to understand its sources better. Also, during the source apportionment, it is understood that all the pollutants contribute in some form or the other to the particulate matter and any regulation or policy measure towards controlling particulate matter has an implicit co benefit towards to the other pollutants. Need of identifying sources of trace elements exist in SPM are vital due to health impacts especially on children's and old age group people. Kolhapur being Tier II city, need to address the problem of Particulate Matter problems and source apportionment study is to be carried out for better Air Quality Management for welfare of human being and nature as a whole.

Chapter 3

Materials and Methods

The present study has been undertaken for identifying the sources of air pollution and their contributions to atmospheric pollutants in the form particulate matter and the trace metal concentration in SPM in Kolhapur and its industrial at suburbs. The PM samples were collected during July 2008 to July 2009 at three different sampling locations in the Kolhapur city (Maharashtra, India) namely Shahu Blood Bank Corner (SBBC) in the city, Gokul Shirgaon MIDC (GS) Area which is on South East of the city and Shiroli MIDC (SS) area which is on East of the city. Total of seven trace elements were analyzed using AAS. The first and most important pre-requisite in trace element analysis of atmospheric SPM is the precautions in processing and analysis of samples, to avoid contamination at each and every stage of sample collection and handling. The chemical composition data in particulate matter were analyzed using the US EPA PMF 3.0 receptor model to estimate the contributions from possible emission sources. After identifying the sources and their contributions, the major contributing source was found out and detailed analysis of source was carried out by sampling SPM at source. This is done to justify and validate the results of observed concentrations of trace elements in air samples as well as in soil samples with the results of predicted concentrations of trace elements in air samples. The present chapter presents the methodologies, standard procedures and protocols used in the experimental studies for obtaining the necessary results to meet the stated objectives listed in chapter 1.

3.1 METHODOLOGY ADOPTED

The following methodology was adopted to carry out experimental work as well as calculations of results to arrive at conclusions.

1. Selected three locations viz. Urban area like Shahu Blood Bank Corner on downwind direction of the city, Industrial area like Shiroli MIDC and Gokul Shirgaon MIDC, both on upwind direction of the city.

2. Measured wind velocity and its direction and constructed Wind Rose Diagram to know the predominant wind direction and wind speed to be used for dispersion studies.

3. Used High Volume Sampler and measured the concentration of SPM for 24 hours during July 2008 to July 2009 at all three locations mentioned above.
4. Simultaneously, the soil samples were collected from each sampling locations.
5. Acid digestion was carried out to extract trace elements from PM collected from air as well as soil for determination and chemical characterization of trace elements like Cu, Pb, Ni, Zn, Cd, Mn, and Fe using Atomic Absorption Spectrophotometer.
6. The observed concentrations of trace elements were given as input to United States Environmental Protection Agency (US EPA) Positive Matrix Factorization (PMF) Receptor model predict the concentrations of trace elements on three locations.
7. The US EPA PMF model was run under standard conditions mentioned and documented by US EPA and sources of each trace elements were found out
8. Source Apportionment which includes quantitative estimation of each source was determined and percentage contribution of each source was calculated.
9. The validation was done on the basis of the results of PMF model with characterization of trace elements in soil samples at locations.
10. The trace element/s with higher concentration at all locations were found out and detailed analysis was carried out to justify the cause of higher concentrations.

3.2 SITE SELECTION AND SAMPLING LOCATIONS

Three distinct areas with different background activities in Kolhapur were selected as sampling sites. Selection of sampling sites was based mainly on the wind direction and speed and the type of activities. Care was taken to maintain sufficient distance between two sampling sites to neutralize the influence of site activities on another. Thus, sites can be differentiated from each other on regional source basis.

Figures 3.1 to 3.3 presents the locations of the three sampling and monitoring stations indicating in red circle selected for the study.

3.2.1 Shahu Blood Bank Corner (SBBC)

Shahu Blood Bank Corner is located in the downwind direction of the city and situated at coordinates of $16^0$42’28.32” N and $74^0$13’45.81”E. It is an institutional cum residential area. This site is about four km from the industrial setups. It is a congested area with high traffic density. There are several small scale industries like Shivaji Udyamnagar which consist of metal processing units etc. located within the city limits.

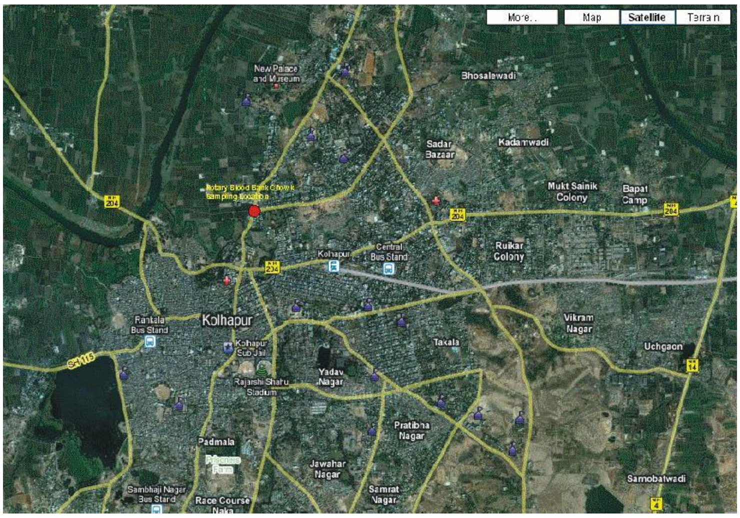


Figure 3.1 Shahu Blood Bank Corner

3.2.2 Gokul Shirgaon (GS) MIDC

Gokul Shirgaon is one of the major industrial clusters in Kolhapur situated at coordinates of 16°38'46"N and 74°17'26"E. The major industries in this cluster mainly produce products such as Steel and ferrous Castings, Alloys, and Bearings, Textiles, etc. The industrialization in Kolhapur is due to the proximity to Bauxite deposits at Radhanagari. Gokul-Shirgaon Industrial Area is situated on National Highway 4 and is 15 km from Kolhapur city. This area is close to the Karnataka State boundary and to Goa also.

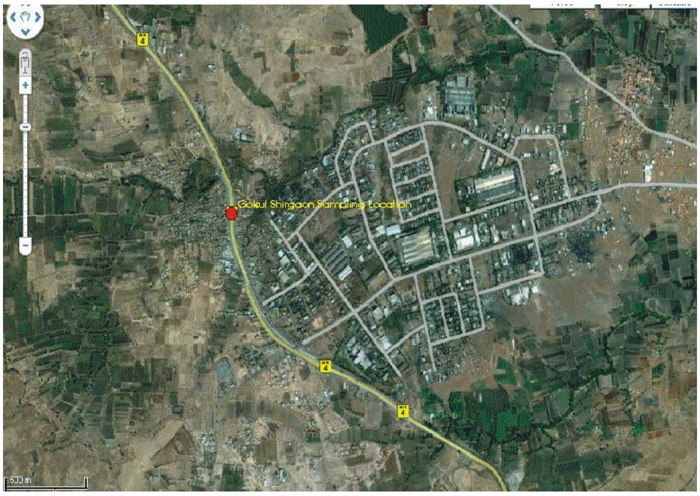


Figure 3.2 Gokul Shirgaon MIDC

The Gokul Shirgaon industrial estate is spread over 220 hectares. It has 850 plots of which 800 are sold. 750 industries function in this estate, most of them relating to engineering and foundry. The major industries are Gokul, Eurotex, Menon Bearings and Indocount.

3.2.3 Shiroli MIDC

Shiroli is another major industrial cluster in Kolhapur and situated at coordinates of $16^0$45’42.75” N and $74^0$16’41.22”E . The major industries in this area include Foundries and Metal Processing industries. It is also located within vicinity of National highway 4.

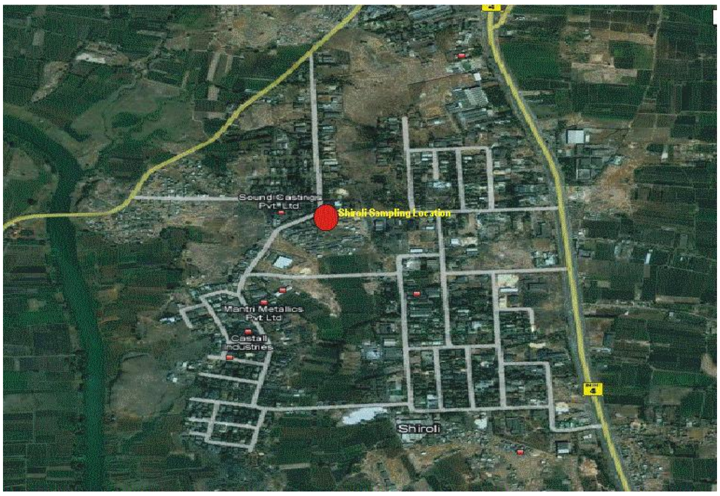


Figure 3.3 Shiroli SMAK MIDC

The Shiroli Industrial estate covers 260 hectares. Of the total 730 plots in this estate, around 650 plots have been sold. 635 industries are currently functioning in this area. MIDC has spent about Rs. 6 crores on providing basic infrastructure in this area. The major industries in this estate are Menon Casting, Manograph Industries, Lokmat, Kolhapur Steel, Saroj Iron Industry, Sriram Foundry, Mahalaxmi Masala Products, Bharat Udyog Ltd. and H.J.Iron.

3.3 METEOROLOGICAL OBSERVATIONS

3.3.1 Methodology for measuring Wind Velocity and Direction and Construction of Wind Rose

Using the Wind Vane / Prismatic compass, eight wind directions were measured on the ground (i.e. N, NE, E, SE, S, SW, W, NW) and then anemometer was adjusted to zero reading in dial gauge. The readings of wind velocity in all eight directions (at least one minute for each reading) were taken and recorded and Wind Rose diagram was prepared by plotting observed wind velocities with respect to its direction.

3.3.2 Methodology for measuring ambient temperature

Ambient temperature at selected sampling locations were measured with the help of a glass thermometer as well as by using thermocouple sensor of Stack Monitoring kit manufactured by Netal India. Maximum temperature was recorded between 12.00 noon to 2.00 pm on the day of sampling of SPM on designated sites.

3.4 PARTICULATE MATTER SAMPLING (US EPA COMPENDIUM METHOD IO-2.1)

Particulate matter samples were collected and monitored by High Volume Sampler (HVS) manufactured by Netal India at Shahu Blood Bank Corner, Gokul Shirgaon MIDC and Shiroli MIDC during July 2008 – July 2009. The average flow rate maintained through sampler was 1.0 m^3/min. The sampling was carried out 24 hours with a frequency of two samples per week at selected three locations in Kolhapur.

The samples were collected on Whatman glass fiber filter papers with 2 µm pore size. The glass fiber filter papers were selected because of their Chemical inertness, Very less moisture absorption and Stability to withstand changing weather conditions. All the filters were pre-conditioned at 40 ^{0}C for 24 hours in an oven before sampling and post-conditioned after sampling at same condition. The SPM concentrations were measured gravimetrically by weighing the particulate matter mass collected and knowing the average suction rate during the sampling. The detailed information about High Volume sampler and calculation of SPM is described in Annexure II and Annexure VIII respectively.

3.5 TRACE METALS EXTRACTION IN PARTICULATE MATTER FROM AIR SAMPLES (US EPA COMPENDIUM METHOD IO- 3.1)

The SPM collected from air using HVS was used for quantitative trace metal constituents in PM. The digestion mixture consists of a mixture of 3 ml Hydrochloric acid (HCl), 2 ml Nitric acid (HNO_3) and 1 ml Perchloric acid ($HClO_4$). The mixture was prepared by adding HCl, $HNO_{3,}$ and HClO4 in the ratio 3:2:1, respectively. The filter paper was reduced to small pieces and kept in each beaker and these beakers were covered by decontaminated watch glasses. These beakers were then kept on a hot plate at about 40-50 ^{0}C where they undergo decomposition. The samples were digested till the black filter paper turns white and 1 -2 ml of acid was left in the beaker. The sample was not digested till evaporation, to avoid the loss of volatile trace metals. Finally the digested sample was extracted by filtration with double distilled water. The digested samples were made up to 25 ml by adding 0.25 % Nitric acid. These prepared samples were then used for trace metal determination using AAS. Annexure III presents the detailed information about trace element extraction.

3.6 SAMPLE ANALYSIS USING ATOMIC ABSORPTION SPECTROSCOPY (AAS) (US EPA COMPENDIUM METHOD IO- 3.2)

The digested samples were then analyzed by using the Chemito Atomic Absorption Spectrophotometer (AAS) for Copper (Cu), Lead (Pb), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Manganese (Mn) and Iron (Fe). The concentrations of trace elements were calculated in microgram per cubic meter by AAS accordingly. Annexure IV presents the detailed working of AAS.

The air-acetylene flame temperature was kept at 2000-2300°C for Zn, Cu, Cd, Pb, Mn, Fe etc. The liquid sample is aspirated into a nebulizer (4-7 ml/min). A steady-state absorbance signal was measured. In Chemito Flame AAS, Sensitivity – a slope of calibration line which is indirectly expressed as characteristic concentration i.e. such concentration of µg/ml of the element that gives the absorbance of 0.0044. Detection limit was kept approx. 2 to 5 times lower than characteristic concentration. Working range was kept approx. 2 to 3 orders of magnitude while Repeatability was under optimum conditions RSD 0.5-1.5 %. Annexure V presents different wavelengths and absorbance for trace element detection.

The Calibration curve is typically linear and involves at least five points from five standards that are at equidistant concentrations from each other. This ensures that the fit is acceptable. A least means squares calculation is used to linearly fit the line. In most cases, the curve is linear only up to absorbance values of 0.5 to 0.8. The absorbance values of the standards should have the absorbance value of a blank subtracted.

The curve is typically linear and involves at least five points from five standards that are at equidistant concentrations from each other. This ensures that the fit is acceptable. A least means squares calculation is used to linearly fit the line. In most cases, the curve is linear only up to absorbance values of 0.5 to 0.8.

3.7 TRACE METALS EXTRACTION FROM SOIL SAMPLES (US EPA COMPENDIUM METHOD IO- 3.1)

To support and validate the results of chemical characterization of trace elements of air samples, the soil samples at each location were taken and the concentrations of trace elements in soil were determined accordingly.

The soil sample were collected from the site and placed in oven at 40^0C for 24 hours. The digestion mixture consists of a mixture of 1 ml Hydrochloric acid (HCl) and 2 ml H_2SO_4. The mixture was prepared by adding HCl and H_2SO_4 in the ratio 1:2, respectively. The dried and sieved soil was poured into the mixture in each beaker and these beakers were covered by decontaminated watch glasses. These beakers were then kept on a hot plate at about 40-50 ^{0}C where they undergo decomposition. The samples were digested till the black filter paper turns white and 1 -2 ml of acid was left in the beaker. The sample was not digested till evaporation, to avoid the loss of volatile trace metals. Finally the digested sample was extracted by filtration with double distilled water. The digested samples were made up to 25 ml by adding 0.25 % Nitric acid. These prepared samples were then used for trace metal determination using AAS.

3.8 APPLICATION OF US EPA PMF MODEL

United States (US) Environmental Protection Agency (EPA) Positive Matrix factorization (PMF) model predicts the concentrations of trace elements, determines the factors for each source and its contribution to each source which is known as Source Apportionment.

Source apportionment analysis was carried out using the positive matrix factorization receptor model (version PMF 3.0) developed by US EPA. In PMF model, any data matrix X with dimension n rows by m columns, where n and m are the number of samples and the number of species, can be factorized into two matrices, namely G (n × p) and F (p × m), and the residual matrix, E, where p is the number of factors or sources extracted. The product of G and F can explain the systematic variations in X. If a p-factor model is being considered, G is an n × p matrix of source contributions, describing the temporal variation of the source strengths.

$$X = GF + E$$

$$\text{or} \quad x_{i,j} = \sum_{k=1}^{p} g_{i,k} f_{k,j} + e_{i,j}$$

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{e_{i,j}^{2}}{s_{i,j}^{2}}$$

The matrix F is a p × m matrix of source chemical compositions, or source profiles. The main process of the PMF is minimizing the Q-value as the sum of square of the residuals (ei,j) weighted inversely with error estimates (si,j) of the data point. It requires two inputs to run PMF, namely concentration and its uncertainty.

In the present work, if the concentration is less than or equal to the method detection limit (MDL) provided, the uncertainty is calculated using the following equation (Polissar *et al.*, 1998; Reff *et al.*, 2007; Norris *et al.*, 2009).

$$\mathrm{Unc} = \frac{5}{6} \times MDL$$

If the concentration is greater than the MDL provided, the uncertainty is then calculated according to

$$\mathrm{Unc} = \sqrt{(Error\ Fraction \times concentration)^2 + (MDL)^2}$$

Missing data were substituted with the median value and their uncertainties were replaced by four times the median value. The model was run 20 times with seven factors and a seed of 25 (in order to replicate the results). All runs converged and a global minimum was found. In this study, the identification of sources was conducted using major marker species that can be estimated according to a number of references. The sources are mainly confirmed based on the percentage of the species for the source. Moreover, analysis on source contributions in relation to seasonal or meteorological conditions helps to understand the source characteristics. The results of observed concentration of trace elements in particulate matter collected in air and quantified by AAS analysis were given as input to US EPA PMF model along with concentrations of uncertainty values of trace elements. US EPA PMF model gives the output like number of factors i.e factorization, the species profile of each source, and the amount of mass contributed by each factor to each individual sample i.e source apportionment. Annexure VII shows the operational procedure of US EPA PMF software.

3.9 SOURCES AND THEIR ASSIGNED FACTORS

Trace elements like Cu, Pb, Ni, Zn, Cd, Mn, Fe were finalized for source apportionment study based on sources available at each selected sampling location and major elements found in air samples. Table no. 3.1 shows the sources which are identified physically on all three locations and it is expected that trace elements of interest may contribute to the concentration from each source. These sources are given to US EPA PMF model and contribution of each trace element to respective source is calculated and predicted by the model.

Table 3.1 Identified sources on the locations

Shahu Blood Bank Corner	Gokul Shirgaon MIDC	Shiroli MIDC
Leather industries	Textile industries	Transportation
Transportation	Foundry	Road dust
Metal industries	Transportation	Automobile service centers
Domestic cooking, burning	Road dust	Foundry
Road dust	Non ferrous metal industries	Stone Crushing plants
Fabrication workshops	Food processing units	Food processing units

The above mentioned sources which are also known as Factors in US EPA PMF model, are classified and grouped as per the standard protocol of US EPA PMF guidelines which are as follows. Table 3.2 present factors assigned to identify source at three sampling locations.

Table 3.2 Sources given to US EPA PMF model as Input

Sources	Factor
Soil & Road Dust	1
Oil & Coal Burning	2
Iron & Steel Industries	3
Non ferrous Metal Industries	4
Refuse Incineration	5
Transportation	6

3.10 US EPA PMF MODEL VALIDATION

The predicted concentrations of trace elements from the model and experimental results of same element from SPM in the atmosphere were compared to check the difference and if the difference is within ±10%, it is accepted. In case of any data set where the variation is more than ±10%, sampling was redone and input was changed. After multiple iterations, the differences between the predicted and experimental values were brought to within ±10%. This ensures validity of the model for the specific region under study and further, this model can be used for Source Apportionment studies for that particular area provided the sources remain same.

3.11 TRACE ELEMENT/S WITH HIGHER CONCENTRATIONS

The highest concentration of trace element/s and its source contribution was calculated at each location. This enables to find out the probable source of Trace element and its contribution. It is observed from past data and literature that the concentration of Pb and Cd in the city seems to be more due to predominantly from transportation sector. Hence the automobile exhaust monitoring was carried out to find out the concentration of SPM in the exhaust gases. Also, the presence of large number of foundries in Gokul Shirgaon and Shiroli MIDC may be a source for metal concentration in particulate matter. Hence the source sampling was carried out at these locations too.

3.11.1 Calculation of SPM from Automobile Exhaust Emission at Shahu Blood Bank Corner

The study was carried out with the use of Guassian Line Source Model to determine the concentration of SPM due to vehicles and compare the results with the Observed Concentration. In the present study, an attempt was made to determine the concentration of SPM due to vehicular emissions at Shahu Blood Bank Corner. The sampling was carried out for 8 hours and the number of vehicles of each category was also counted during the period. Annexure IX presents detailed analysis of automobile exhaust and results.

The source strength or the emission rate was calculated for each type of vehicle with the use of emission factor. Emission Factor was obtained from CPCB, 2007 for diffrent type of vehicle. As Shahu Blood Bank Corner is signal point, two cases were assumed. Case1- when the vehicle is at rest position and Case 2- when the vehicle is accelarating as the signal goes green. For both the cases the speed was assumed , case 1- 2m/sec and case 2- 15m/sec.

Emission rate, q, is determined from the product of emission rate per vehicle times the number of vehicleper unit lenght. The latter quantity is found by dividing the rate of vehicle passeage through a point by average speed:

Vehicle/meter = flow(vehicle / hr)/ average speed (km/hr)

Using the following formula, SPM concntration was found out.

$$c = \left(q/\left(\sqrt{2\pi}.u.dz\right)\right)$$

3.11.2 Calculation of SPM from foundries at Shiroli MIDC and Gokul Shirgaon

The study was carried out with the use of Gaussian Plume Model to detrmine the concntration of SPM due to release of emission from foundries. The number of foundries, their fuel emission factors and working hours were taken into consideration for calculation of source strength and then calculation of SPM was done at sampling location using plume model. Annexure X presents detailed analysis of SPM calculation from foundries at Shiroli MIDC and Gokul Shirgaon MIDC.

The source strength calculation for foundry at Shiroli MIDC and Gokul Shirgaon MIDC was necessary to get to know SPM concentrations and some trace elements from foundry. It was calculated based on the Emission Factor for the particular source in consideration. In the present study, the furnace used in the Foundry Industry is the source.

The data for the duration of working hours and the production capacity was collected from Suyash Foundry, Kolhapur. From the available data, it was assumed that all the foundries in consideration for the present study run for 10 hours and have production capacity of 7000 kg/day. Thus based on the type of furnace, the emission factor was selected and emission strength was calculated with the use of working hours, production capacity and the area of the box under study. The input is given to the following Gaussian Area source model to calculate SPM concentration at ground level along the plume centerline.

$$C(x,0,0) = \frac{Q}{\pi u \sigma_y \sigma_z} e^{-\frac{H^2}{2\sigma_z^2}}$$

Where,

C = Concentration of the pollutant (µg/m^3)

Q = Source emission strength (gm/m-sec)

u = Wind speed (m/sec)

σ_z = Vertical dispersion Parameter (m)

σ_y = Horizontal dispersion Parameter (m)

H = Effective Stack Height (m)

Chapter 4

RESULTS AND DISCUSSSIONS

The present studies on Source Apportionment of Different Pollutants and trace elements released from different sources was carried out in the city of Kolhapur, Maharashtra, India as well as in two industrial areas namely Gokul Shirgaon MIDC and Shiroli MIDC which are 3 km away from Kolhapur city on upstream side. Sampling location i.e. Shahu blood bank corner (SBBC) was selected due to its heavy traffic as well as the presence of some small scale industries. This location is on downwind side of industrial suburb and it is expected that most of the suspended particulate matter (SPM) in the city shall come from industrial activities. The trace elements concentration in SPM was found out. The data collected at these locations was provided as an input to EPA PMF model for source apportionment and chemical characterization of trace elements which is objective of the present study. Table 4.1 shows the Latitude, longitude and attitude of these locations.

Table 4.1 Positioning data of sampling locations

Location	Latitude	Longitude	Attitude from Mean Sea level
Shahu Blood Bank Corner (SBBC)	16^{0}42’28.32”	74^{0}13’45.81”	548 m
Gokul Shirgaon (GS)	16^{0}38’17.48”	74^{0}16’47.84”	613 m
Shiroli SMAK (SS)	16^{0}45’42.75”	74^{0}16’41.22”	573 m

4.1 AVERAGE MONTHLY WIND SPEED AND DIRECTION

In any dispersion study, location topography, wind velocity and its direction and other meteorological parameters plays a vital role in the movement of pollutants. The wind speed and direction are recorded at selected sampling locations. This data is represented with windrose diagrams. The wind speed recorded on eight sides and average monthly wind speeds are shown here for the purpose of input in the present study.

Prior to selection of sampling location, wind velocity and direction was measured at three different locations chosen for the study. SBBC is on the downstream of Kolhapur city and one of the busiest commercial places in the Kolhapur city and has heavy vehicular movements. Similarly, sampling location at Gokul Shirgaon MIDC and Shiroli MIDC were selected for measurement of wind velocity and direction. The measurement of wind velocity was carried out in many sites in these MIDC locations and also, few readings were taken in the NH4 highway which divides Industry and City.

The sampling was started in October 2008 and finished by June 2009. July, August and September in 2008 was eliminated from the study due to heavy rainfall in Kolhapur city as well as in western Maharashtra. Almost, 15% of city goes under flood water and SBBC is one of the flooded places.

North-West (NW) & South-West (SW) sides of Kolhapur city are covered with hills and mountains, which come in western Ghat at Maharashtra. The gateway to Konkan region starts from Kolhapur city. Most of the winds come from (SE) side of Kolhapur city and very few times from NE & E also and enters into the city.

Gokul Shirgaon MIDC and Shiroli SMAK MIDC (SS) are on upstream side and the release sources from industries in these areas are at an attitude of $\geq$ 15 m. Due to release of pollutant at higher altitude, it is expected that these may be carried towards Kolhapur city.

Kolhapur city has got many seven storied buildings which are commercial and more two storied buildings in residential area.

Wind rose diagram was constructed manually from the readings of average monthly wind speed. All 9 months data was given to wind rose plotter software to construct wind rose. Wind rose diagrams explain the graphical representation of wind speed and direction. It also explains magnitude and frequency of winds in particular direction. The wind speed and direction was recorded at every hour in 24 hrs duration but average monthly wind speed and direction data is used to know the monthly and seasonal variations in a year at different sampling locations.

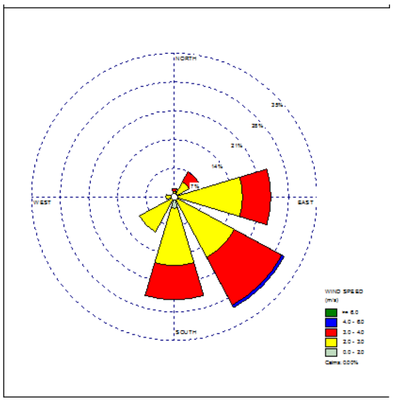


Figure 4.1 Average yearly Wind Rose diagrams for Shahu Blood Bank Corner

Figure 4.1 shows most of the winds are seen in SE, ESE, NE directions and blowing towards NW, W directions. Highest wind speed observed is 3.5 meter per second in the month of November while lowest is 1.7 meter per second in months of December, which are well above calm wind speed. Sampling location i.e. Shahu blood bank corner is located downwind side of city.

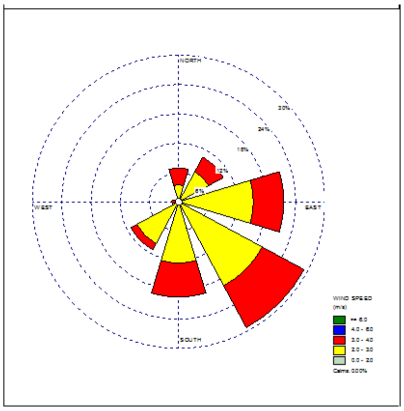


Figure 4.2 Average Yearly Wind Rose Diagrams for Sampling location Gokul Shirgaon

Figure 4.2 shows most of the winds are seen in SE, SEE directions and blowing towards NW, W directions. Highest wind speed observed is 3.3 meter per second while lowest is 1.8 meter per second which are well above calm wind speed. Sampling location i.e. Gokul Shirgaon MIDC is located downwind side of MIDC.

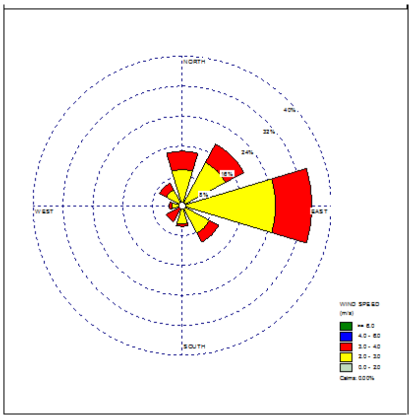


Figure 4.3 Average Yearly Wind Rose Diagram for Shiroli MIDC

Figure 4.3 shows most of the winds are seen in E, SEE directions and blowing towards W direction. Highest wind speed observed is 3.5 meter per second while lowest is 1.8 meter per second which are well above calm wind speed. Sampling location i.e. Shiroli MIDC is located downwind side of MIDC.

4.2 AMBIENT TEMPERATURES

The volume of gases is dependent upon ambient temperatures and hence the pollutant concentrations vary accordingly. Ambient temperature was measured in ^{0}C at selected sampling locations and average temperature of the day is recorded for measurement and calculation of SPM concentrations. Table 4.2 shows highest temperature recorded on each sampling dates during sampling.

Table 4.2 Ambient temperatures at different sampling locations (^{o}C)

2008-09	Dates	SBBC	GS	SS
October	2-Oct-08	26.0	28.2	27
	9-Oct-08	27.0	30.8	28.2
	16-Oct-08	26.0	27.8	27
	23-Oct-08	26.0	30.5	28
	30-Oct-08	28.0	27.5	29
November	6-Nov-08	27.5	27.4	28

	13-Nov-08	27.8	28.2	28.1
	20-Nov-08	28.1	29.8	29
	27-Nov-08	28.4	26.1	29
December	4-Dec-08	28.7	29.6	29
	11-Dec-08	29.0	30.5	29.9
	18-Dec-08	29.3	30.3	30.1
	25-Dec-08	29.6	30.9	30.5
January	1-Jan-09	29.9	30.6	30.1
	8-Jan-09	30.2	30.3	30.5
	15-Jan-09	30.5	30.2	30.9
	22-Jan-09	30.8	30.7	30.9
	29-Jan-09	31.1	31.4	32
February	5-Feb-09	31.4	31.3	32
	12-Feb-09	31.7	31.8	32.2
	19-Feb-09	32.0	32.6	32.5
	26-Feb-09	32.3	32.2	32.8
March	5-Mar-09	32.6	32.9	33
	12-Mar-09	32.9	32.6	33
	19-Mar-09	33.2	33.4	33.5
	26-Mar-09	33.5	33.0	33.9
April	2-Apr-09	33.8	33.7	34
	9-Apr-09	34.1	31.4	34.5
	16-Apr-09	34.4	34.2	34.9
	24-Apr-09	34.7	34.3	35
May	7-May-09	35.0	34.4	35.4
	14-May-09	35.3	35.1	35.7

	21-May-09	35.6	35.2	35.9
	28-May-09	35.9	35.1	36.1
June	4-Jun-09	36.2	36.1	36.5
	11-Jun-09	36.5	36.7	36.9

Temperatures observed at SBBC during sampling period is ranging from 26 to 36.5 degree Celsius, which are highest, recorded on respective day while Temperatures observed at GS during sampling period is ranging from 27.4 to 36.7 degree Celsius. Also, Temperatures observed at SS during sampling period is ranging from 27 to 36.9 degree Celsius.

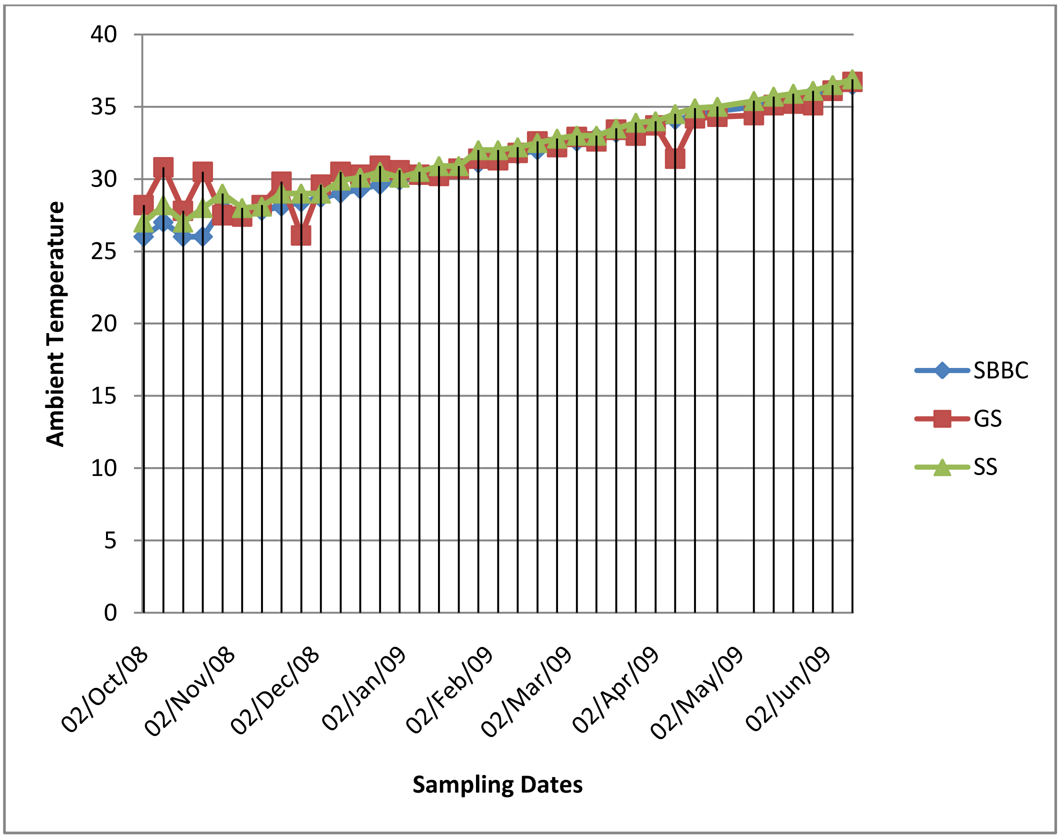


Figure 4.4 Temperature variations during study period

It is seen that from Figure 4.4, there is not much deviations in temperature readings at each location during most of the months. Also, range of temperature at each locations is not having large difference.

4.3 SUSPENDED PARTICULATE MATTER (SPM) IN µg / m^3

The sampling device, high volume samplers (HVS) was kept at all three locations simultaneously at a height of 10 m. Many commuter vehicles and residents of Kolhapur district come to city for shopping and other commercial activity.

The sampling time was chosen as 24 hours continuously with all precaution. Every hour, suction rate was recorded and average suction rate was taken for calculation of volume of air sampled at average ambient temperature. SPM concentration was found at NTP condition i.e. 25^{0}C and 1 atm pressure. The quantification of SPM is the primary objective in any source apportionment study.

SPM concentration was found out as per standard procedure of USEPA and CPCB, New Delhi. Compliance to NAAQS was checked. After sampling, precaution was taken to preserve the filter paper on which SPM was deposited and subsequently the same particulates were used for the analysis of trace elements. Process of chemical characterization of trace elements was done just after taking final weight of the paper. This was done to avoid addition of more organic matter in filter paper.

Table 4.3 SPM Concentrations at sampling locations

2008-09	**DATE**	**SPM Concentrations, µg/m^3**		
		SBBC	**GS**	**SS**
October	2-Oct-08	478	465	423
	9-Oct-08	480	500	440
	16-Oct-08	470	460	455
	23-Oct-08	490	460	460
	30-Oct-08	495	495	480
November	6-Nov-08	492	490	495
	13-Nov-08	495	480	460

	20-Nov-08	490	485	465
	27-Nov-08	495	460	470
December	4-Dec-08	500	480	475
	11-Dec-08	510	550	480
	18-Dec-08	505	540	485
	25-Dec-08	510	550	480
January	1-Jan-09	510	510	485
	8-Jan-09	520	515	490
	15-Jan-09	505	520	460
	22-Jan-09	525	525	500
	29-Jan-09	530	550	490
February	5-Feb-09	540	545	520
	12-Feb-09	545	540	510
	19-Feb-09	550	540	520
	26-Feb-09	565	530	540
March	5-Mar-09	550	525	535
	12-Mar-09	545	535	525
	19-Mar-09	540	540	530
	26-Mar-09	540	520	540
April	2-Apr-09	580	510	540
	9-Apr-09	590	520	545
	16-Apr-09	585	455	550
	24-Apr-09	590	485	525
May	7-May-09	580	470	520
	14-May-09	575	490	515
	21-May-09	565	440	510

	28-May-09	585	480	550
June	4-Jun-09	590	423	540
	11-Jun-09	565	475	550

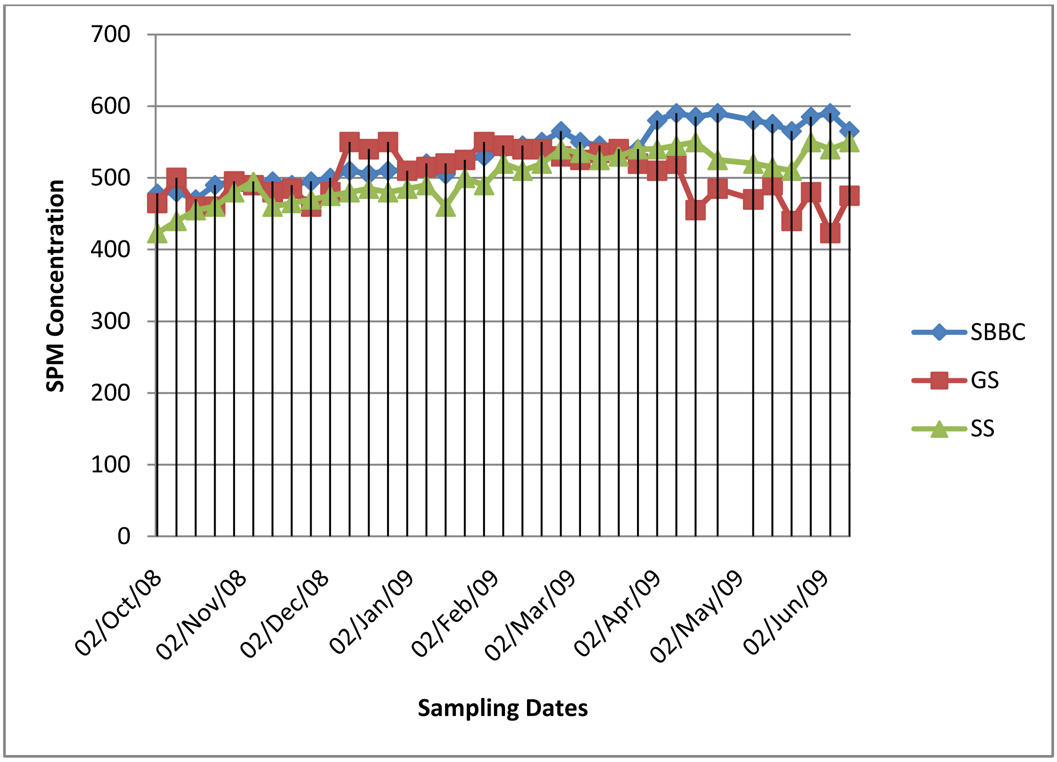


Figure 4.5 Suspended Particulate Matter Concentrations

Table 4.3 presents the data collected for SPM concentration at all selected sampling locations. Months from July to September were excluded from the sampling due to monsoon. During the rainy season the concentration of aerosols are much less as compared to the other season, this is because rainfall or precipitation exerts a two-fold cleansing action on the pollutant discharged into the atmosphere. It accelerates the deposition of particulate matter on the ground and hence the removal from the atmosphere.

It is seen from Table 4.3 and Figure 4.5 that SPM concentrations at Shahu Blood Bank corner at Kolhapur city is increasing from October in Winetr season to June in Post Summer season. Highest concentration observed is 590 microgram per cubic meter while lowest is 470 microgram per cubic meter. Both concentrations are above NAAQS standards which are set by Central Pollution Control Board, New Delhi. SPM concentrations may be due to soil and road dust as well as heavy transportation. The major source contributing to SPM may be automobiles in the city and particularly, at Shahu Blood Bank Corner. The increase in the level may also be due to festival season in Kolhapur, which is observed in the month of December to February. The highest observed concentration is 560 µg / m^3, which is very high and can lead to various kinds of damages to the humans as well as the local environment. The other sources of SPM in the above area may be Road Dust due to the movement of Vehicles, the construction activities taking place in the nearby locality, pollen grains, burning of municipal garbage, wood burning.

It is seen from Table 4.3 and Figure 4.5 that SPM concentrations at Gokul Shirgaon MIDC observed is ranging from 423 microgram per cubic meter to 550 microgram per cubic meter. Both concentrations are above standards, which are set by Central Pollution Control Board, New Delhi. SPM concentrations are high due to soil and road dust as well as release from textile industries and heavy transportation on NH4 highway. Highest concentration observed is 535 µg/ m3 while lowest is 415 µg/ m3. All concentrations are above standards, which are set by CPCB, New Delhi. The higher SPM concentrations are due to road dust as well as heavy transportation on National Highway 4 (Pune Bangalore) situated near sampling location.

It is seen from Table 4.3 and Figure 4.5 that SPM concentrations at Shiroli MIDC are increasing with seasonal variations like from monsoon to summer. Highest concentration observed is 550 microgram per cubic meter while lowest is 423 microgram per cubic meter. Both concentrations are above standards which are set by Central Pollution Control Board, New Delhi. SPM concentrations may be high due to foundries, transportation in NH4 highway.

4.4 CHEMICAL CHARACTERIZATION OF TRACE ELEMENTS

Table 4.4, 4.5 and 4.6 represents the trace element concentrations in ug/m^{3}at different sampling locations. Concnetration on Y Axis of all the graphs has unit of ug/m^3.

Table 4.4 Observed concentrations of trace elements in µg / m^3 at Shahu Blood Bank Corner

DATE	Cu	Pb	Ni	Zn	Cd	Mn	Fe
2-Oct-08	0.048	3.0480	0.003	0.1760	1.2670	0.001	0.032
9-Oct-08	0.047	3.0500	0.004	0.1800	1.2660	0.001	0.035
16-Oct-08	0.048	3.0510	0.004	0.1850	1.2700	0.002	0.036
23-Oct-08	0.048	3.0550	0.005	0.1860	1.2600	0.001	0.037
30-Oct-08	0.049	3.0560	0.005	0.1890	1.2700	0.002	0.032
6-Nov-08	0.049	3.0550	0.005	0.1800	1.2400	0.002	0.035
13-Nov-08	0.05	3.0550	0.004	0.1900	1.3000	0.003	0.036
20-Nov-08	0.05	3.0640	0.004	0.2000	1.3400	0.003	0.037
27-Nov-08	0.05	3.0650	0.005	0.2400	1.3500	0.001	0.04
4-Dec-08	0.052	3.0620	0.0045	0.2200	1.3500	0.002	0.041
11-Dec-08	0.053	3.0520	0.005	0.2400	1.3900	0.002	0.042
18-Dec-08	0.054	3.0700	0.003	0.2500	1.3500	0.002	0.045
25-Dec-08	0.055	3.0660	0.0055	0.2600	1.3400	0.003	0.045
1-Jan-09	0.053	3.0650	0.005	0.2200	1.3600	0.003	0.041
8-Jan-09	0.052	3.0550	0.004	0.2100	1.3800	0.002	0.042
15-Jan-09	0.06	3.0600	0.005	0.2300	1.3400	0.001	0.046
22-Jan-09	0.051	3.0610	0.005	0.2400	1.3400	0.003	0.045
29-Jan-09	0.065	3.0680	0.004	0.2800	1.3900	0.002	0.045
5-Feb-09	0.052	3.0640	0.004	0.2400	1.4000	0.002	0.046
12-Feb-09	0.061	3.0700	0.003	0.2100	1.4500	0.004	0.04
19-Feb-09	0.05	3.0740	0.004	0.1980	1.4700	0.003	0.035
26-Feb-09	0.045	3.0450	0.005	0.2000	1.4800	0.004	0.036
5-Mar-09	0.04	3.0400	0.003	0.2200	1.4900	0.0045	0.037

12-Mar-09	0.045	3.0450	0.004	0.2500	1.5000	0.004	0.04
19-Mar-09	0.055	3.0660	0.005	0.2200	1.5500	0.003	0.041
26-Mar-09	0.053	3.0650	0.0045	0.2300	1.5500	0.004	0.042
2-Apr-09	0.052	3.0550	0.004	0.2400	1.5000	0.0045	0.045
9-Apr-09	0.06	3.0600	0.004	0.2500	1.5200	0.0035	0.05
16-Apr-09	0.051	3.0610	0.004	0.2400	1.5400	0.004	0.05
24-Apr-09	0.065	3.0680	0.005	0.2200	1.5400	0.0045	0.055
7-May-09	0.052	3.0640	0.005	0.2400	1.5600	0.0045	0.054
14-May-09	0.061	3.0700	0.003	0.2100	1.6000	0.004	0.056
21-May-09	0.05	3.0740	0.003	0.2600	1.6500	0.004	0.06
28-May-09	0.045	3.0450	0.003	0.2000	1.4000	0.003	0.05
4-Jun-09	0.04	3.0400	0.002	0.1900	1.3400	0.002	0.035
11-Jun-09	0.045	3.0450	0.002	0.1800	1.3000	0.001	0.035
Highest Concentration	0.0650	3.0740	0.0060	0.2800	1.6500	0.0060	0.0320
Lowest Concentration	0.0400	3.0400	0.0020	0.1760	1.4000	0.0010	0.5500

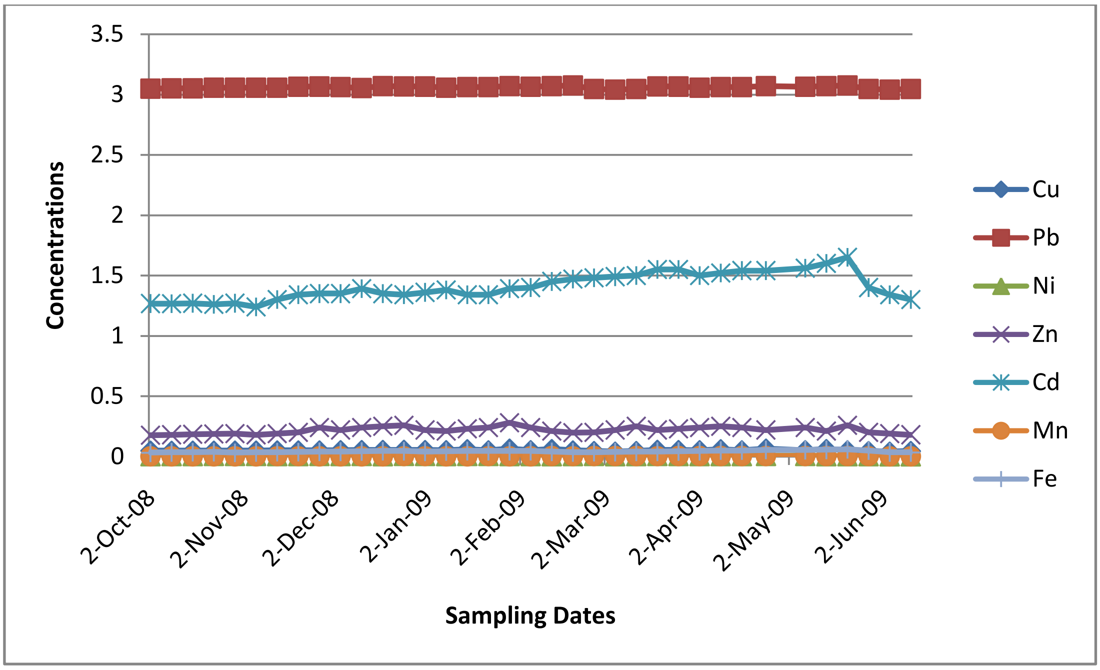


Figure 4.6 **Observed Trace Elements concentrations at Shahu Blood Bank Corner**

It is seen from Table 4.4 and Figure 4.6 that concentrations of trace elements like Pb, Cd at Shahu Blood Bank Corner are above Threshold Limit Values (TLVs) set by US EPA standard limit which are harmful to citizens of Kolhapur city. Other trace element concentrations are below standard but their existence in the atmosphere of Kolhapur city should not be ignored. The presence of excess concentrations of Pb and Cd may be coming from mostly the transportation sector, which is high in the city of Kolhapur. Other sources like non ferrous industries may also be contributing to Pb and Cd concentrations which will be found out with the help of the model.

Table 4.5 Observed concentration of trace elements in µg / m^3 at Gokul Shirgaon MIDC

DATE	Cu	Pb	Ni	Zn	Cd	Mn	Fe
2-Oct-08	2.0500	0.1020	0.0870	0.35	0.0030	0.0001	1.4000
9-Oct-08	2.0300	0.1020	0.0870	0.35	0.0040	0.0001	1.4000
16-Oct-08	2.0400	0.1040	0.0870	0.36	0.0020	0.0001	1.4500
23-Oct-08	2.0500	0.1030	0.0870	0.37	0.0040	0.0001	1.4200
30-Oct-08	2.0900	0.1050	0.0890	0.36	0.0050	0.0001	1.4600
6-Nov-08	2.0900	0.1070	0.0920	0.37	0.0060	0.0001	1.4500
13-Nov-08	2.0500	0.1060	0.0910	0.36	0.0050	0.0001	1.4400
20-Nov-08	2.0700	0.1050	0.0920	0.38	0.0060	0.0001	1.4600
27-Nov-08	2.0800	0.1040	0.0900	0.37	0.0060	0.0001	1.4500
4-Dec-08	2.0600	0.1050	0.0900	0.35	0.0040	0.0001	1.4700
11-Dec-08	2.0500	0.1060	0.0900	0.36	0.0050	0.0001	1.4700
18-Dec-08	2.0700	0.1080	0.0900	0.37	0.0060	0.0001	1.4900
25-Dec-08	2.0900	0.1090	0.0910	0.39	0.0070	0.00015	1.4800
1-Jan-09	2.0800	0.1000	0.0910	0.38	0.0080	0.0001	1.4900
8-Jan-09	2.0900	0.1200	0.0910	0.39	0.0080	0.0001	1.5000
15-Jan-09	2.0900	0.1150	0.0910	0.39	0.0070	0.00015	1.4900
22-Jan-09	2.1000	0.1100	0.0930	0.4	0.0090	0.00015	1.4900
29-Jan-09	2.1000	0.1200	0.0950	0.41	0.0090	0.0001	1.4800
5-Feb-09	2.1100	0.1250	0.0940	0.42	0.0090	0.00015	1.4700
12-Feb-09	2.1000	0.1110	0.0960	0.43	0.0080	0.00015	1.6000
19-Feb-09	2.1300	0.1110	0.0940	0.41	0.0100	0.0001	1.6500
26-Feb-09	2.1200	0.1120	0.0950	0.44	0.0100	0.0001	1.7000
5-Mar-09	2.1400	0.1140	0.0960	0.45	0.0120	0.0001	1.7500

12-Mar-09	2.1500	0.1130	0.0970	0.44	0.0150	0.0001	1.6500
19-Mar-09	2.1900	0.1130	0.0960	0.45	0.0120	0.0001	1.5400
26-Mar-09	2.2000	0.1120	0.0950	0.46	0.0120	0.0001	1.6000
2-Apr-09	2.1700	0.1040	0.0960	0.48	0.0120	0.0001	1.6800
9-Apr-09	2.2000	0.1200	0.0960	0.42	0.0120	0.0001	1.6500
16-Apr-09	2.2000	0.1140	0.0970	0.44	0.0130	0.0001	1.8900
24-Apr-09	2.1500	0.1120	0.0970	0.44	0.0110	0.0001	1.9000
7-May-09	2.1400	0.1150	0.0980	0.4	0.0110	0.0001	1.6500
14-May-09	2.1000	0.1150	0.0980	0.4	0.0100	0.00015	1.8500
21-May-09	2.1200	0.1130	0.0880	0.39	0.0090	0.00015	1.8500
28-May-09	2.0400	0.1140	0.0900	0.38	0.0090	0.0001	1.9000
4-Jun-09	2.0000	0.1190	0.0940	0.37	0.0100	0.0001	1.9000
11-Jun-09	2.1000	0.1140	0.0950	0.36	0.0110	0.0001	1.9000
Highest Concentration	2.2000	0.1250	0.0980	0.4800	0.0150	0.0002	1.9000
Lowest Concentration	2.0000	0.1000	0.0870	0.3500	0.0020	0.0001	1.4000

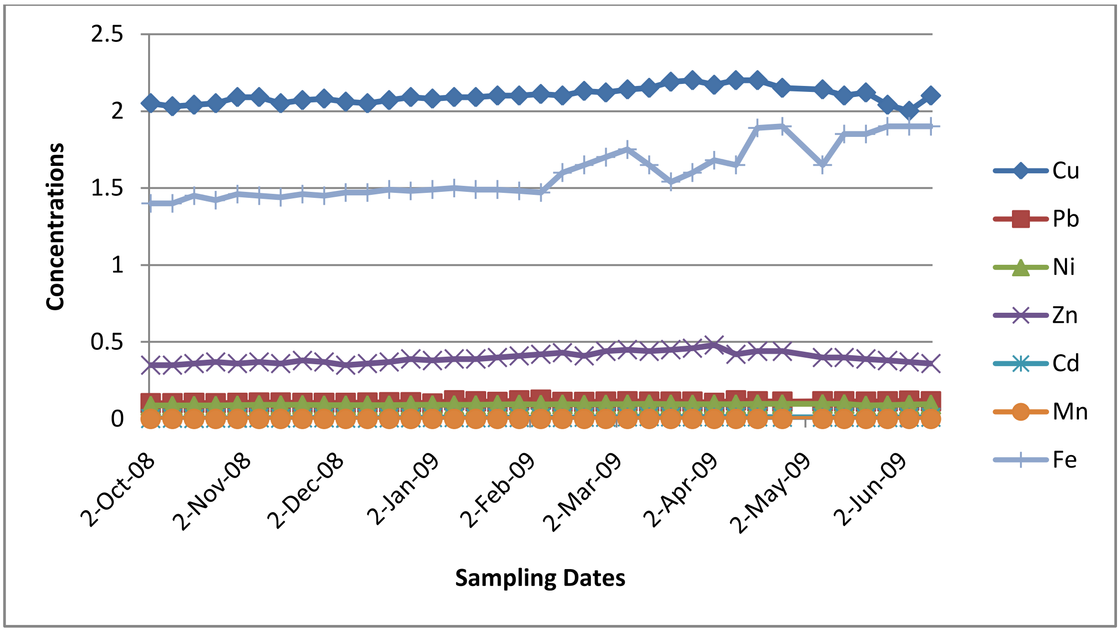


Figure 4.7 Observed Trace Elements concentrations at Gokul Shirgaon

It is seen from Table 4.5 and Figure 4.7 that concentrations of trace element like Cu at Gokul Shirgaon are above TLVs, which are harmful. Other trace element concentrations are below standard but their existence in the atmosphere should not be ignored. Trace elements like Pb, Ni and Fe are closer to limit. The presence of excess concentration of Cu may be coming from mostly the copper plating and pot-manufacturing unit. Other trace elements source may be transportation sector and battery refilling and charging units as well as automobile service centers, which is high in Gokul Shirgaon MIDC.

Table 4.6 Observed concentration of trace elements in µg / m^3 at Shiroli MIDC

DATE	Cu	Pb	Ni	Zn	Cd	Mn	Fe
2-Oct-08	1.4500	0.0490	0.1060	0.8370	0.0020	0.004	2.0100
9-Oct-08	1.5000	0.0480	0.1070	0.8450	0.0020	0.006	2.0100
16-Oct-08	1.5500	0.0480	0.1080	0.8500	0.0020	0.009	2.0100
23-Oct-08	1.500	0.0450	0.1000	0.8600	0.0010	0.01	2.0100

30-Oct-08	1.9700	0.0980	0.1120	0.8670	0.0030	0.024	2.0200
6-Nov-08	1.9700	0.0650	0.1150	0.8700	0.0030	0.025	2.0300
13-Nov-08	1.9800	0.0550	0.1140	0.8800	0.0030	0.03	2.0400
20-Nov-08	2.0000	0.0750	0.1150	0.8600	0.0030	0.025	2.0400
27-Nov-08	2.0100	0.0830	0.1150	0.8890	0.0040	0.026	2.0500
4-Dec-08	2.1500	0.0800	0.1160	0.8800	0.0040	0.02	2.0500
11-Dec-08	2.1000	0.0800	0.1140	0.8500	0.0040	0.02	2.0900
18-Dec-08	2.2000	0.0850	0.1170	0.8800	0.0030	0.025	2.0600
25-Dec-08	2.2200	0.0890	0.1170	0.8850	0.0040	0.029	2.0900
1-Jan-09	2.2500	0.0900	0.1150	0.9000	0.0030	0.03	2.0800
8-Jan-09	2.2500	0.0990	0.1140	0.9500	0.0030	0.03	2.0900
15-Jan-09	2.4000	0.1000	0.1130	0.9500	0.0040	0.031	2.1000
22-Jan-09	2.5000	0.1200	0.1190	0.9540	0.0050	0.031	2.1500
29-Jan-09	2.6000	0.1500	0.1900	0.9400	0.0040	0.032	2.1400
5-Feb-09	2.5000	0.1400	0.2000	0.9300	0.0030	0.035	2.1800
12-Feb-09	2.4000	0.1300	0.2450	0.9400	0.0050	0.035	2.1800
19-Feb-09	2.4500	0.1500	0.2430	0.9450	0.0060	0.03	2.1900
26-Feb-09	2.5000	0.1400	0.2500	0.9300	0.0050	0.039	2.2000
5-Mar-09	2.5500	0.1300	0.2400	0.9250	0.0050	0.035	2.1900
12-Mar-09	2.9000	0.1500	0.2700	1.0000	0.0070	0.034	2.2100
19-Mar-09	3.7000	0.1900	0.2850	1.2540	0.0065	0.035	2.2000
26-Mar-09	3.0000	0.2000	0.2900	1.3000	0.0070	0.065	2.2200
2-Apr-09	2.5000	0.2500	0.3000	1.4000	0.0070	0.06	2.2000
9-Apr-09	2.7500	0.2000	0.3000	1.3000	0.0080	0.065	2.2100
16-Apr-09	2.7000	0.2500	0.3470	1.2600	0.0080	0.07	2.2200
24-Apr-09	3.8000	0.2500	0.3500	1.2500	0.0050	0.065	2.1000

7-May-09	3.6000	0.2200	0.3000	1.2000	0.0040	0.07	2.1500
14-May-09	3.7000	0.2000	0.3000	1.2400	0.0060	0.075	2.1400
21-May-09	3.5000	0.1900	0.2980	1.2400	0.0060	0.025	2.1300
28-May-09	3.0000	0.1200	0.2600	1.2500	0.0050	0.03	2.1200
4-Jun-09	2.9000	0.1000	0.2500	1.2500	0.0040	0.04	2.1400
11-Jun-09	2.5000	0.1000	0.2400	1.1000	0.0030	0.05	2.1900
Highest Concentration	3.8000	0.2500	0.3500	1.4000	0.0080	0.075	2.2000
Lowest Concentration	1.4500	0.0450	0.1060	0.8370	0.0010	0.0040	2.0100

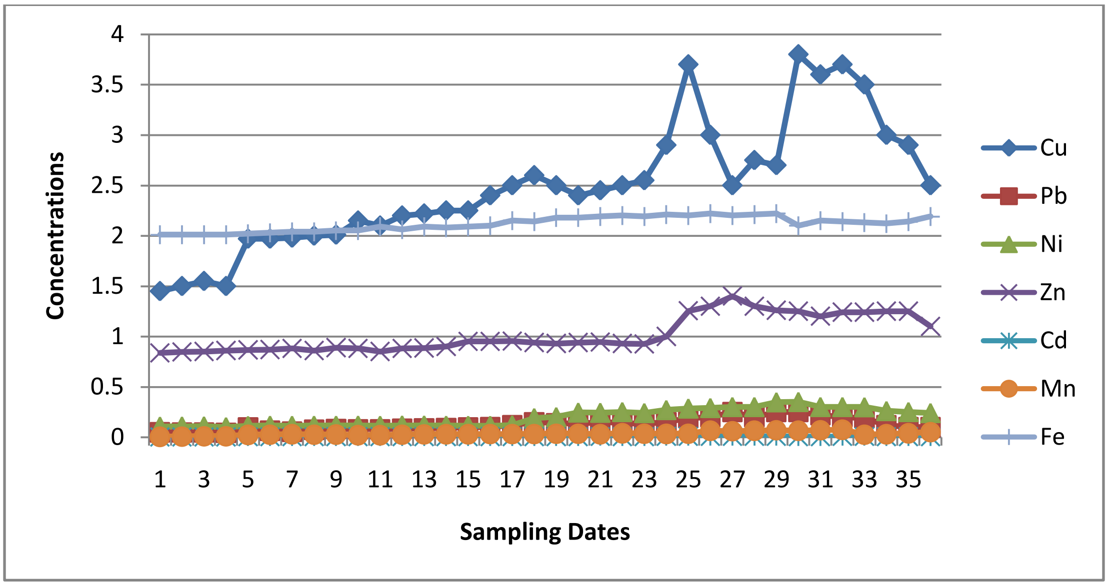


Figure 4.8 Observed Trace Elements concentrations at Shiroli MIDC

It is seen from Table 4.6 and Figure 4.8 that concentrations of trace elements like Cu, Pb, Ni and Fe at Shiroli MIDC are above TLVs. Other trace element concentrations like Cd and Mn are below standard. Zn concentrations are closer to limits but should not be ignored. The possible source for higher concentrations may be foundries, textile industries, stone crushing units and transportation sector.

4.5 PREDICTED CHEMICAL CHARACTERIZATION OF TRACE ELEMENTS IN µG / M^3 BY US EPA PMF MODEL

Observed concentration of trace elements at all selected sampling locations were given as an input to US EPA PMF model for prediction of concentrations of Trace elements of study interest. Model generated the concentration of trace elements, which were predicted at location on same sampling date. Another input to model was Uncertainty values of trace elements observed during sampling at selected locations. Uncertainty values were calculated on the basis Method Detection Limit (MDL) of each trace element set by US EPA PMF model. As per the guidelines of US EPA PMF model, predicted concentrations of trace elements should not exceed ±10% with respect to observed concentrations of trace elements. Table 4.7, 4.8 and 4.9 shows the predicted concentrations of Trace elements at each sampling locations.

Table 4.7 Predicted Concentration of Trace Elements in µg / m^3 at Shahu Blood Bank Corner

DATE	Cu	Pb	Ni	Zn	Cd	Mn	Fe
2-Oct-08	0.0470	2.9000	0.0039	0.1950	1.2500	0.0010	0.0320
9-Oct-08	0.0470	2.8500	0.0035	0.2000	1.2500	0.0012	0.0350
16-Oct-08	0.0410	2.6000	0.0040	0.1800	1.2000	0.0024	0.0360
23-Oct-08	0.0520	2.9500	0.0045	0.1950	1.2500	0.0010	0.0370
30-Oct-08	0.0460	3.0000	0.0041	0.2050	1.3500	0.0027	0.0320
6-Nov-08	0.0500	2.9500	0.0046	0.2000	1.3500	0.0025	0.0350
13-Nov-08	0.0490	2.9000	0.0045	0.2050	1.4000	0.0030	0.0360
20-Nov-08	0.0470	3.0000	0.0037	0.2050	1.3200	0.0018	0.0370
27-Nov-08	0.0540	3.3000	0.0044	0.2200	1.4000	0.0010	0.0400
4-Dec-08	0.0460	2.8000	0.0032	0.2050	1.3000	0.0027	0.0410
11-Dec-08	0.0550	3.3000	0.0066	0.2200	1.5000	0.0025	0.0420
18-Dec-08	0.0560	3.2000	0.0031	0.2400	1.4300	0.0018	0.0450

25-Dec-08	0.0630	3.6000	0.0040	0.2650	1.7000	0.0031	0.0450
1-Jan-09	0.0540	3.5000	0.0043	0.2450	1.5000	0.0024	0.0410
8-Jan-09	0.0490	2.9500	0.0039	0.2100	1.3500	0.0010	0.0420
15-Jan-09	0.0490	3.0000	0.0043	0.2000	1.2800	0.0011	0.0460
22-Jan-09	0.0510	2.9500	0.0042	0.2200	1.4000	0.0027	0.0450
29-Jan-09	0.0550	3.4000	0.0034	0.2400	1.5000	0.0023	0.0450
5-Feb-09	0.0510	3.2500	0.0039	0.2350	1.4800	0.0026	0.0460
12-Feb-09	0.0530	3.0000	0.0038	0.2100	1.4000	0.0029	0.0400
19-Feb-09	0.0490	3.0000	0.0040	0.2050	1.3500	0.0028	0.0350
26-Feb-09	0.0440	2.7500	0.0036	0.2000	1.3200	0.0032	0.0360
5-Mar-09	0.0480	3.0500	0.0038	0.2100	1.3500	0.0023	0.0370
12-Mar-09	0.0500	2.9000	0.0044	0.2050	1.3800	0.0028	0.0400
19-Mar-09	0.0600	3.5000	0.0048	0.2500	1.6500	0.0027	0.0410
26-Mar-09	0.0490	2.8000	0.0033	0.2050	1.3000	0.0024	0.0420
2-Apr-09	0.0490	2.9000	0.0043	0.2000	1.3000	0.0023	0.0450
9-Apr-09	0.0570	3.2000	0.0040	0.2400	1.6000	0.0038	0.0500
16-Apr-09	0.0530	3.1500	0.0047	0.2200	1.5800	0.0022	0.0500
24-Apr-09	0.0590	3.4000	0.0044	0.2500	1.6200	0.0036	0.0550
7-May-09	0.0550	3.3000	0.0035	0.2500	1.6000	0.0033	0.0540
14-May-09	0.0540	3.0500	0.0039	0.2150	1.4000	0.0024	0.0400
21-May-09	0.0550	3.3000	0.0037	0.2400	1.5800	0.0034	0.0500
28-May-09	0.0480	2.8000	0.0032	0.2100	1.3800	0.0032	0.0400
4-Jun-09	0.0400	2.4000	0.0026	0.1850	1.1500	0.0025	0.0350
11-Jun-09	0.0480	2.3000	0.0020	0.1800	1.1000	0.0013	0.0350

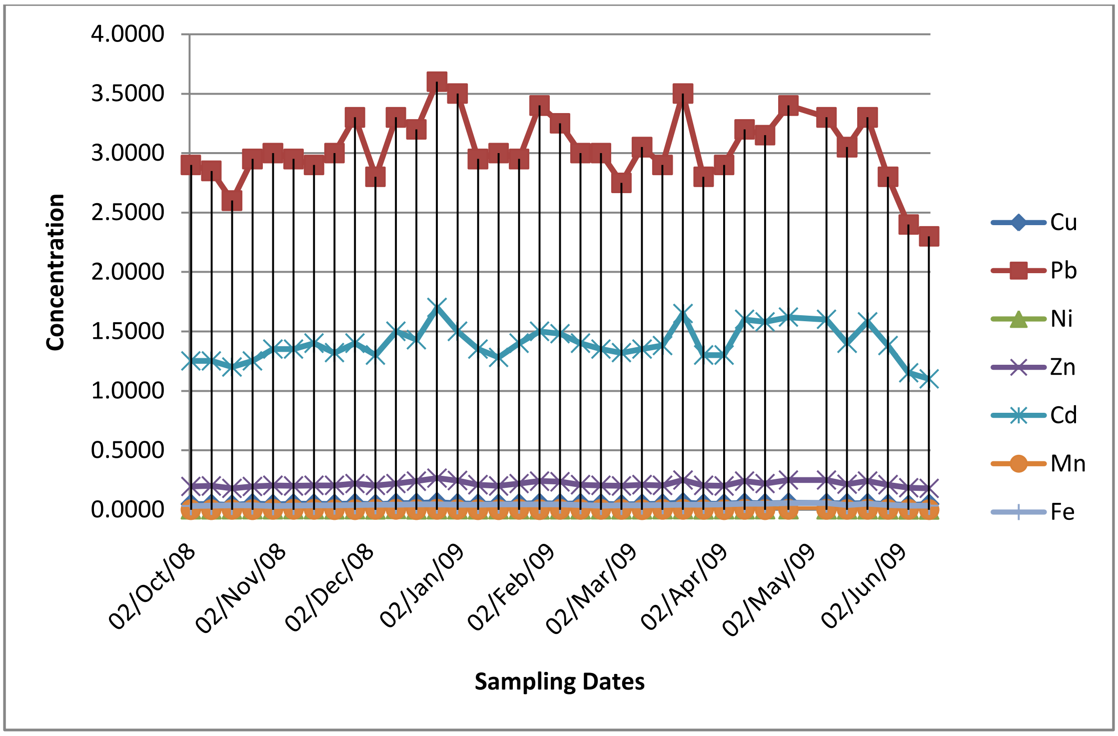


Figure 4.9 **Predicted Trace Elements concentrations at Shahu Blood Bank Corner**

Table 4.8 shows Predicted Concentration of Trace Elements at Gokul Shirgaon MIDC.

Table 4.8 **Predicted Concentration of Trace Elements in µg / m^3 at Gokul Shirgaon MIDC**

DATE	Cu	Pb	Ni	Zn	Cd	Mn	Fe
2-Oct-08	1.5500	0.0800	0.0680	0.3000	0.0040	0.00007	1.2000
9-Oct-08	1.9000	0.0980	0.0860	0.5000	0.0040	0.00010	1.4000
16-Oct-08	1.5000	0.0780	0.0650	0.2800	0.0025	0.00010	1.0000
23-Oct-08	1.9000	0.0980	0.0840	0.3600	0.0040	0.00009	1.4000
30-Oct-08	1.7500	0.0950	0.0750	0.3200	0.0070	0.00010	1.3200
6-Nov-08	1.8800	0.1000	0.0820	0.3300	0.0060	0.00012	1.4000
13-Nov-08	1.8400	0.0980	0.0800	0.3200	0.0065	0.00009	1.5000

20-Nov-08	2.0000	0.1200	0.0880	0.3700	0.0065	0.00010	1.5200
27-Nov-08	2.2000	0.1020	0.0880	0.3900	0.0060	0.00011	1.4500
4-Dec-08	2.0000	0.1030	0.0860	0.3600	0.0040	0.00010	1.4500
11-Dec-08	2.0000	0.1020	0.0860	0.3700	0.0055	0.00010	1.4800
18-Dec-08	2.1500	0.1020	0.0940	0.4000	0.0070	0.00010	1.6200
25-Dec-08	2.3000	0.1120	0.1000	0.4300	0.0060	0.00015	1.6200
1-Jan-09	2.3500	0.1200	0.1040	0.4200	0.0055	0.00015	1.7000
8-Jan-09	2.2000	0.1240	0.0950	0.4200	0.0070	0.00014	1.5500
15-Jan-09	2.1800	0.1150	0.0920	0.4000	0.0060	0.00013	1.5500
22-Jan-09	2.4000	0.1120	0.1050	0.4300	0.0055	0.00016	1.7000
29-Jan-09	2.1000	0.1220	0.0940	0.4200	0.0100	0.00010	1.6500
5-Feb-09	2.3000	0.1100	0.1000	0.4400	0.0085	0.00016	1.6200
12-Feb-09	2.1000	0.1220	0.0920	0.4200	0.0080	0.00013	1.5000
19-Feb-09	2.1200	0.1100	0.0940	0.4100	0.0085	0.00013	1.6000
26-Feb-09	2.2800	0.1120	0.0850	0.4300	0.0055	0.00013	1.6200
5-Mar-09	1.9500	0.1150	0.0950	0.4100	0.0130	0.00010	1.6200
12-Mar-09	2.000	0.1060	0.1020	0.4100	0.0060	0.00010	1.6000
19-Mar-09	1.8000	0.1040	0.0970	0.3700	0.0070	0.00012	1.3800
26-Mar-09	2.1000	0.1000	0.1020	0.4200	0.0130	0.00010	1.8000
2-Apr-09	2.1800	0.1160	0.1000	0.4600	0.0100	0.00011	1.7200
9-Apr-09	2.2000	0.1170	0.0950	0.4300	0.0110	0.00012	1.7000
16-Apr-09	2.3200	0.1200	0.1020	0.4300	0.0060	0.00012	1.8000
24-Apr-09	2.3800	0.1220	0.1020	0.4500	0.0085	0.00013	1.7800
7-May-09	2.1500	0.1140	0.0950	0.4000	0.0090	0.00011	1.7000
14-May-09	2.3500	0.1240	0.1060	0.4400	0.0110	0.00011	1.9000
21-May-09	2.1500	0.1150	0.0950	0.3900	0.0090	0.00011	1.7200

28-May-09	2.1000	0.1120	0.0920	0.3900	0.0090	0.00010	1.6500
4-Jun-09	2.1000	0.1100	0.0950	0.3600	0.0070	0.00011	1.7000
11-Jun-09	1.9600	0.1040	0.0880	0.3500	0.0110	0.00010	1.5000

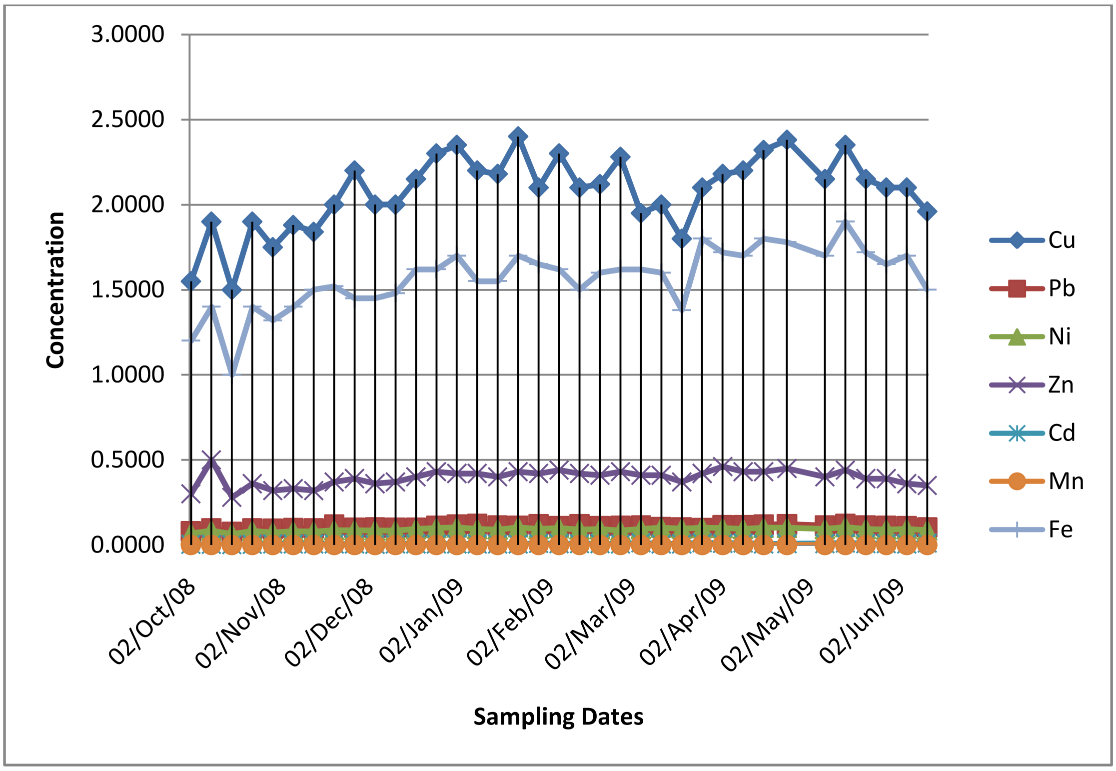


Figure 4.10 Observed Trace Elements concentrations at Gokul Shirgaon

The following Table 4.9 shows Predicted Concentration of Trace Elements in µg / m^3 at Shiroli MIDC

Table 4.9 Predicted Concentration of Trace Elements in µg / m^3 at Shiroli MIDC

DATE	Cu	Pb	Ni	Zn	Cd	Mn	Fe
2-Oct-08	1.5000	0.0490	0.1100	0.7000	0.0020	0.0020	1.7000
9-Oct-08	1.5000	0.0480	0.0700	0.7200	0.0020	0.0060	1.7500
16-Oct-08	1.6000	0.0480	0.0950	0.7700	0.0020	0.0090	1.8000

23-Oct-08	1.2500	0.0450	0.0900	0.6700	0.0010	0.0120	1.6500
30-Oct-08	2.1500	0.0980	0.1300	0.9700	0.0030	0.0220	2.3000
6-Nov-08	2.0000	0.0650	0.1300	0.8200	0.0032	0.0200	1.8000
13-Nov-08	1.9500	0.0550	0.1350	0.8400	0.0029	0.0250	2.0000
20-Nov-08	2.1500	0.0750	0.1250	0.8200	0.0034	0.0200	1.800
27-Nov-08	2.2500	0.0830	0.1350	0.9100	0.0031	0.0240	2.0700
4-Dec-08	2.1500	0.0800	0.1350	0.9400	0.0032	0.0200	2.1500
11-Dec-08	2.1000	0.0800	0.1200	0.8500	0.0035	0.0240	2.1500
18-Dec-08	2.0500	0.0850	0.1400	0.9200	0.0027	0.0230	2.1000
25-Dec-08	2.2900	0.0890	0.1450	0.9000	0.0039	0.0310	1.9500
1-Jan-09	2.2000	0.0900	0.1400	0.8200	0.0039	0.0290	1.7500
8-Jan-09	2.0500	0.0990	0.1400	0.8900	0.0030	0.0280	1.9500
15-Jan-09	2.1500	0.1000	0.1550	0.9200	0.0031	0.0190	2.0000
22-Jan-09	2.3000	0.1200	0.1570	0.9500	0.0039	0.0220	2.0500
29-Jan-09	2.6300	0.1500	0.1800	1.0200	0.0042	0.0350	2.1500
5-Feb-09	2.7500	0.1400	0.1950	1.1000	0.0041	0.0380	2.3900
12-Feb-09	2.5500	0.1300	0.2150	1.0900	0.0039	0.0420	2.200
19-Feb-09	2.4000	0.1500	0.1850	1.0200	0.0036	0.0320	2.1900
26-Feb-09	2.6000	0.1400	0.2100	1.0200	0.0046	0.0420	2.0000
5-Mar-09	2.6500	0.1300	0.1950	1.0200	0.0042	0.0310	2.1000
12-Mar-09	3.3900	0.1500	0.2400	1.3000	0.0060	0.0400	2.5500
19-Mar-09	2.9800	0.1900	0.2200	1.1000	0.0050	0.0420	2.1000
26-Mar-09	3.3000	0.2000	0.2800	1.1200	0.0060	0.0610	2.0000
2-Apr-09	3.4000	0.1700	0.2800	1.3000	0.0058	0.0550	2.5000
9-Apr-09	3.4500	0.1700	0.2750	1.0900	0.0059	0.0620	1.9000
16-Apr-09	3.5000	0.1700	0.2900	1.3100	0.0060	0.0610	2.4500

24-Apr-09	3.4000	0.2000	0.3100	1.1200	0.0069	0.0650	1.8000
7-May-09	3.5000	0.1700	0.2450	1.2400	0.0057	0.0510	2.2500
14-May-09	3.4000	0.1700	0.2800	1.2200	0.0064	0.0610	2.4000
21-May-09	2.8000	0.1500	0.2050	1.2900	0.0059	0.0350	2.7000
28-May-09	2.8000	0.1500	0.2090	1.0000	0.0050	0.0420	1.9000
4-Jun-09	2.5000	0.1500	0.2000	1.1300	0.0045	0.0390	2.4000
11-Jun-09	2.8000	0.1000	0.1700	1.1300	0.0035	0.0310	2.5700

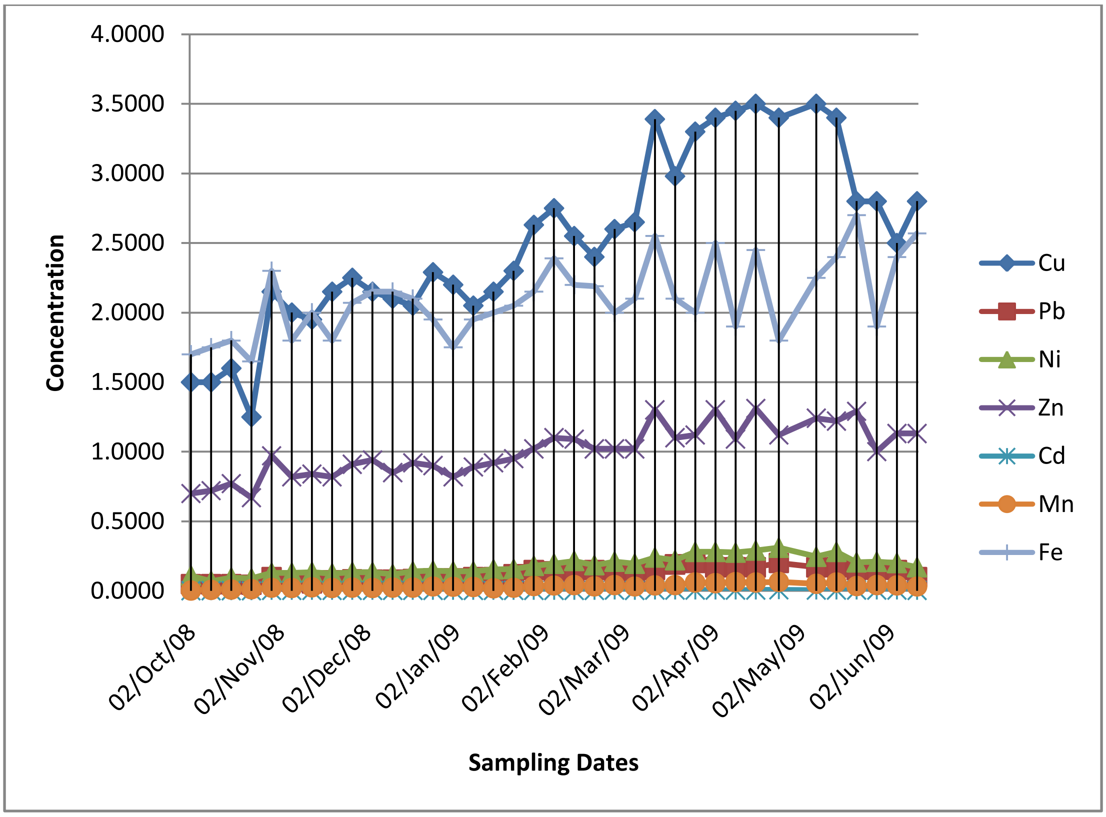


Figure 4.11 Observed Trace Elements concentrations at Shiroli MIDC

The predicted concentration of trace elements from the model and experimental observation of trace elements were taken together and compared to see any variations in values such that both readings match with permissible limit ± 10%. Multiple iterations were carried out. This ensures applicability of model for further studies i.e. source apportionment. If there is a deviation beyond ±10%, resampling is done for specific trace element and again given as input to model. PMF model can be run for many times to arrive at minimum deviations. Model validation is must and should be accurate to arrive at specific conclusions on source apportionment study at any vicinity and in any air pollution episodes, and condition.

It can be inferred by comparison of the values in Table 4.7, 4.8 and 4.9 to Table 4.10, 4.11 and 4.12 respectively, Predicted concentrations of trace elements are within the range of ± 10% in comparison with observed concentrations of Trace elements at each sampling locations. Hence, US EPA PMF model is successfully applied to present study. The following Figure 4.12 to 4.32 presents comparison of concentrations of each trace element at each sampling locations.

4.6 OBSERVED CONCENTRATION VERSUS PREDICTED CONCENTRATIONS

4.6.1 Observed concentration versus predicted concentrations at Shahu Blood Bank Corner

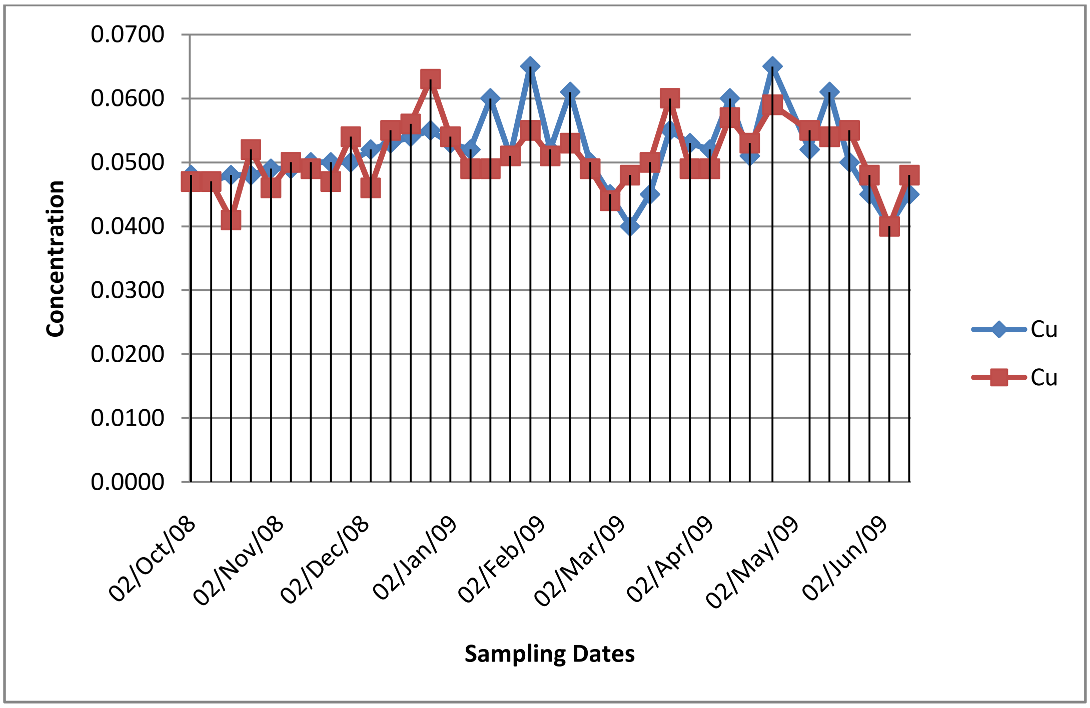


Figure 4.12 Observed versus Predicted Concentration of Cu at Shahu Blood Bank Corner

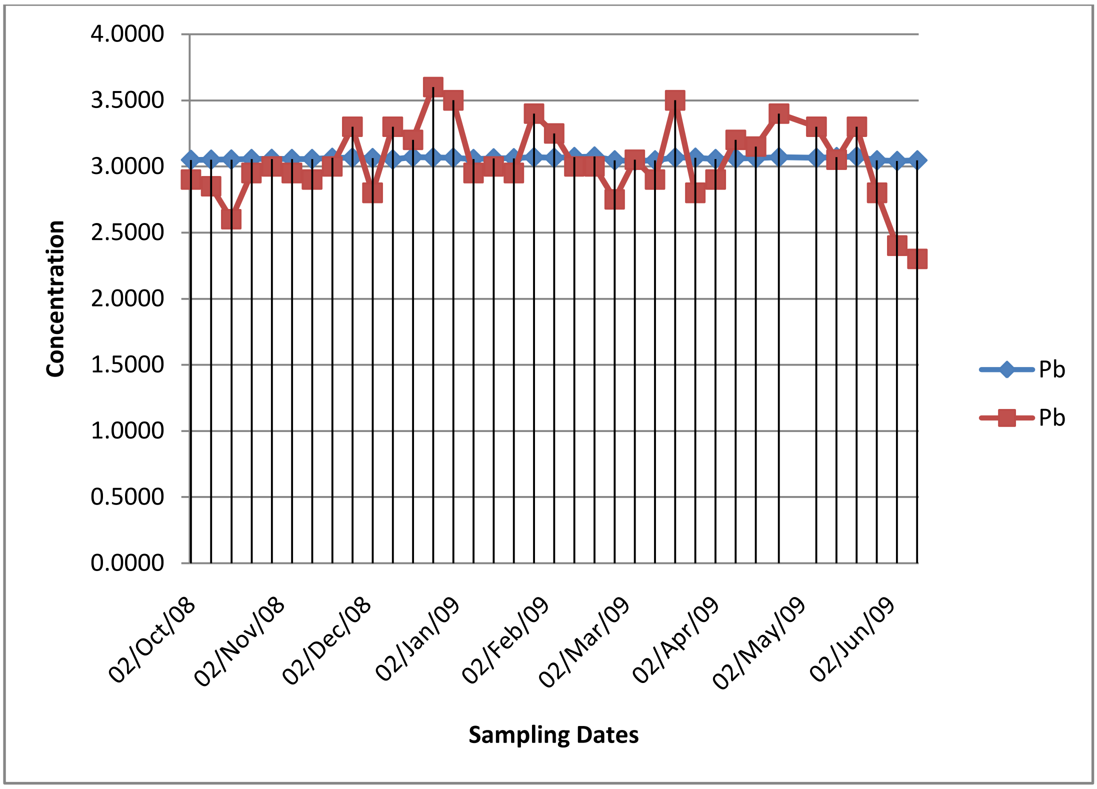


Figure 4.13 Observed versus Predicted Concentration of Pb at Shahu Blood Bank Corner

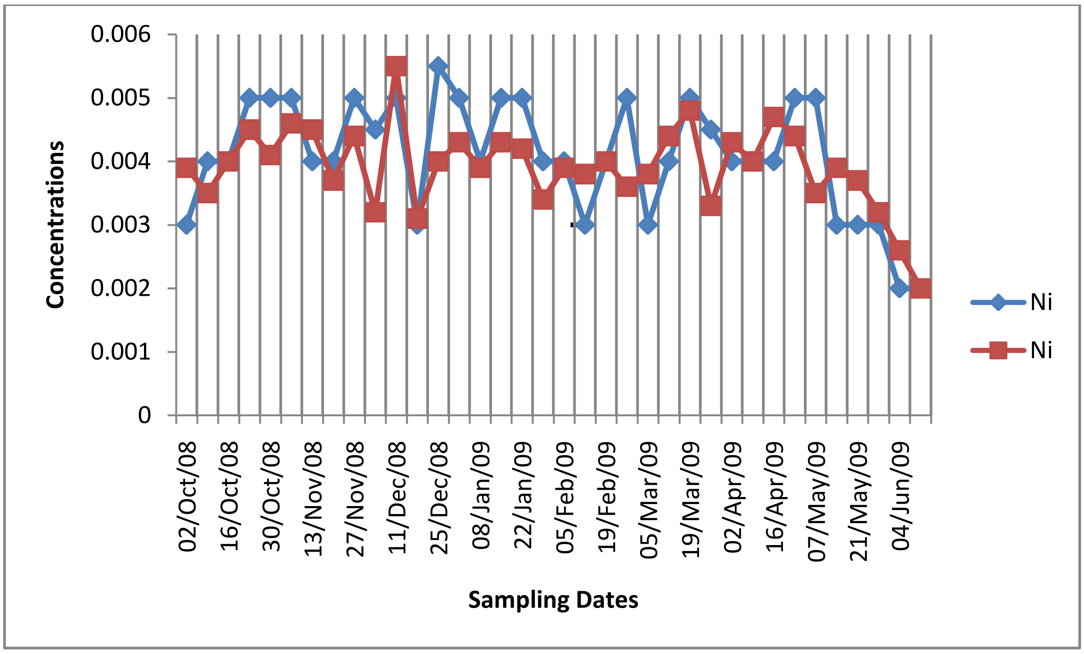


Figure 4.14 Observed versus Predicted Concentration of Ni at Shahu Blood Bank Corner

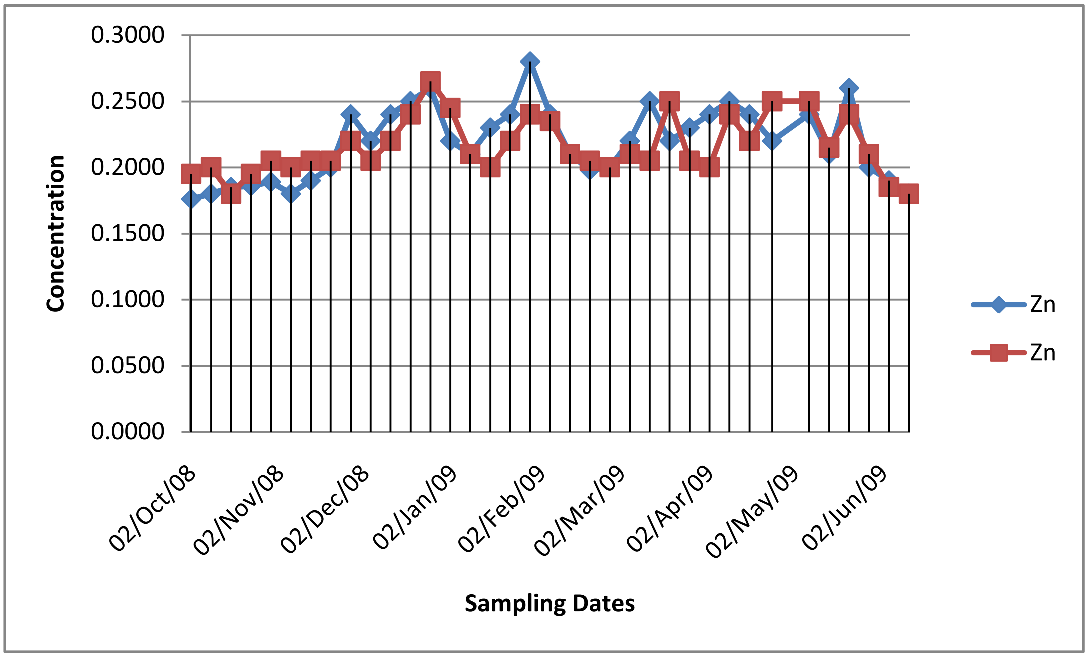


Figure 4.15 **Observed versus Predicted Concentration of Zn at Shahu Blood Bank Corner**

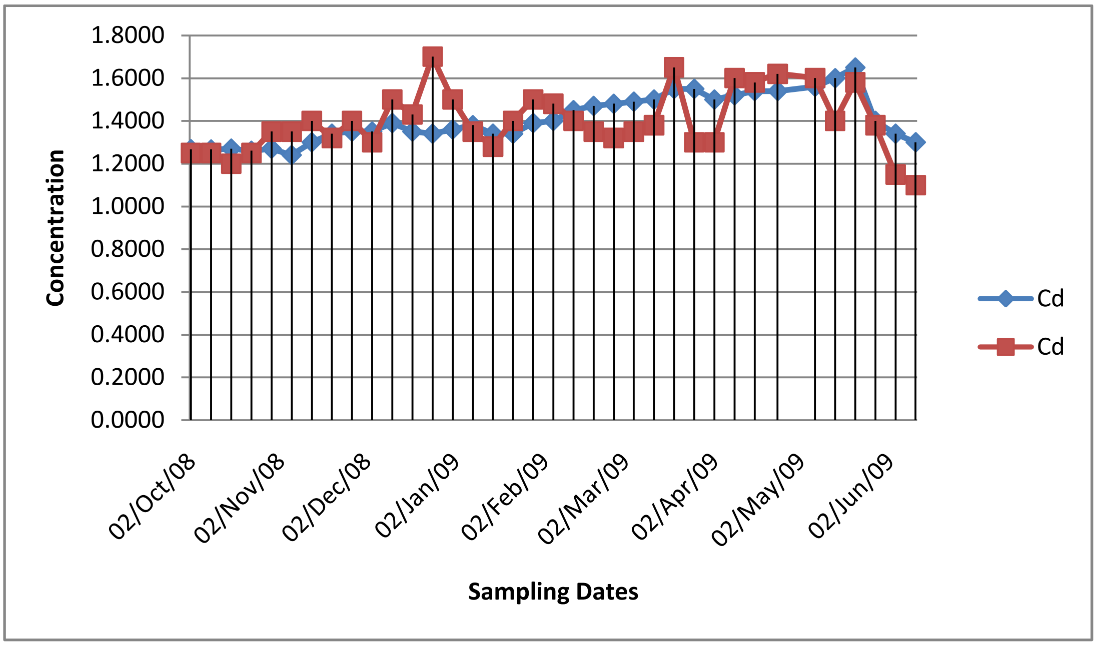


Figure 4.16 **Observed versus Predicted Concentration of Cd at Shahu Blood Bank Corner**

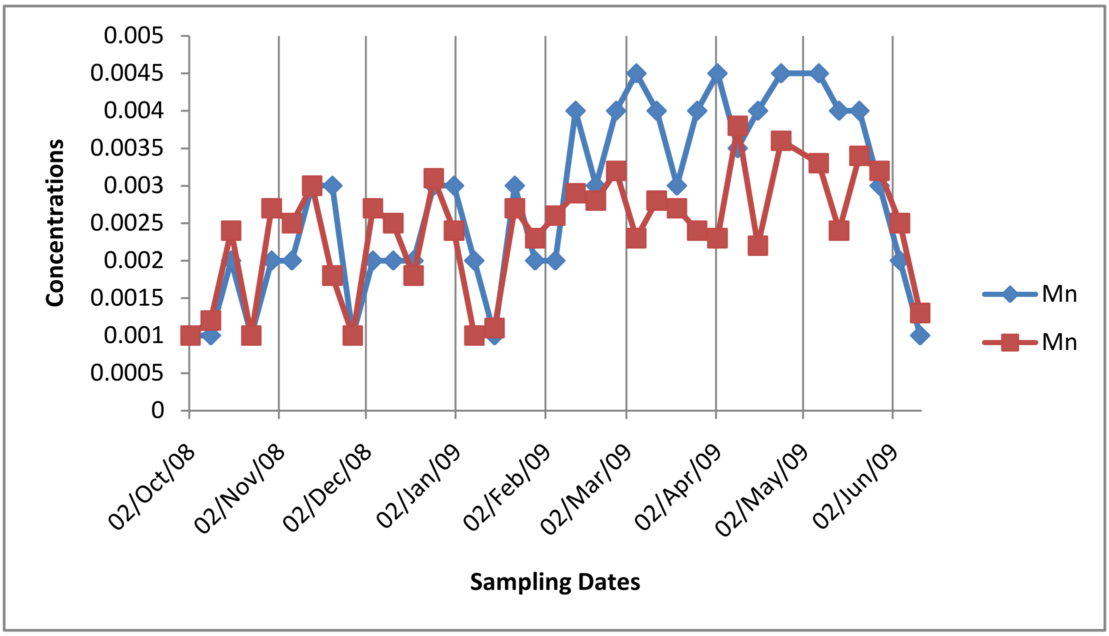


Figure 4.17 Observed versus Predicted Concentration of Mn at Shahu Blood Bank Corner

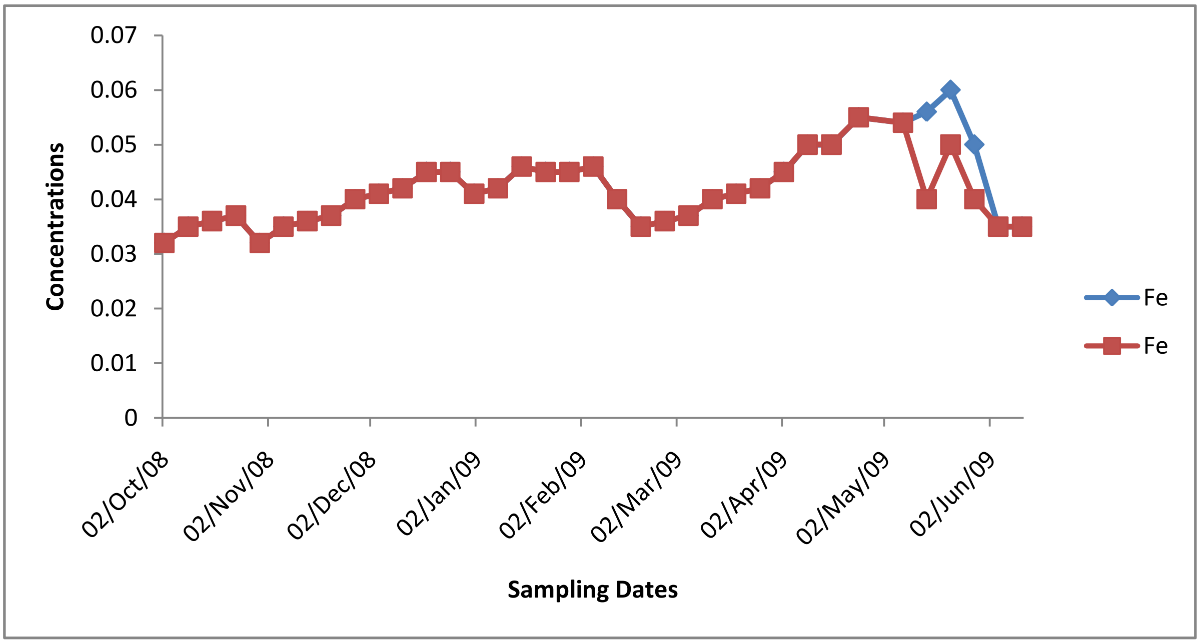


Figure 4.18 Observed versus Predicted Concentration of Fe at Shahu Blood Bank Corner

4.6.2 Observed versus Predicted Concentration at Gokul Shirgaon

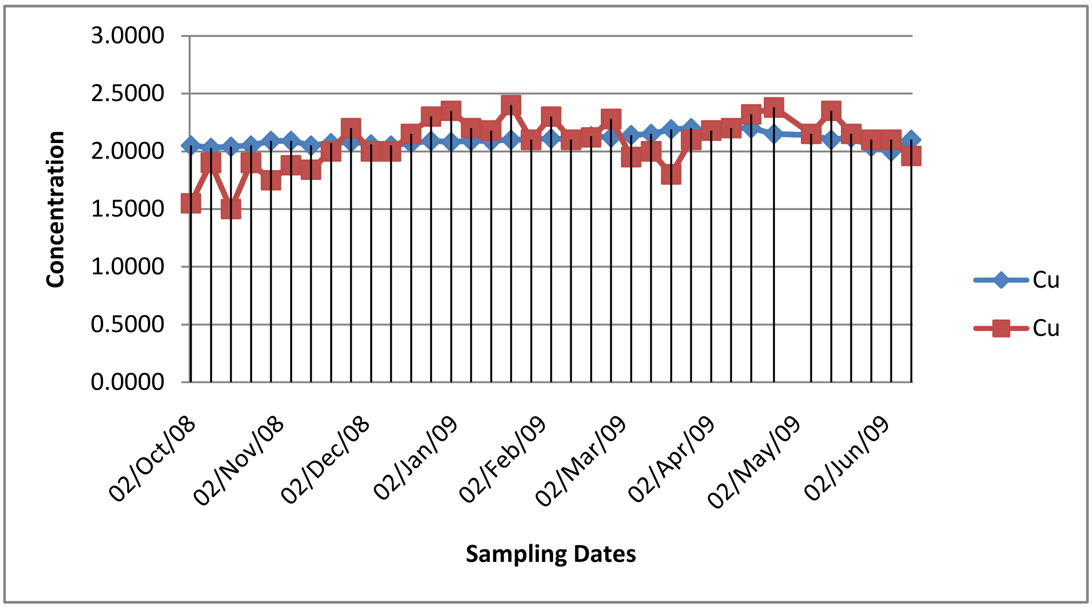


Figure 4.19 Observed versus Predicted Concentration of Cu at Gokul Shirgaon

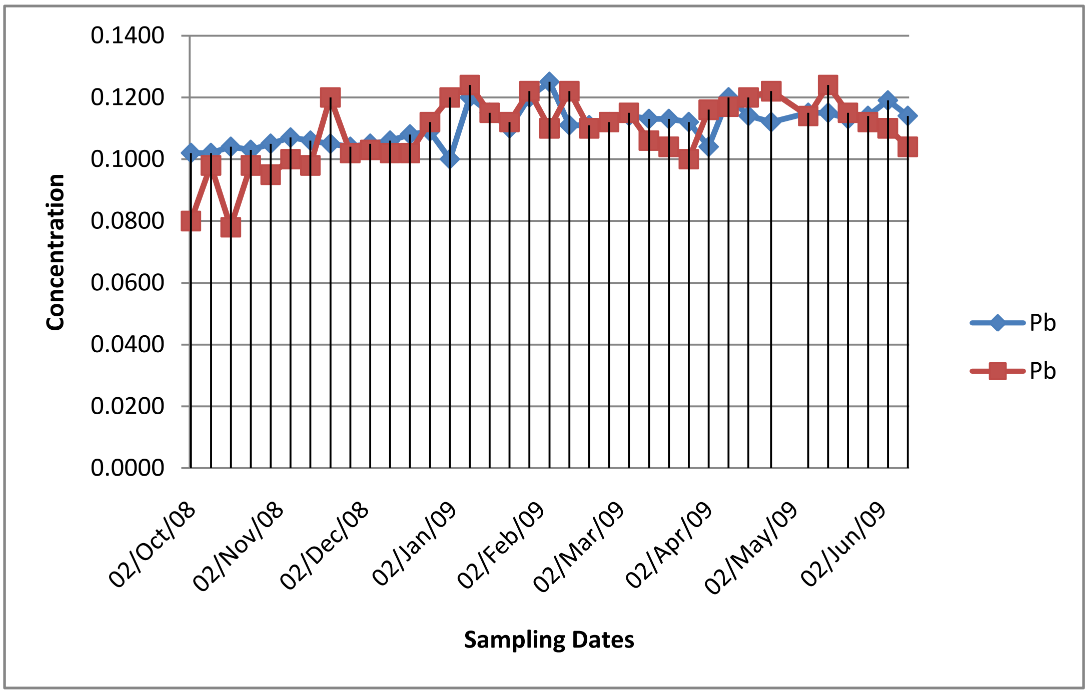


Figure 4.20 Observed versus Predicted Concentration of Pb at Gokul Shirgaon

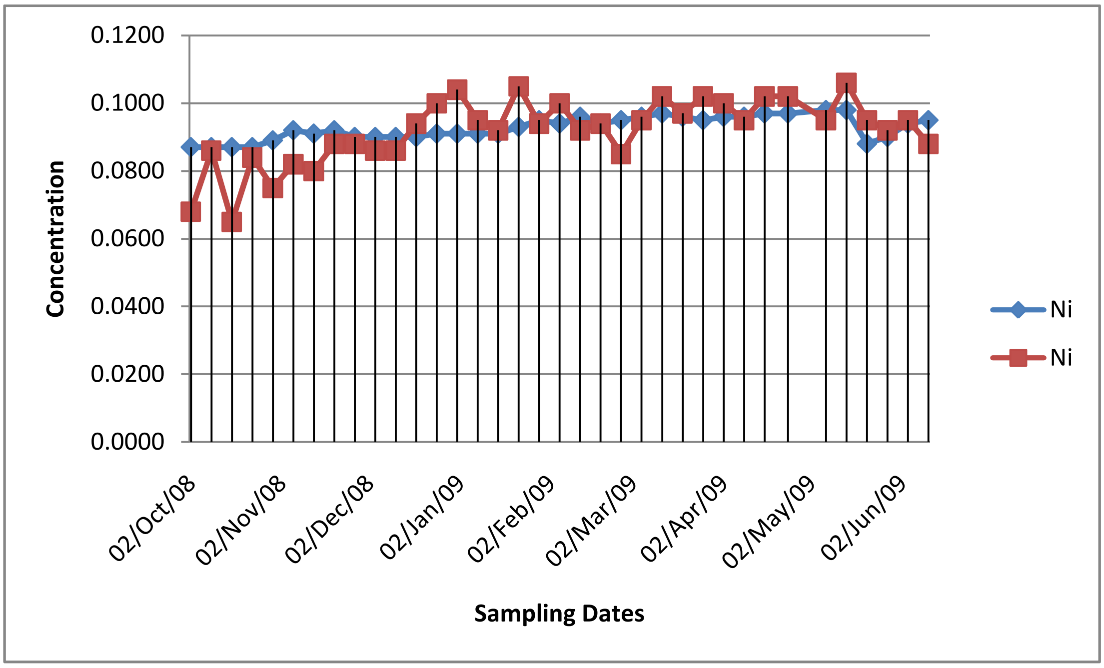


Figure 4.21 Observed versus Predicted Concentration of Ni at Gokul Shirgaon

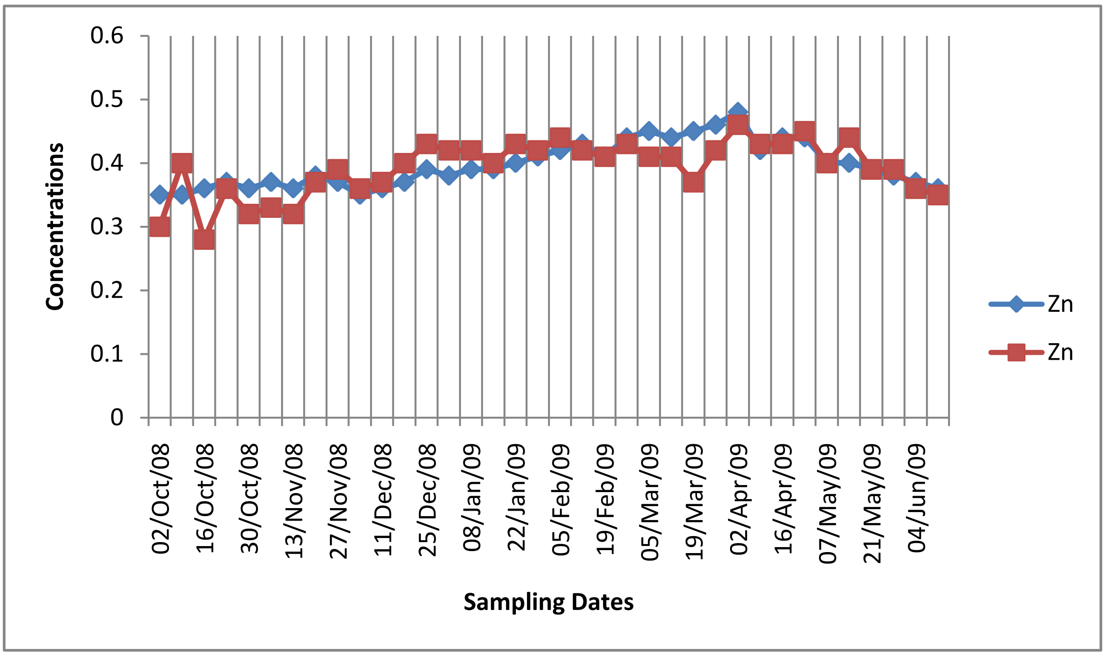


Figure 4.22 Observed versus Predicted Concentration of Zn at Gokul Shirgaon

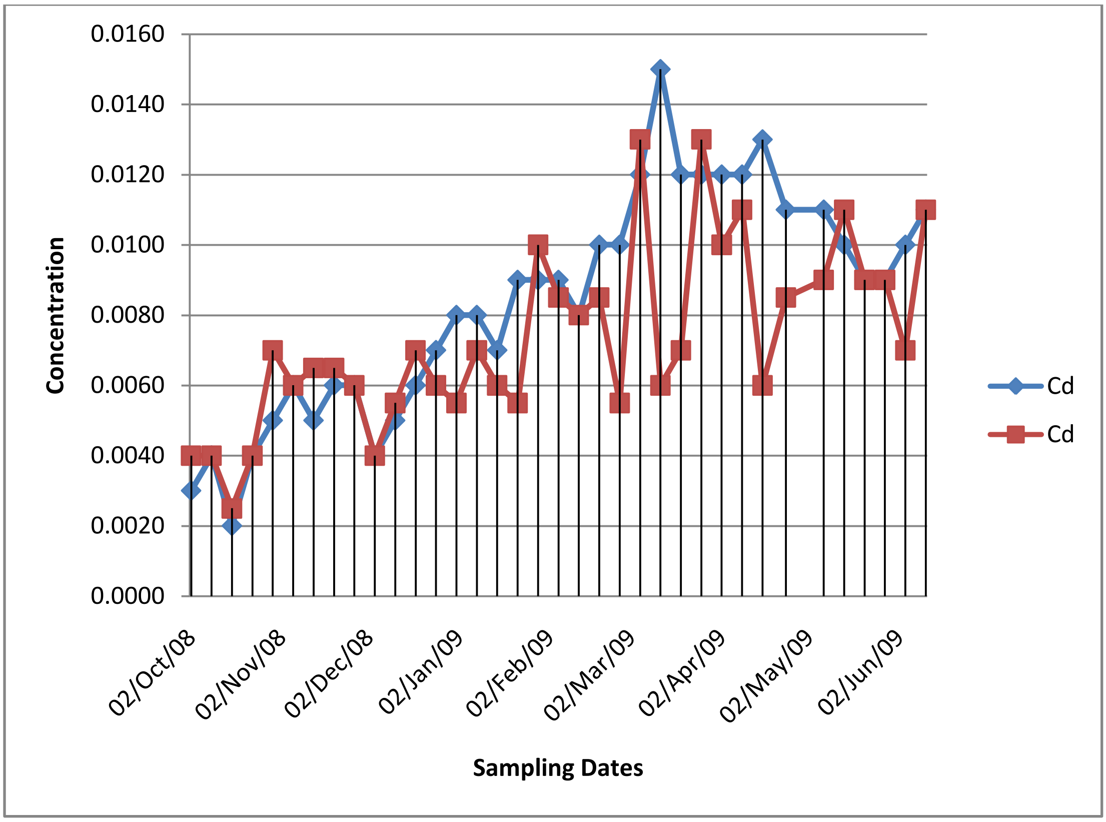


Figure 4.23 **Observed versus Predicted Concentration of Cd at Gokul Shirgaon**

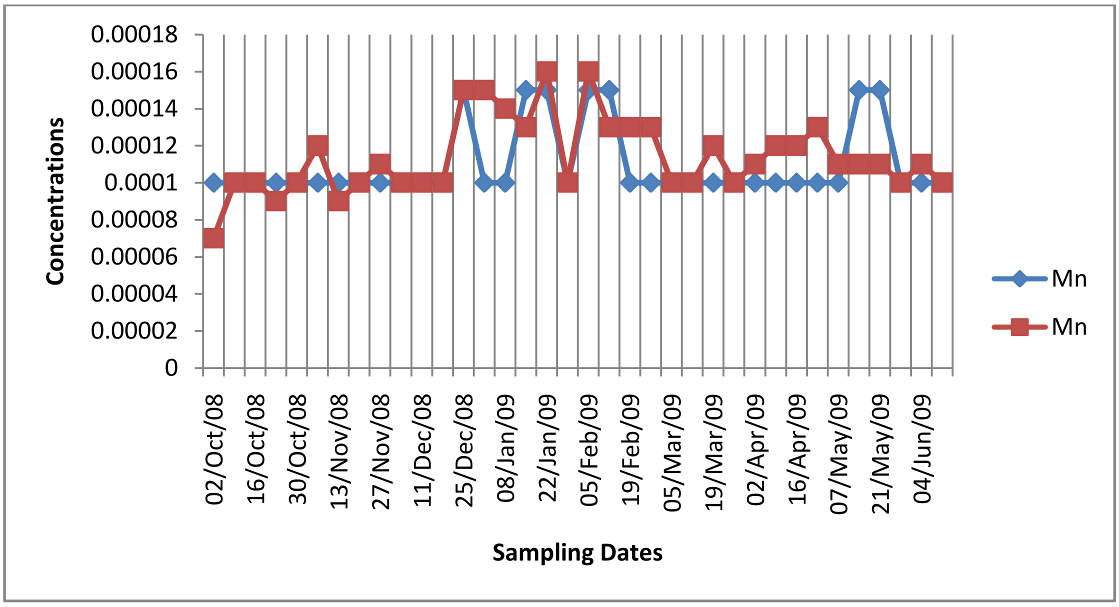


Figure 4.24 **Observed versus Predicted Concentration of Mn at Gokul Shirgaon**

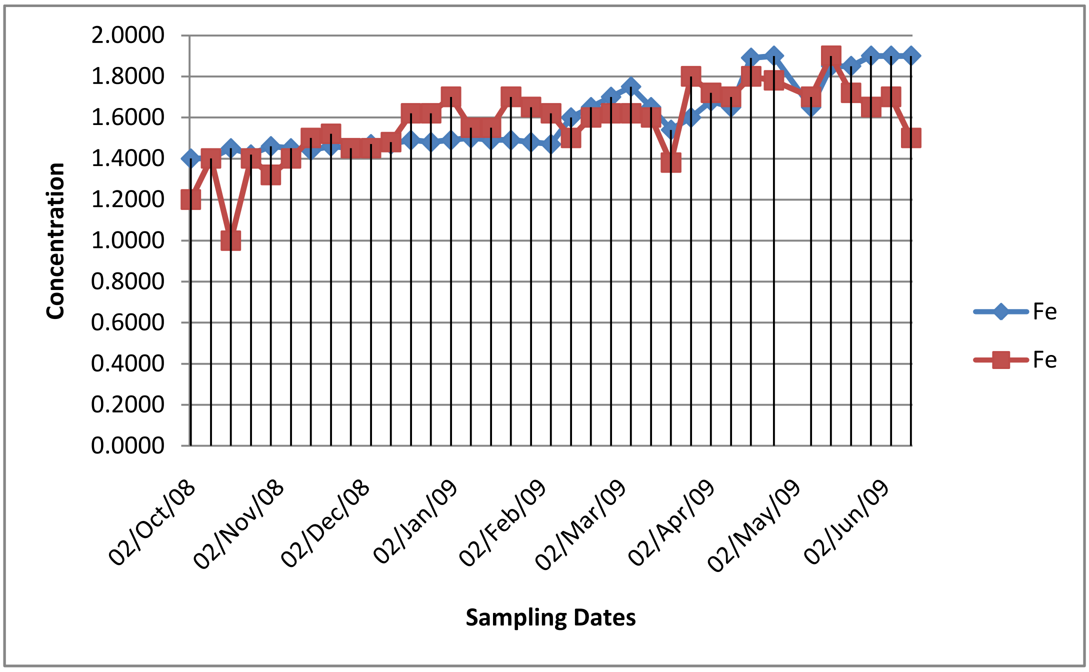


Figure 4.25 Observed versus Predicted Concentration of Fe at Gokul Shirgaon

4.6.3 Observed versus Predicted Concentration at Shiroli MIDC

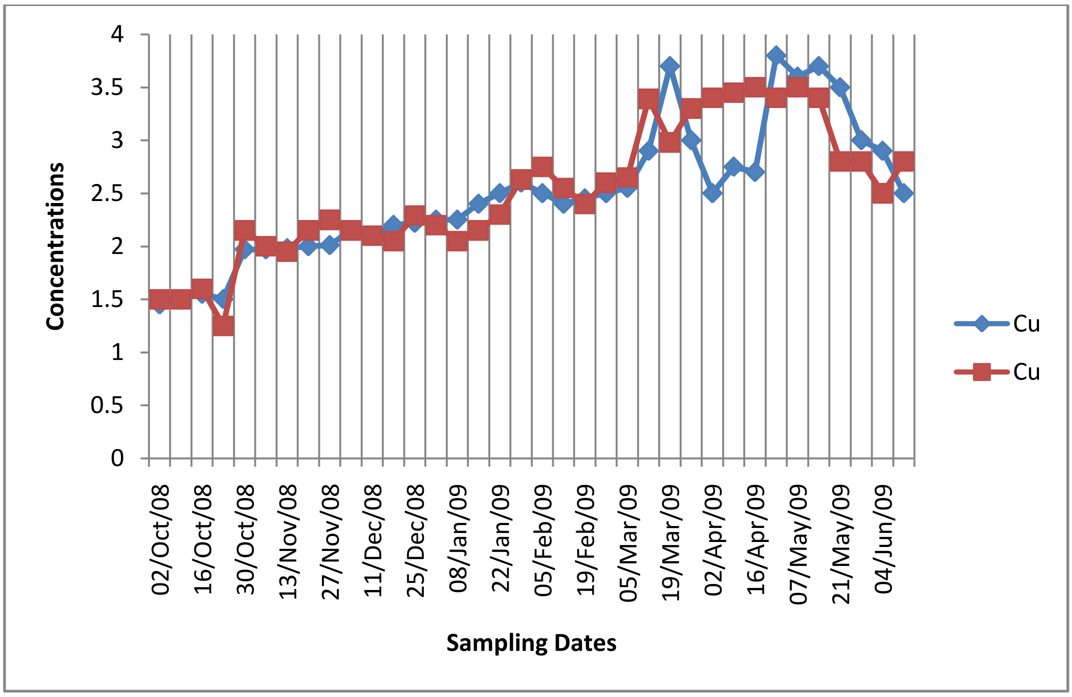


Figure 4.26 Observed versus Predicted Concentration of Cu at Shiroli MIDC

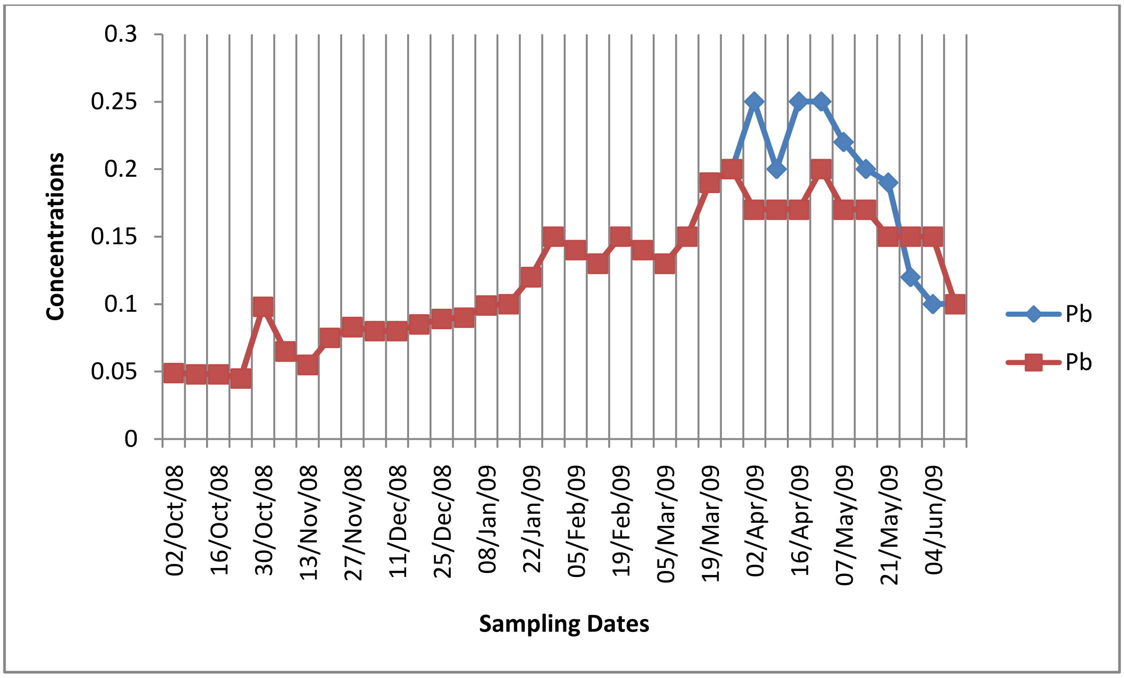


Figure 4.27 **Observed versus Predicted Concentration of Pb at Shiroli MIDC**

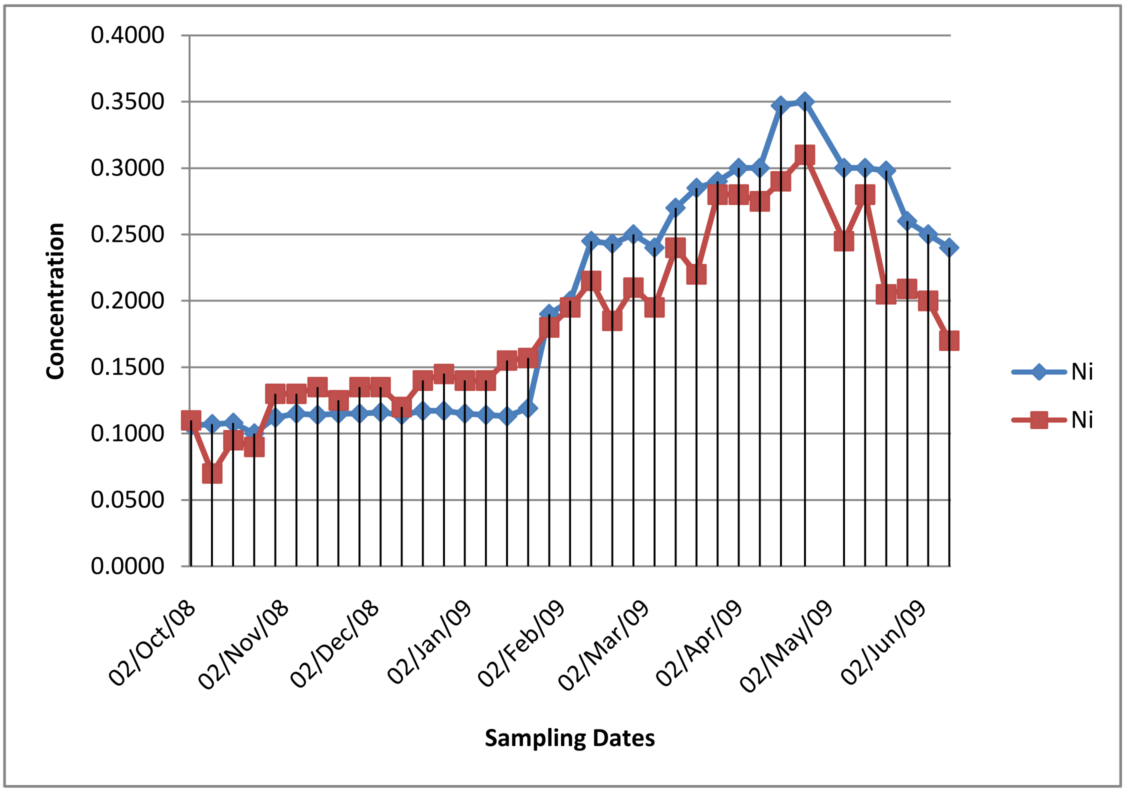


Figure 4.28 **Observed versus Predicted Concentration of Ni at Shiroli MIDC**

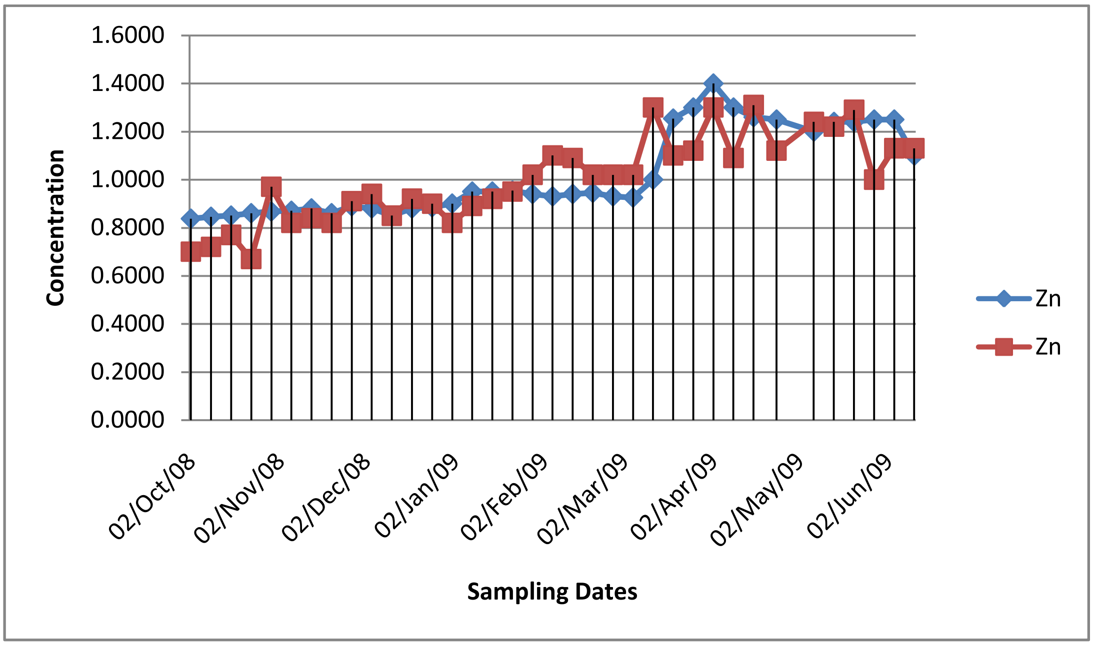


Figure 4.29 **Observed versus Predicted Concentration of Zn at Shiroli MIDC**

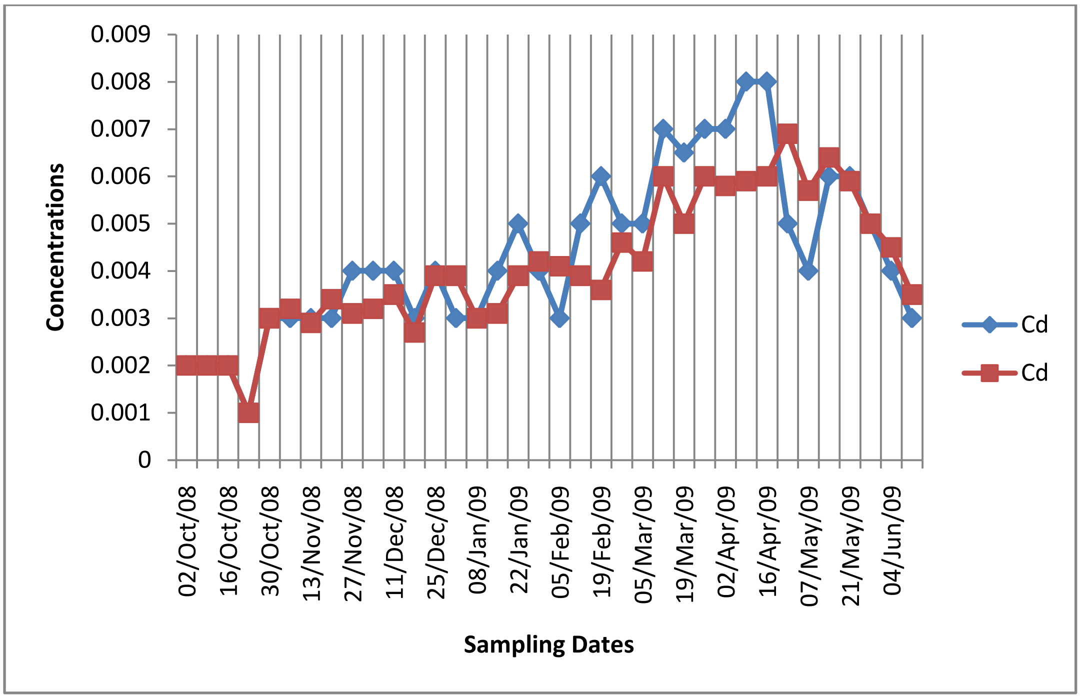


Figure 4.30 **Observed versus Predicted Concentration of Cd at Shiroli MIDC**

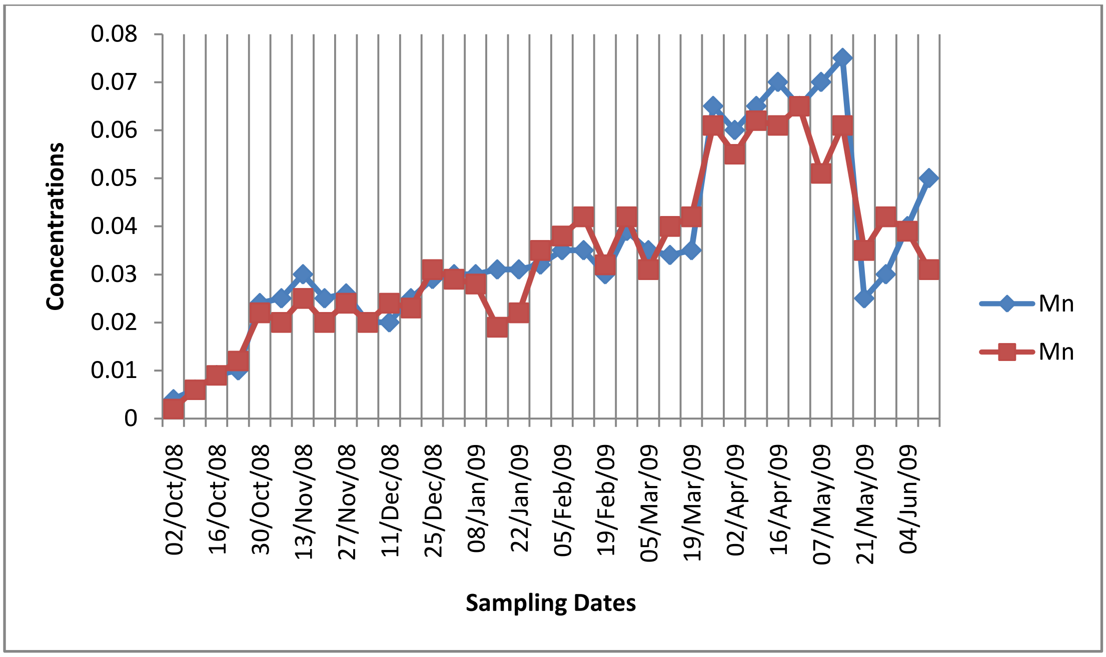


Figure 4.31 Observed versus Predicted Concentration of Mn at Shiroli MIDC

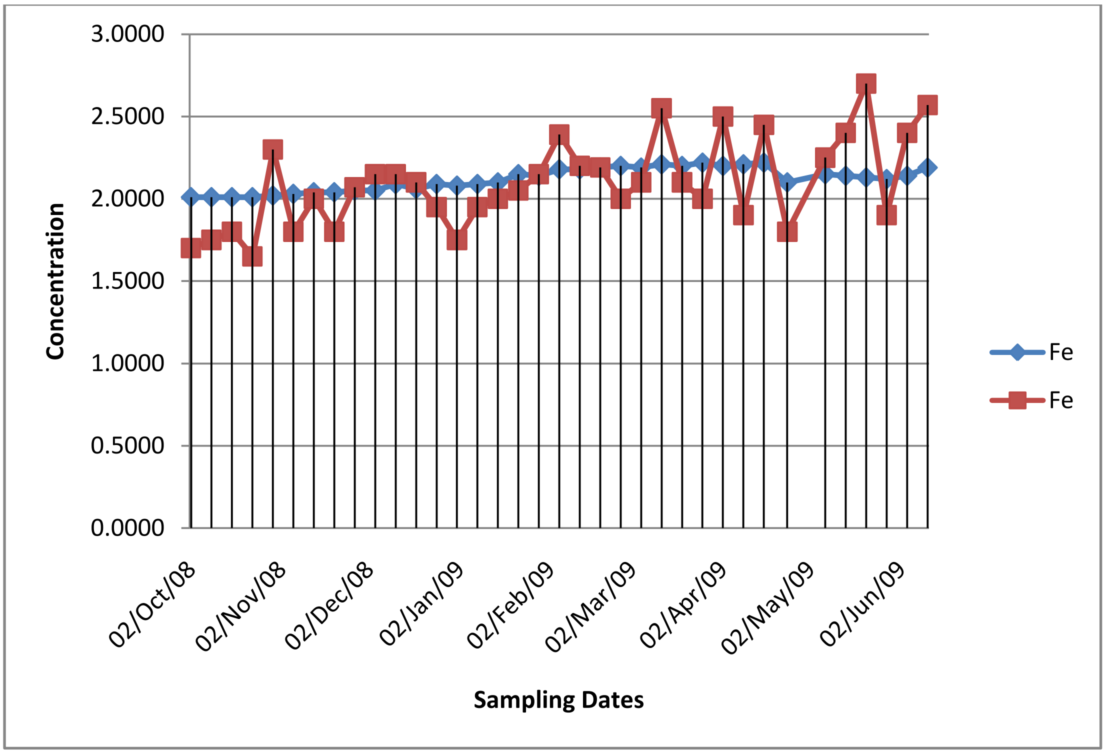


Figure 4.32 Observed versus Predicted Concentration of Fe at Shiroli MIDC

4.7 SOURCE APPORTIONMENT OF TRACE ELEMENTS

The main objective of the present study is source apportionment which means identification of sources for trace elements as well as quantifying estimate of contribution of each trace element to its source. This is vital to check the existing sources at particular location and compare with the results of source apportionment given by model. Table 4.10, 4.11 and 4.12 presents the contribution of trace elements from each source at selected particular locations.

Table 4.10 Source Apportionment of trace elements in percentage Shahu Blood Bank corner

Factor	Source	Cu	Pb	Ni	Zn	Cd	Mn	Fe
1	**Soil & Road Dust, %**	12.1	16.1	01.8	18.0	14.6	Nil	14.4
2	**Oil & Coal Burning, %**	**27.5**	**23.6**	20.3	**25.0**	**22.6**	Nil	**29.4**
3	**Iron & Steel Industries, %**	15.8	19.1	**34.7**	13.1	14.3	Nil	09.2
4	**Non ferrous Metal Industries, %**	11.4	08.1	13.4	06.7	09.8	09.6	05.0
5	**Refuse Incineration, %**	15.7	13.6	Nil	17.8	17.0	44.9	20.7
6	**Transportation, %**	17.6	19.5	29.7	19.4	21.8	**45.4**	21.4

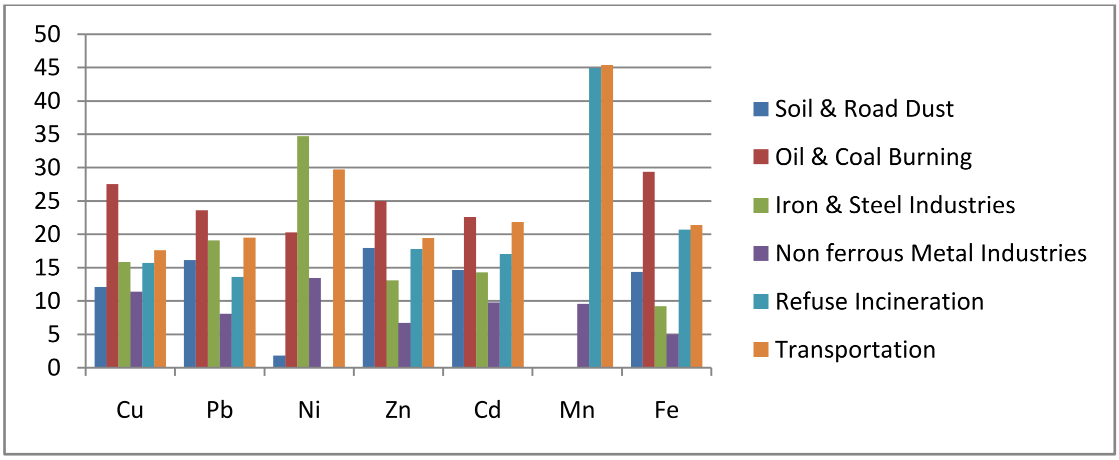


Figure 4.33 Source Apportionment of trace elements in percentage at Shahu Blood Bank corner

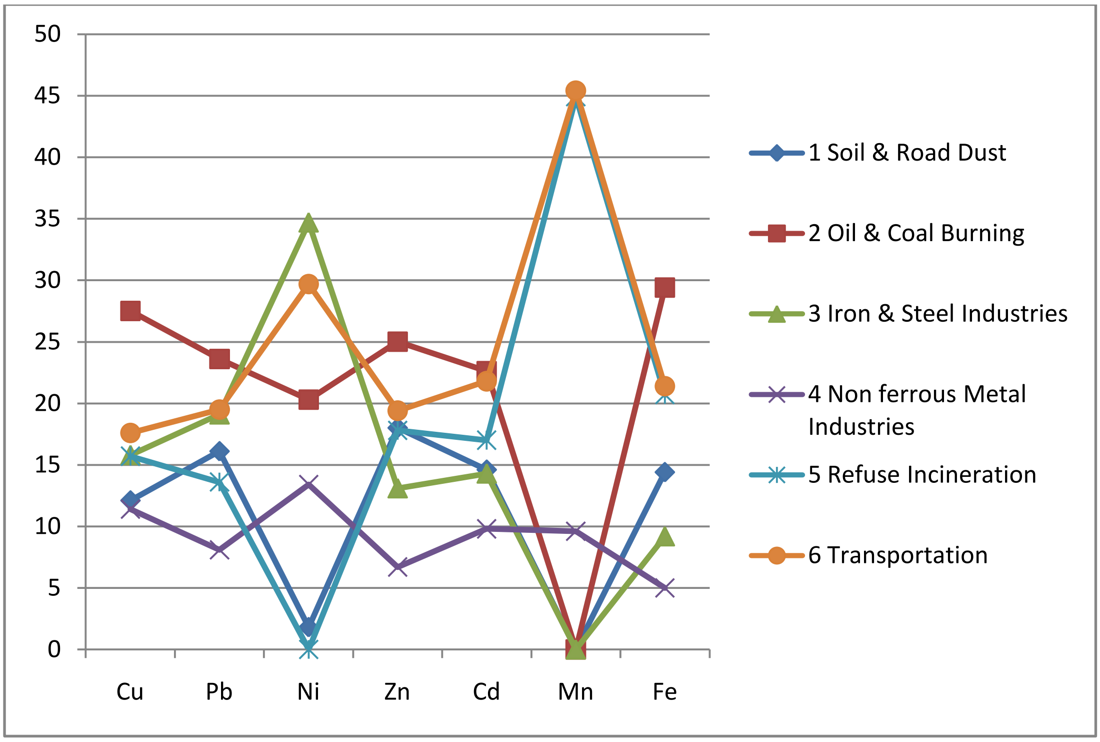


Figure 4.34 **Summary of Source Apportionment of trace elements in percentage at Shahu Blood Bank corner**

It is seen from Figure 4.34 that factor 1 (Source: Soil and Road dust) of each trace element shows lowest contribution of soil and road dust source. Trace element like Zn and its source contribution is very high i.e. 18% relative to other trace elements. Deposit of Cd in soil and road dust comes from batteries of vehicles running in the city. Mn contribution is nil since such element’s source is industry which is far away from sampling location. Other trace elements and their contribution to soil and road dust range from 12.1% to 16.1%. Contribution of other trace elements present is due to small scale industrial units located within the city.

Factor 2 (Source: Oil and Coal Burning) of each trace element shows higher contribution from the source of oil and coal burning domestic and commercial application in the city. Citizens of Kolhapur city are still using conventional coal and oil for cooking, heating and other domestic purpose. Except Mn, all trace element concentrations range from 20.3% (Ni) to 29.4% (Fe). Kolhapur city has small scale industrial cluster within the city. Fe, Cu, Zn, Cd concentrations is high due to such industrial units. This sector has many battery refilling shops in turn Cd is high. Mn contribution to oil and coal burning is Nil.

Factor 3 (Source: Iron and Steel Industries) and factor 4 (Source: Non Ferrous Metal Industries) of each trace element shows very low contribution to the source of Iron & Steel industries as well as Non ferrous metal industries respectively. The contribution ranges from Nil to 34.7% from the source of iron & Steel industries while source like non-ferrous metal industries range from 5.0% to 13.4%. Since these two sources are far away from sampling location, sufficient wind speeds disperse the concentrations of all trace elements while traveling towards city.

Factor 5 (Source: Refuse Incineration) shows highest contributions of Mn from the source of refuse incineration i.e. 44.9%. Ni contribution is nil while Pb contribution is 13.6% which is lowest in the range of 13.6% to 44.9%. Release of Mn is high due to industrial gaseous burning or emission incineration process. Since the wind direction is towards the city, Mn contribution is highest for factor 5.

Factor 6 (Source: Transportation) of each trace element shows, also, higher contribution from the source of transportation especially Mn. Since the sampling location is at downwind of Kolhapur city as well as industrial areas, Ni, Cd and Fe from transportation as well local industry are highest contributors to the factor 6. Cu contribution is less while other trace elements are observed with little higher contributions. Similarly, other sources and their respective trace element contributions are contributing the source of transportation.

It is observed from Figure from 4.34 that Pb and Cd concentrations may be due to heavy transportation at Shahu Blood Bank Corner. Recent developments in constructions of residences, commercial complexes and expansion of road by IRB Infrastructure Private Limited may have contributed Pb and Cd in the air as well as soil samples. Since, road at SBBC connects to NH4 highway at Shiroli MIDC, traffic movements are fast and higher in traffic density too. Such circumstances may lead to building up of higher concentrations of SPM and subsequent Pb and Cd concentrations which may affect residents and other living, non living elements of Environment.

Table 4.11 Source Apportionment of trace elements in percentage at Gokul Shirgaon MIDC

Factor	Source	Cu	Pb	Ni	Zn	Cd	Mn	Fe
1	**Soil & Road Dust, %**	23.9	**26.1**	25.3	**29.7**	**77.8**	17.5	**28.7**
2	**Oil & Coal Burning, %**	10.3	09.1	11.3	08.8	Nil	Nil	14.2
3	**Iron & Steel Industries, %**	12.0	12.1	12.3	08.5	05.0	14.6	14.6
4	**Non ferrous Metal Industries, %**	25.0	22.9	24.3	27.4	04.9	27.4	19.3
5	**Refuse Incineration, %**	01.9	02.4	Nil	0.01	Nil	Nil	01.2
6	**Transportation, %**	**26.8**	27.4	**26.8**	25.5	12.3	**39.4**	22.1

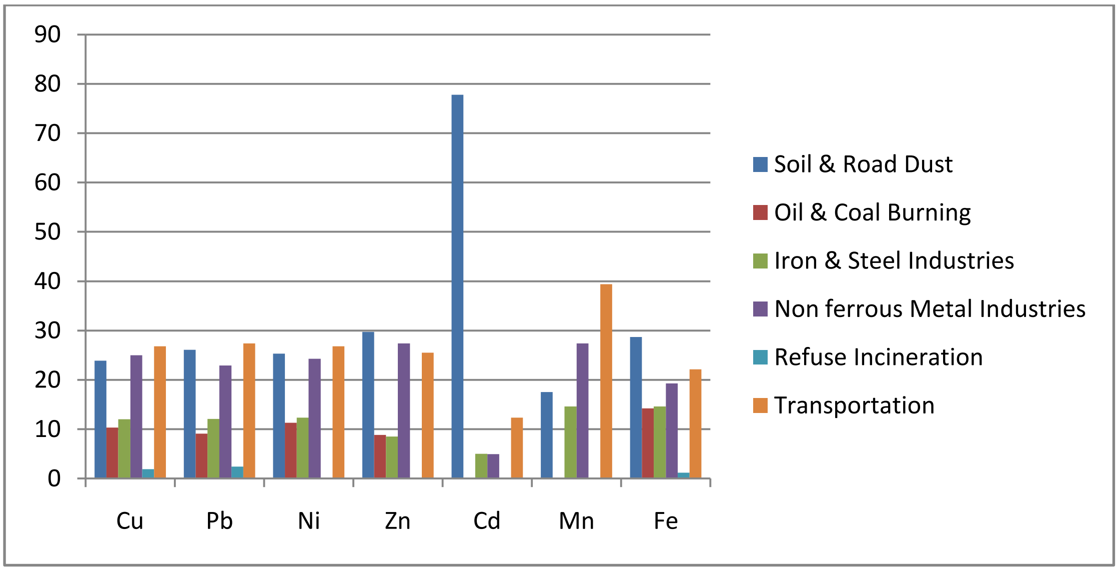


Figure 4.35 Source Apportionment of trace elements in percentage at Gokul Shirgaon MIDC

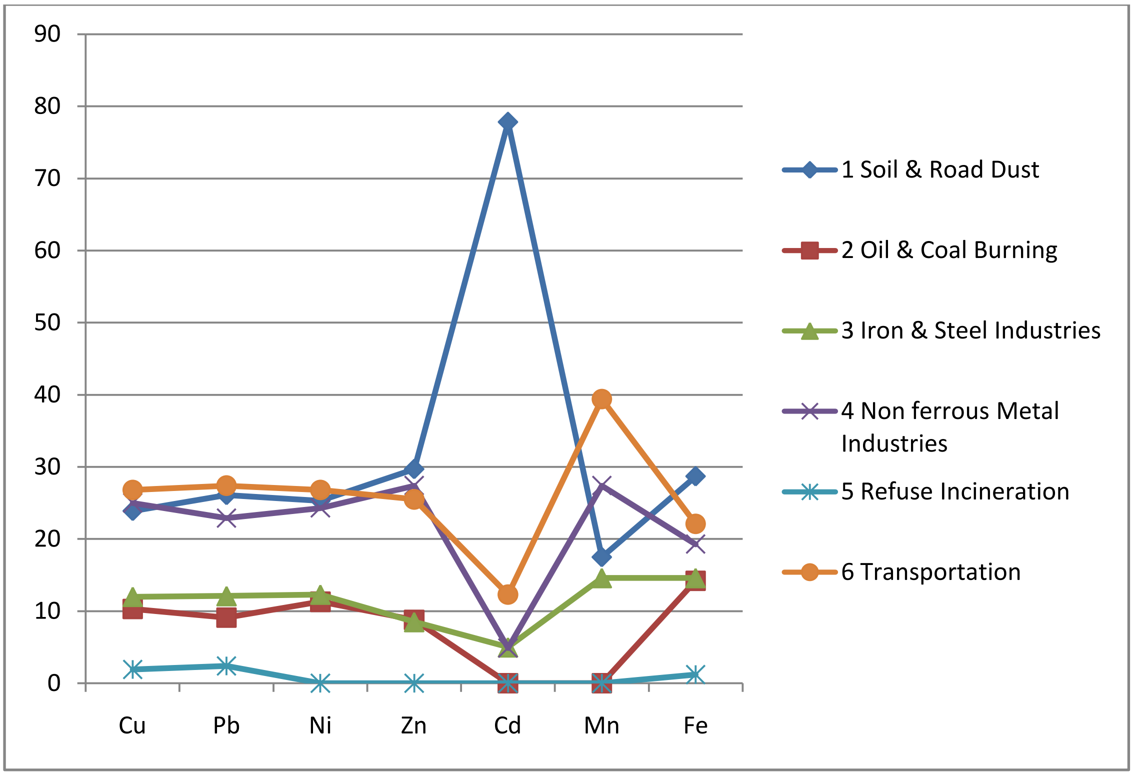


Figure 4.36 **Summary of Source Apportionment of trace elements in percentage at Gokul Shirgaon MIDC**

It is seen from Figure 4.36 that , factor 1 (Source: Soil and Road Dust) of each trace element shows highest contribution of soil and road dust source. Trace element like Cd and its source contribution is very high i.e. 77.8% relative to other trace elements. Deposit of Cd in soil and road dust comes from battery industries are more in Gokul Shirgaon. Mn contribution is very less in the source of soil and road dust. Other trace elements and their contribution to soil and road dust range from 23.9% to 29.7% which are lower contributions.

Factor 2 (Source: Oil and Coal Burning), factor 3 (Source: Iron and Steel Industries) and factor 5 (Refuse Incineration) of each trace element shows very low contribution to the source of Oil and Coal burning, Iron and steel Industries and Refuse incineration respectively. Such types of industries are very few. Of course, use of coal and oil is abundant in such units but still combustion process is fastening due to some of additives. The factor 2 contributions rang from Nil to 14.2% for all trace elements coming from the source of oil and coal burning while 5.0% to 14.6% is for factor 3 which is iron and steel industries. Foundry units are also less. Sufficient wind speeds disperse the concentrations of all trace elements while traveling towards city. Source like refuse incineration of factor 5 shows very lower contributions of each trace element ranging from Nil to 1.9%.

Factor 4 (Source: Non Ferrous Industries) of each trace element except Cd shows higher contribution from the source of Non ferrous metal industries. The range is from 19.3% to 27.4%. The existence of non-ferrous metal industries is increasing at five star Kagal MIDC which is upstream of Gokul Shirgaon MIDC. So contributions may get increased in the future. Cd contributions from such source are predicted 4.9% only.

Factor 6 (Source: Transportation) of each trace element except Cd shows again, higher contribution from the source of transportation. Sampling location was on NH4 Highway and on downwind side of MIDC. Automobile emissions are playing important role in Gokul Shirgaon MIDC. The main trace elements like Pb, Cu, Ni, Zn and Fe are contributing more than Cd. Mn is very high i.e. 50.9% as compared to other trace elements which is due to auto components manufacturing, body building units at MIDC.

Table 4.12 Source Apportionment of trace elements in percentage at Shiroli MIDC

Factor	Source	Cu	Pb	Ni	Zn	Cd	Mn	Fe
1	**Soil & Road Dust, %**	17.4	16.5	10.0	16.8	19.8	Nil	16.9
2	**Oil & Coal Burning, %**	**29.2**	**40.2**	**37.3**	18.1	**39.0**	49.1	09.5
3	**Iron & Steel Industries, %**	14.4	06.8	16.3	**21.7**	04.9	Nil	**25.7**
4	**Non ferrous Metal Industries, %**	14.5	00.9	03.8	18.4	14.6	Nil	23.2
5	**Refuse Incineration, %**	10.2	Nil	Nil	15.6	Nil	Nil	23.5
6	**Transportation, %**	14.4	35.6	32.6	09.4	21.7	**50.9**	01.2

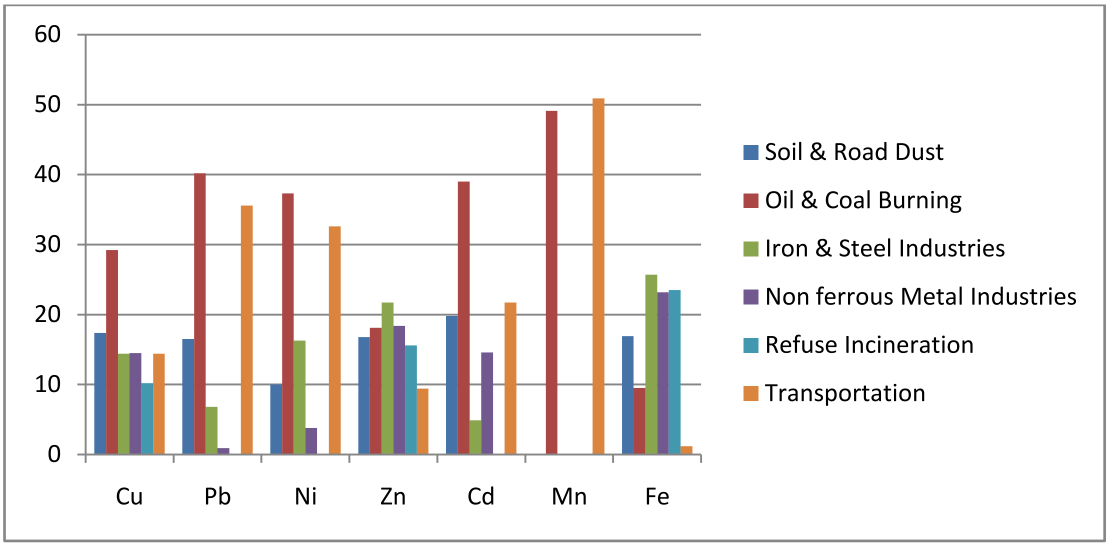


Figure 4.37 **Source Apportionment of trace elements in percentage at Shiroli MIDC**

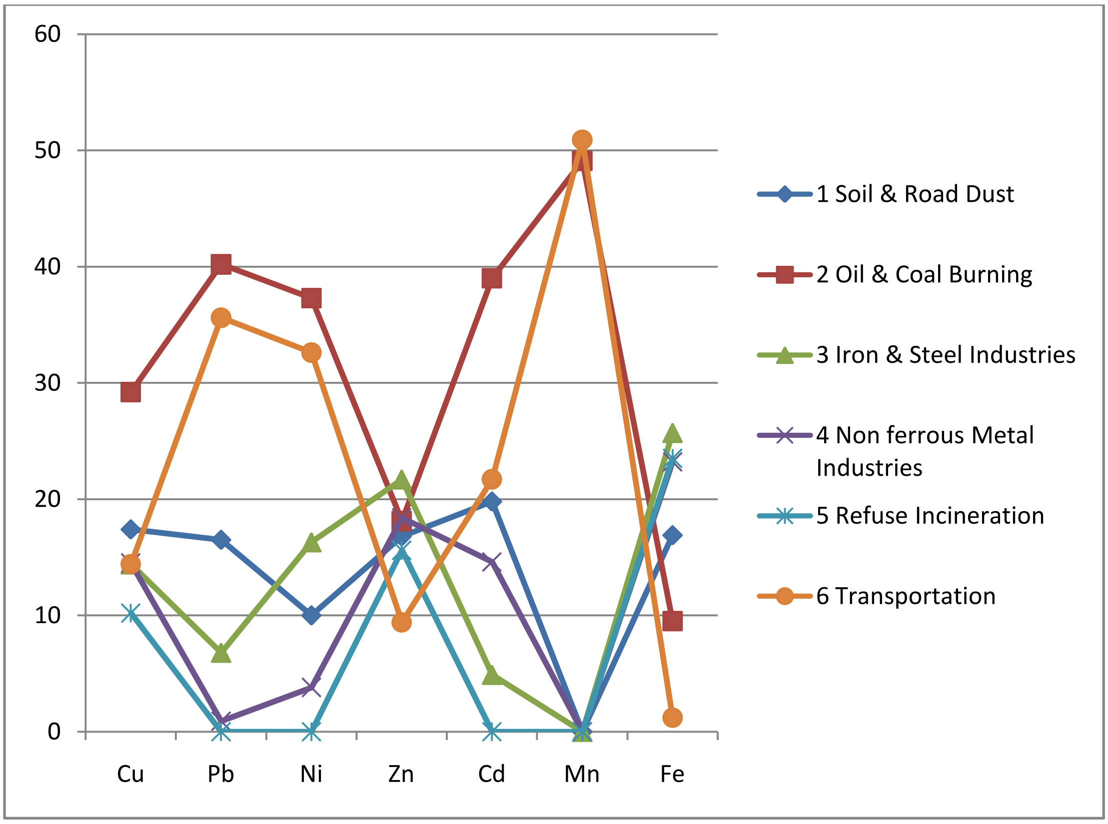


Figure 4.38 **Summary of Source Apportionment of trace elements in percentage at Shiroli MIDC**

It is seen from Figure 4.38 that factor 1 (Source: Soil and Road Dust) of each trace element shows lower contribution of soil and road dust source ranging from 10% to 19.8%. Trace element like Cd and its source contribution is very high i.e. 19.8% relative to other trace elements. Deposit of Cd in soil and road dust comes from batteries of vehicles running on NH$ national Highway called Pune-Bangalore. Also there are many battery refilling and charging units in Shiroli MIDC. Mn contribution is Nil in the source of soil and road dust.

Factor 2 (Source: Oil and Coal Burning) of trace element like Ni, Cd, Pb and Mn shows very high contribution to the source of Oil and Coal burning ranging from 37.3% to 49.1%. In Shiroli MIDC, there are many industrial units which use oil lubricants as well as Diesel for combustion process. The coal is main source of foundry units which are more in this MIDC. Mn and Ni contribution is high i.e 49.1% and 37.3% respectively due to foundries, Crushing, Combustion and automobile service centers. Since NH4 Highway is running through this MIDC, Pb contribution is also high as 40.2% while Cd of the source contributes around 39%. Cu contribution is also somewhat higher i.e. 29.2 which comes from copper plating and pot manufacturing units.

Factor 3 (Source: Iron and Steel Industries) of each trace element shows low contribution to the source of Iron and steel Industries ranging from 6.8% to 25.7%. Fe contribution is high i.e. 25.7% which comes from steel industries which are very less in MIDC. Lowest contribution is recorded for Pb i.e. 6.8%. Mn is Nil.

Factor 4 (Source: Non Ferrous Industries) of each trace element shows low contribution to the source of Non ferrous metal industries ranging from 0.9% to 23.2%. Fe contribution is high i.e. 23.2% which comes from some of the industries which are less as compared to foundries. Lowest contribution is recorded for Pb i.e. 0.9%. Mn is Nil also.

Factor 5 (Source: Refuse Incineration) of each trace element shows very low contribution to the source of Refuse incineration. The contribution rang from Nil to 23.5%. Refuse incineration plants are very few in MIDC. Only Fe i.e. 23.5%, Zn i.e.

15.6% and Cu i.e. 10.2% have been predicted as lowest contributor to the source of Refuse incineration.

Factor 6 (Source: Transportation) of each trace element shows highest contribution of Mn, Pb and Ni coming from transportation sources. They are predicted as 50.9%, 35.6% and 32.6% respectively. Since NH4 Pune-Bangalore highway is on upstream of sampling location and winds are blowing from south-East to North-west and West direction, Pb trace element is contributing 35.6% which is very high. Some of the automobile service centers are also present. Vehicle Body building at these service centers is the main source for trace elements like Mn and Ni. Paint booth is also important source of these elements which are 50.9% and 32.6% respectively.

4.8 SOIL SAMPLING

The presence of trace elements in the particulate matter suspended in the air at different designated sampling locations was quantified and compared with the predicted values using USEPA PMF model. The results were presented and discussed in the earlier paragraph. Concentrations of trace elements at different locations were apportioned from different sources releasing particulate in the form of metals. It has been observed from the earlier experimental results that the soil and road dust contributes significantly to the presence of trace elements in all the selected locations. Since from the monitoring results, SPM concentration in the atmosphere is fairly high and particulate matter is coarse in nature, it was felt that theses particulate matter may settle nearer to Kolhapur city and enhance the concentration of trace elements in soil. Therefore it was desired to undertake soil sampling in and around designated sampling locations as per established standard protocols and subject the sample for trace element analysis. The soil sampling was carried out during the month of March 2009 after source apportionment study. The soil samples were analyzed for few metals, which exhibited fairly high concentration in air samples. Table 4.13 shows concentration of trace elements in soil samples collected at different designated sampling locations. Soil samples were taken on same date at all location during 12 noon – 1 p.m. Dry soil were collected and analyzed as per standard laboratory procedures.

Table 4.13 Observed concentration of trace elements in Soil Samples at sampling locations (μg/m^3)

DATE	SBBC		GS		SS		
	Pb	Cd	Cu	Fe	Cu	Fe	Zn
5-Mar-09	3.0200	1.3160	0.4950	4.4280	1.6140	2.4300	1.1800
12-Mar-09	3.0245	1.1720	0.0010	4.6500	1.8080	2.0390	0.9840
19-Mar-09	3.0240	0.9580	0.0730	3.3232	0.7820	2.0350	1.2860
26-Mar-09	3.0300	1.4010	0.0841	1.4020	1.2170	2.4040	1.2515
2-Apr-09	3.0305	0.7830	0.1770	3.8240	1.7034	2.4500	1.1520
9-Apr-09	3.0300	0.5620	0.2680	2.9800	0.4100	2.0041	0.8170
16-Apr-09	3.0405	0.6650	0.1780	3.6400	2.9610	2.4600	0.9820
24-Apr-09	3.0358	1.0750	0.3230	4.8820	2.6690	2.4540	1.3540
7-May-09	3.0378	1.0750	0.3650	1.1320	0.6790	2.7000	1.4040
14-May-09	3.0402	0.6630	0.2890	1.2400	2.9720	2.4450	0.8950
21-May-09	3.0420	0.9200	0.1050	4.7430	1.6200	2.3205	1.1320
28-May-09	3.0400	1.0270	0.3370	1.8760	0.7430	1.9850	1.6190
4-Jun-09	3.0450	1.0980	0.3270	1.0090	0.7120	2.0031	1.5360
11-Jun-09	3.0500	1.3090	0.1660	1.3800	0.3220	2.0400	1.1640
18-Jun-09	3.0540	0.7740	0.3480	3.7910	0.2880	1.9000	1.0740
25-Jun-09	3.0570	0.7440	0.0914	2.7450	0.5790	3.0390	1.1470
Highest Concentration	3.0570	1.3160	0.3650	4.8820	2.9720	3.0390	1.6190
Lowest Concentration	3.0200	0.5620	0.0010	1.0090	0.2880	1.9000	0.8170

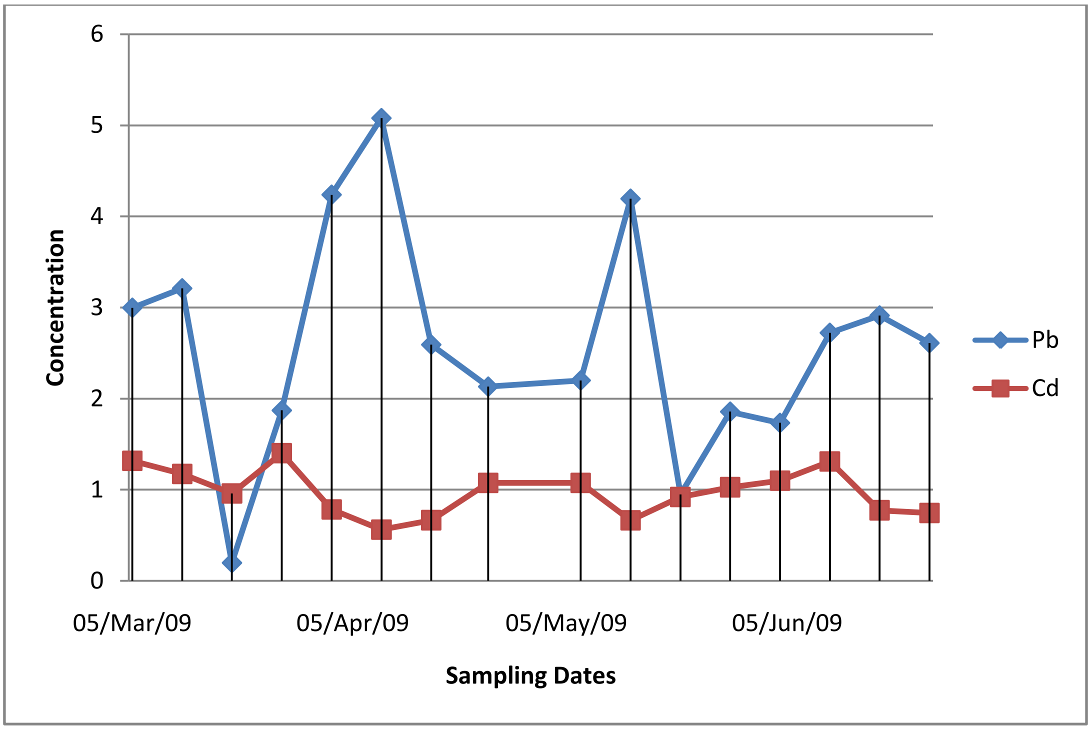


Figure 4.39 **Observed concentrations of trace elements in Soil Samples in µg / m^3 at Shahu Blood Bank Corner**

Lead and Cd have been confirmed as major metals in soil resulting from road traffic pollution in Kolhapur City. This form of pollution is attributed to emissions from motor vehicles (Jardat and Momani, 1999; Akhteer, 1993; Martin *et al*., 1988). The amount of Pb deposited along the roads was variable, being dependent on factors such as traffic volume and distance from the road. Results of this study show that the traffic volume caused a significant increase in Pb content in roadside soils. Higher Pb concentrations were found in sites with a higher traffic volume on main roads and in the entrance of petrol station. It seems reasonable to conclude that Pb and Cd in roadside soil levels are significantly higher on dusty roads compared to residential roads. Pb and Cd concentration levels in roadside soil decline with distance from the main road. It can be inferred from the results that the soil nearer to highway is getting lot of deposits of Pb and Cd from traffic.

It can also be observed that the frequencies with which motor vehicles stop, start, and accelerate, especially at traffic lights, may help to explain differences in the Pb levels in roadside soil. It is clear that Pb levels vary from time to time and depend on the volume of traffic. The enrichment factors for Pb and Cd were high, indicating that both main roads of this study are significantly contaminated with Pb and Cd. The high enrichment coefficient for Pb and Cd (non-crustal) indicates the role of anthropogenic sources of contamination for these metals, i.e. automobile emissions. The degree of such pollution is apparently dependent on the type, intensity, and duration of the activity.

It is commonly agreed that automobile exhaust has been the most important source of Pb pollution in urban areas, and that Cd may come from wear and tear of tyres. Pb is identified as an element originating from vehicles, petrol, paints (especially near old painted buildings), smelters and coal combustion plant and in rubber and plastic industries.

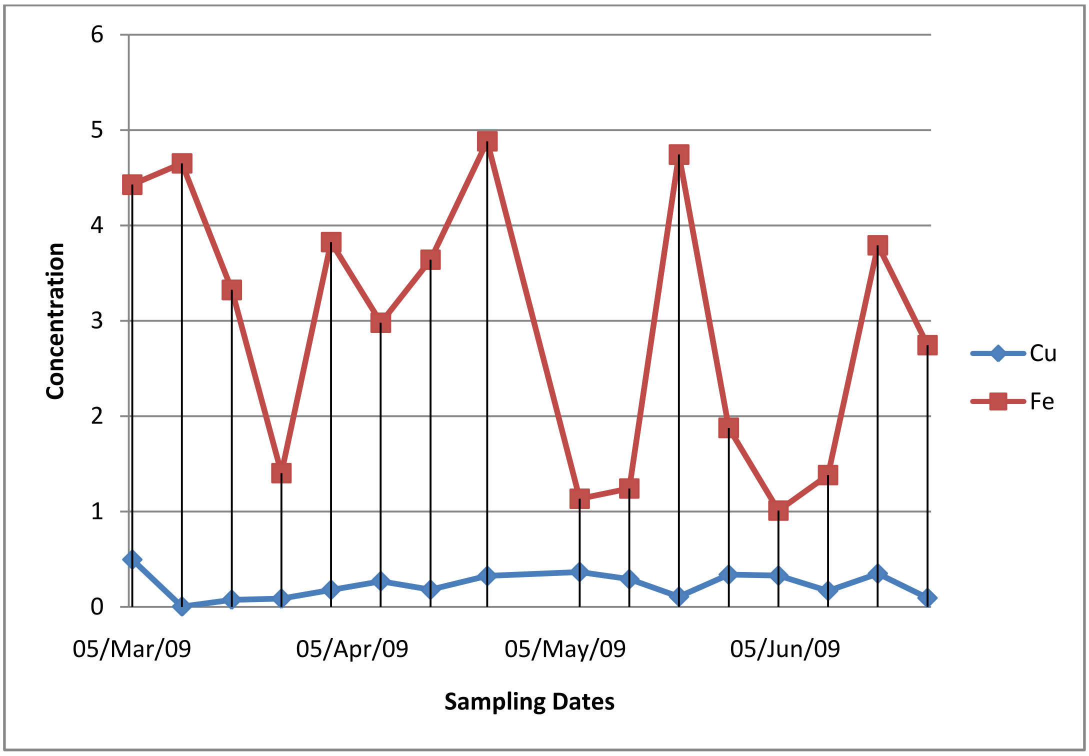


Figure 4.40 Observed concentration of trace elements in Soil Samples in µg / m^3 at Gokul Shirgaon MIDC

The level of Fe in Gokul Shirgaon MIDC and Shiroli MIDC was high in soil nearer to Rubber Factory, fabrication units as well as Iron and Steel Industries soil. Highest amount of Fe was found in soil at Gokul Shirgaon which could be due to proximity of Steel Industries. Iron comes from corrosion of pipes, containers and wear and tear of vehicles (Ara et al., 1996). Iron is a metallic element, one of the most useful of all metals. Iron is best known for its uses as a high strength structural material (Iqbal and Rahmati et al., 1992).

The level of Cu in soil at Shiroli MIDC was high at this location also. Soil of some other metal industries Factory had low amount of Cu. Therefore accumulation of Cu in root and aerial parts could be possibly through other sources like aerial deposition. Toxic levels of Cu occur naturally in some soils whereas others may contain high levels of Cu as a result of the anthropogenic release of heavy metals into the environment through mining, smelting, manufacturing, and agriculture and waste disposal technologies (Yruela et al., 2005).

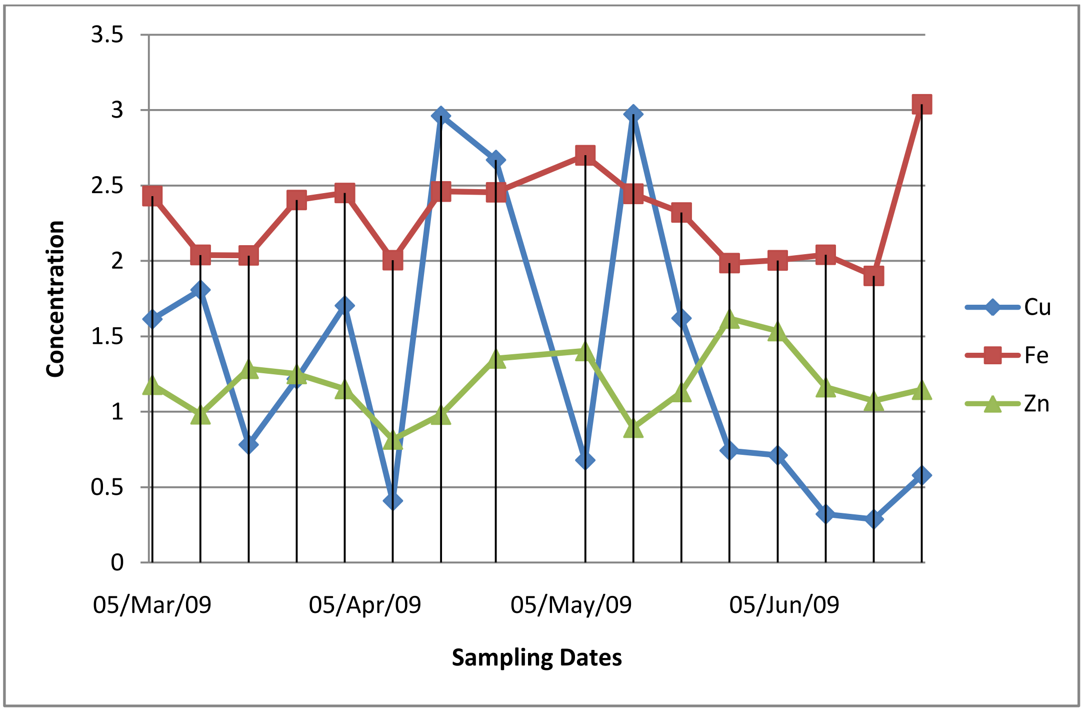


Figure 4.41 Observed concentration of trace elements in Soil Samples in µg / m^3 at Shiroli MIDC

Zn is used in the industries for many purposes. Fe and Zn did not show any correlation in the level of accumulation in root and aerial parts of Shiroli MIDC. High accumulation of Fe and Zn in the roots and aerial parts of Shiroli was recorded in soil.

4.9 SPM CONCENTRATIONS FROM AUTOMOBILE EXHAUST AT SHAHU BLOOD BANK CORNER

From the earlier paragraphs of results of SPM concentrations at selected sampling locations, it is seen that SPM concentrations are exceeding National Ambient Air Quality Standards (NAAQS). Also, it is seen that Pb and Cd are found higher than that of other trace elements at SBBC in Kolhapur city. It may be observed that Automobile exhaust may play important role in generating higher concentrations of SPM in city. Hence, Concentrations of SPM from automobile was calculated at SBBC. It is found that concentration of SPM releasing from automobile exhaust at SBBC on 28th May 2010 during 10 am – 6 pm is 359.49µg/m^3. Observed concentration of SPM during Source Apportionment study on 28th May 2009 (One year earlier) was 585µg/m^3 (Table 4.3). It is concluded that automobile exhaust may contribute 62% of total SPM at SBBC and hence trace elements like Pb and Cd are more at SBBC. Annexure VII shows the calculation of SPM concentrations from Automobile Exhaust.

4.10 SPM CONCENTRATIONS FROM FOUNDRIES AT GOKUL SHIRGAON MIDC

It is seen from Table 4.5, Cu, Fe are found more than other trace elements. As per soil samples taken at Gokul Shirgaon, Concentrations of Cu, Fe are found high. Hence concentration of SPM releasing from foundries was calculated to measure the contribution in Total SPM found during Source apportionment study. As per Annexure VII, it is seen that concentration of SPM releasing from major foundries is 311µg/m^3. The concentration of SPM during source apportionment study at Gokul Shirgaon was found 550µg/m^3. Hence it is concluded that SPM from foundries at Shiroli MIDC may contribute 57% of Total SPM. This enable trace elements like Cu, Fe to exist in atmosphere as well as soil at sampling locations due to foundry activities. Other trace elements are found comparatively less.

4.11 SPM CONCENTRATIONS FROM FOUNDRIES AT SHIROLI MIDC

It is seen from Table 4.6, Cu, Fe and Zn are found more than other trace elements at Shiroli MIDC. Also, As per soil sample taken at Shiroli MIDC, Concentrations of Cu, Fe and Zn are found high. Hence concentration of SPM releasing from foundries was calculated to measure the contribution in Total SPM found during Source apportionment study. As per Annexure no. VIII, it is seen that concentration of SPM releasing from major foundries is 466µg/m^3. The concentration of SPM during source apportionment study at Shiroli MIDC was found 550µg/m^3. Hence it is concluded that SPM from foundries at Shiroli MIDC may contribute 85% of Total SPM. Also, it may seen that trace elements like Cu, Fe and Zn may exist in atmosphere as well as soil at sampling locations due to foundry activities.

Other industries present in Shiroli MIDC and Transportation on NH4 highway may contribute 15% of total SPM found at the location. Hence, other trace elements are found less in comparison with Cu, Fe and Zn.

4.12 SOME SALIENT POINTS

Kolhapur where present study was carried out is growing faster in terms of transportation and industries. The population rise due to new setup of industries and other infrastructure developments in and around city has led to increase in automobiles and other private utility vehicles. Being a Tier II city, Kolhapur is a major tourism place due to its scenic places around and especially Mahalaxmi temple known as Dakshin Kashi flooded with pilgrims.

It is found that SPM concentrations in city as well as at all three sampling locations have exceeded above National Ambient Air Quality Standards (NAAQS), CPCB, New Delhi. It may be due to unplanned road structures and infrastructure being developed recently. Also, government authorities like RTO and Urban Land Development Authority failed to create systematic and sustainable way of implementing developments for ease of people and Environment safeguards. Higher concentrations of SPM have trace element contaminants from different sources mentioned in source apportionment results. It is found that Pb and Cd have found higher in city as well as Industrial areas of interests. This may be due to transportation, batteries and its allied industries, paints and pigments used for exterior walls as well as new products at manufacturing units. The results of observed concentrations of trace elements in air samples have validated with concentrations of trace elements found in soil samples nearby sampling locations. The PMF model was validated accordingly with minimum deviations in results. The sources responsible for higher concentrations of trace elements at each sampling location were resampled for SPM analysis and found out the share of SPM from such specific source to total SPM found at each location. At SBBC, SPM due to transportation accounted 62% of total SPM observed during sampling. Similarly, SPM due to foundry that is main source found in source apportionment accounted 57% at Gokul Shirgaon MIDC and 85% at Shiroli MIDC respectively. Transportation and industries like foundry were found out be main contributors of critical pollutants in Kolhapur. This has proven the failure of government authorities like RTO, Transportation department, Industrial Estates authorities of Maharashtra and Kolhapur District Industrial Authorities for unplanned and unorganized Road Infrastructure in Kolhapur and around as well as siting and zoning of Industries in Kolhapur. Maharashtra Pollution Control Board (MPCB) is also, equally responsible for not issuing closer notices to industries polluting beyond the limits.

Dealing with air pollution from mobile sources requires an integrated approach. Transport planning including Travel Demand Management (TDM) and Transport Systems Management (TSM) is a fundamental part of such an approach. Significant political will and technical capacity are required for successful implementation and vigorous efforts should be made to create and sustain both. An integrated approach requires combining: land use and transport planning; travel demand management; and transport systems management and regulation. These three elements should be supported by appropriate policies and actions on resource mobilization, taxation, pricing, subsidies; institutional and legal aspects; as well as promotion and awareness raising.

RTO and other transportation authorities of India should take necessary actions to reduce Automobile exhaust as well as control of vehicular emission at source only. Proper traffic planning shall serve as the best method to minimize emissions from tailpipe of all variants. The strategies to reduce vehicle emissions should include the following.

1. Cleaner vehicles: regulating emission standards for new vehicles/engines;
2. Cleaner fuels: regulating fuel composition to reduce emissions;
3. Vehicle inspection programs: mandatory vehicle emissions testing;
4. Vehicle scrappage programs: incentive programs designed to get old higher polluting vehicles off the road;
5. Consumer education: on items like idling, vehicle operation and maintenance; and
6. Programs to encourage cleaner, alternative transportation: such as carpooling, public transit, walking and biking.

Similarly, Industrial estate authorities and local Industrial Associations should take some measures to reduce industrial emission from its processes. Proper selection of new industrial estate or industrial locations as per EIA study, zoning of industries, setting up of SEZ's shall prove to be sustainable practice for industrial organizations and authorities. Adoption of cleaner production technologies shall serve the purpose of being Eco-Friendly and Zero Discharge Industry. Process change, effective material handling, advanced quality control inspections, proper control equipments, fuel switching, use of sustainable technologies, use of renewable energies shall be beneficial to industry to curb industrial emission problems.

The successful phase-out of leaded gasoline, the partial introduction of lower sulfur diesel, the adoption of stricter emissions standards for vehicles in several Asian countries and experiments with greater citizen involvement in managing mobile sources of pollution all show that it is possible to make a difference.

Chapter 5

SUMMARY AND CONCLUSIONS

Individual particles in an urban airshed can contain both primary and secondary components, and the composition of ambient aerosols have been found to reflect source SPM emission characteristics differences over space (e.g., between cities) and time (e.g., across seasons). Because the composition of particle types varies greatly, it is probable that some types of particles are more toxic than others. Thus, treating all particles that contribute to the mass concentration equally in the regulatory process may lead to inefficient protection of public health. A potentially more effective regulatory approach would be to address the individual types of particles independently, focusing control efforts on the most toxic categories. However, because toxicities of individual source components are not yet certain, and because virtually all published SPM health effects studies to date have used SPM mass (in various size categories) as the particle pollution index, the current NAAQS for airborne SPM use airborne particle mass as the indicator for making air quality compliance determinations. Equal treatment of all particles that contribute to mass, irrespective of composition, may be leading to less-optimal control strategies to avoid the adverse human health effects of SPM, potentially causing the present SPM ambient standard to be less protective of health in some areas of the nation than in others. There is a need for epidemiologic and toxicologic evaluation of the extent to which the toxicity of ambient SPM mass varies by particle type and source.

Because source composition and/or physical properties of particles vary between different source categories, the mass can be statistically apportioned into contributions from various source categories, opening the possibility of evaluating SPM component effects using epidemiologic methods presently used on the SPM mass. Receptor modeling has been active for over 3 decades. A number of accepted methods are being used to apportion the total mass into source categories, and these source apportionment methods can now be used as inputs to epidemiologic models of the human health effects of air pollution. However, to date only a small number of published efforts have related source-apportioned SPM impacts to human health effects (Laden et al. 2000). The effect of the imputation of these apportionments on the ability of epidemiologic methods to evaluate the health effects associated with various SPM components is uncertain. Because a number of methods are used to determine source contributions to SPM mass impacts, and application of these methods varies among researchers, their application, although providing new insights, can also be expected to introduce added uncertainty into the derivation of estimates of SPM toxicity. The scientific and regulatory community is uncertain whether meaningful and reliable source apportionments of SPM health effects are possible with today's data and methods.

Measurements of urban air quality at monitoring stations in developed countries have frequently involved the criteria gaseous pollutants, particulates, hazardous air pollutants, perceived air quality and relevant meteorological conditions. Large numbers of indicators have therefore been established to quantify emissions, concentrations and environmental and human health impacts of each of these groups of substances. To simplify the data for management, several indicators have been grouped together to form urban air quality indices but the weightings of individual variables is contentious. In industrializing and developing countries, data may be limited and traditional air pollutant indicators cannot often be constructed. The emphasis therefore has to be placed on the development of policy-relevant indicators, such as Response Indicators that reflect different policy principles for regulating air pollutant emissions. Indices that quantify the air quality management capabilities and capacities at the city level provide further useful decision-relevant tools. Four sets of indices, namely, air quality measurement capacity, data assessment and availability, emissions estimates, and management enabling capabilities, and a composite index to evaluate air quality management capability, were constructed and applied to 80 cities. The indices revealed that management capability varied widely between the cities. In some of the cities, existing national knowledge on urban air quality could have been more effectively used for management. It was concluded that for effective urban air quality management, a greater emphasis should be given, not just to monitoring and data capture programmes, but to the development of indicators and indices that empower decision-makers to initiate management response strategies. Over-reliance on restricted, predetermined sets of traditional air quality indicators should be avoided (Peterson PJ, Williams WP et at. 1999).

The rate at which urban air pollution has grown across India is alarming. A vast majority of cities are caught in the toxic web as air quality fails to meet health-based standards. Almost all cities are reeling under severe particulate pollution while newer pollutants like oxides of nitrogen and air toxics have begun to add to the public health challenge. Only a few mega cities where action has started show some improvement in air quality but in most cases the particulate levels are still unacceptably high. But medium and small sized towns and cities are witnessing phenomenal spurt in pollution as severe as or more than any mega city.

Improve air quality monitoring to include more pollutants and more areas in cities to assess the risk of air pollution, make appropriate policies to control it and to create awareness amongst people about hard policy decisions. Ambient air quality standards are constantly evolving to address the emerging health challenges. The most recent attempt by CPCB to revise the ambient air quality standards will set tighter benchmark for air quality. These standards will set new and tighter targets for air quality improvement in our cities -- one uniform health based standards for all land-use classes; tighter standards for sensitive area; introduction of more short terms standards, among others.

Despite a very small minority using cars in cities, the available road space and transport-related investments are getting locked up only to cater to them. Public transport, bicycles and pedestrian facilities used by the vast urban majority, especially the urban poor, remain neglected. The poor end up paying an enormous cost for their travel, while car users do not even pay the full cost of car travel. Indian cities, in fact, penalise public transport with higher taxes compared to personal vehicles.

There is no roadmap yet that sets the milestones for uniform and tighter emissions standards for the entire country. Yet the Auto Mission Plan is proposing to make India the auto hub without linking the new investments with the effective roadmap.

The worrying factor is the rate of increase in air pollution in smaller Tier II cities/towns. Among the 12 most polluted cities in India, at least seven are smaller towns such as Kanpur, Amritsar and Jamshedpur. Among major cities, Kolkata ranks sixth on the list, Bangalore 11th, and Mumbai 12th.

Tier II Cities/smaller cities have witnessed a huge increase in personal vehicles since 2005, leading to greater congestion due to inadequate increase in road space. According to road transport ministry data, road space in India has increased at an annual rate of 2.5%, compared to an over 10% increase in vehicular population. The government had taken several measures to check air pollution but the failure of many cities to provide an alternative and viable public transport system had caused a huge jump in the number of private vehicles on the roads.

5.1 FOCUS OF SOURCE APPORTIONMENT STUDIES IN INDIA

It is important to note that the health impacts of urban air pollution are not entirely dependent on the particulate pollution. The health impacts observed or estimated are also dependent on other pollutants, such as ozone, hydrocarbons, acidity in the air due to sulfur and nitrogen compounds, carbon monoxide, etc. However, in the developing countries, the particulate matter forms the major contributor and hence the pressure to understand its sources better. Also, during the source apportionment, it is understood that all the pollutants discussed here, contribute in some form or the other to the particulate matter and any regulation or policy measure towards controlling particulate matter has an implicit co-benefit towards to the other pollutants.

Building an effective air quality management system requires a process of continual improvement in knowing where the pollution is coming from and how much each of the sources are contributing to the ambient air quality. The source apportionment techniques are now well established to develop this information for informed decision making. There are two ways in apportioning pollution - (a) A top-down approach starting with monitoring of pollution and (b) A bottom-up approach starting with the activity data (like fuel consumption). Both the methods are well studied and documented. The literature available on these approaches to successfully conduct a source apportionment study is immense.

Source apportionment studies, which are primarily based on measurements and tracking down the sources through emission characteristics profiling, and receptor modeling, help in identifying the sources & extent of their contribution. The Auto Fuel Policy document of Government of India also recommended for carrying out source apportionment studies. Accordingly, source apportionment studies have been initiated in six major cities viz. Delhi**,** Mumbai**,** Chennai**,** Bangalore**,** Pune and Kanpur. The scope for source apportionment studies include**d** preparation of emission inventories, monitoring of ambient air quality for various pollutants (SPM, PM_{10}, $PM_{2.5}$, SO_2, NO_x, CO, HC, VOC, etc.) at selected locations (07 – 10 locations covering different land use viz. residential, industrial, kerbside, background, etc.), chemical speciation of PM_{10} & $PM_{2.5}$ as well as source emissions, application of dispersion & CMB8 models to assess the contribution from various sources, future projections and evaluation of various control options to develop cost-effective action plans. Besides, separate projects on development of emission factors for vehicles and Development of emission profiles for vehicular as well as non-vehicular sources have also been taken up, which would provide necessary inputs to source apportionment studies (CPCB, 2011).

Oil companies, led by Indian Oil Corporation Limited (IOCL) initiated source apportionment studies in August 2003 with National Environmental Engineering Research Institute (NEERI), Nagpur for source apportionment study in Delhi and with Automotive Research Association of India (ARAI), Pune for development of emission factors for vehicles. Subsequently, Memoranda of Collaborations (MoCs) were entered into with The Energy and Resources Institute (TERI) in December 2004 and The Automotive Research association of India (ARAI) in January 2005 for studies in Bangalore and Pune respectively. The focus of the above studies was on PM_{10} (particles of size less than or equal to10μm) (CPCB, 2011).

The air pollution levels especially in the urban areas are increasing in India. The efforts so far for pollution control mainly focused on monitoring and pollution control in the industry and vehicular sectors. However, quantitative/ qualitative assessments of pollution loads form individual sources viz. vehicular, industry, domestic etc. is important to prioritise the pollution control needs and take appropriate pollution control an abatement measures. In view of the high requirements for controlling air pollution due to its potential impact on human health, there is a need to have advanced assessment and apportionment of the pollution loads from various sources viz. traffic, industry etc. Source Apportionment is relatively new technique to assess air pollution problem in the vicinity and quantifications of each responsible source contributions of trace elements. This study addresses the characteristics of culprit source which emits non-essential trace elements in air which later on deposits in the soil by gravity.

Considering the need of Source Apportionment study, Tier II cities are facing adverse effects of local industries and transportation. Tier II cities in India are growing faster due to availability of land for infrastructure development, New SEZ policies by government, tax relief for some states/cities, political will to bring new industry at their cities and thereby creating employment opportunities for local citizens etc. New economic policies are favoring entrepreneurs and businessperson to invest their capital amount in some projects at Tier II cities with airport and other transport facilities. In addition, investments in real estate at such cities are attracting nearby metropolitan and Tier I citizens.

Kolhapur has always been looked at as a city with lovely weather, green landscapes and people with immense potential. With changing times and need of the hour, younger energetic entrepreneurs have given Kolhapur a new look. Positive change, development and fast pace of growth. This is evident with the changing skyline of Kolhapur. Better infrastructure, public facilities, shopping malls, multinational franchises are now prominently visible. Industries, retailers and other prospecting businesses are eying Kolhapur as the next big developing market. There also seems to a political willingness to help Kolhapur develop. With almost 220 crores being put into developing almost 50 Kms of internal arterial and access roads, Upgraded infrastructure like night landing facilities at the airport in the pipeline, possible availability of developmental funds through JNNRUM scheme, Kolhapur is truly being pushed onto the growth path.

Kolhapur is changing, developing and growing that too at a rapid pace. With availability of better infrastructure & key geographical location, Kolhapur foresees a tremendous boost in industrial growth. No city can make progress merely on industrial development. The retail market too has to support this developmental process. The influx of people into Kolhapur for work and business has increased the demand for more commercial and residential premises. One major indicator of this is the fact that Kolhapur has grown to its limits. The city boundaries are being extended. As a result, there is a huge potential for further investments, more business opportunities and larger availability of land and properties in general at affordable prices. Kolhapur is now Tier II city which is in top 5 in list of cities with highest per capita income.

Keeping eye on existing and proposed development of Kolhapur as well as current levels of Air pollution in city, which are beyond the NAAQS, the present study was conducted at Kolhapur city and industrial estates around city. The objective of the present study was to analyze trace elements present into SPM in Kolhapur and quantification of such trace elements with identification of responsible sources by US EPA PMF modeling, which was being used prominently, and only for Tier II city like Kolhapur. The sampling locations viz. Shahu Blood Bank Corner (SBBC), Gokul Shirgaon MIDC (GS) and Shiroli MIDC (SS) were selected due to their importance with respect to traffic density, industries and its process, commercial complexes, malls and other recreational facilities. Sampling of SPM at three sampling locations was done with High Volume Sampler for 24 hours weekly during 2008-09 and recording of meteorological data like Ambient Temperature and Wind Velocity were done simultaneously. SPM samples were subject to trace element extraction and accordingly trace elements like Cu, Pb, Ni, Mn, Zn, Cd, Fe were analyzed by Atomic Absorption Spectrophotometer. Observed concentrations of Trace Elements were given as Input to US EPA PMF modeling to get out of predicted concentrations of such trace elements. In addition, identification of responsible sources and its contribution to each trace element were found out which was main objective of the study. Model validation was done by sampling of soil as well as sampling of SPM from major sources like transportation and foundry at Kolhapur. The standard protocols and procedures of US EPA and CPCB were followed for Source Apportionment and Chemical Characterization of Trace Elements in Suspended Particulate Matter in Kolhapur City.

5.2 FINDINGS OF THE PRESENT STUDY

The main finding of the present study is the source identification of the trace metals found in Suspended Particulate Matter and its control at source. The study is aimed at understanding the present Ambient Air Quality and its concentrations in Tier II developing city of Kolhapur in Maharashtra, presence of Trace elements in SPM and the sources which contribute to their surces.

1. The sampling locations selected for the study were SBBC, GS and SS. The latitudes of SBBC, GS and SS are 16042’28.32”, 16038’17.48” and 16045’42.75” respectively while longitudes are 74013’45.81”, 74016’47.84” and 74016’41.22” respectively for above-mentioned locations.
2. Suspended Particulate Matter at SBBC ranges from 470 µg/m^3 to 590 µg/m^3. And in the case of GS, it ranges from 423 µg/m^3 to 550 µg/m^3. The SPM values ranges from 415 µg/m^3 to 535 µg/m^3 at SS. SPM exceeds the standard limit of 200 µg/m^3 as per NAAQS, CPCB, New Delhi at all three locations of study.
3. Presently, there are no threshold limit values available for trace elements selected for the study but their presence in air as well as soil in Kolhapur is warning and threat of being contamination in air as well as ground water through soil leading to adverse effect on human being as well as other components of Environment.
4. Pb and Cd are emerging as major trace elements in the air and soil of Kolhapur due to transportation and foundries nearby. Batteries and its allied industries and paints/pigments are also other sources releasing higher concentrations of Cd in city.

5. The two major contributors to the atmospheric particulate matter at Kolhapur are Transportation sector and the Industrial emissions. The SPM contributions from transportation sector can be effectively controlled by taking measures like Engine Modifications, Fuel substitution and Use of Catalytic Converters while the contributions from industrial sector can be controlled by adapting Process changes, Good operating practices, Source control, Use of air pollution control equipments, and Dispersion at higher levels, etc.
6. In addition, Cu and Fe are emerging as major trace elements in the air and soil of Gokul Shirgaon MIDC and Shiroli MIDC due to large number of foundries and casting industries available.
7. The presence of Zn in Kolhapur city is also threatening to the citizens of Kolhapur. Small-scale industries at Shivaji Udyamnagr, Y. P. Powar Nagar, and Panjarpol are playing vital role in emitting Zn and Cd into atmosphere of Kolhapur.
8. It is seen that 62% of Total SPM observed are released from tailpipe of Automobiles at SBBC. Unplanned traffic and shorter margins of road widths are leading to traffic congestions and chaos at SBBC during 10 am to 8 pm every day.
9. Presently, only one sampling station of MPCB at Shivaji University is operating. Shivaji University is situated on upstream of Kolhapur city on higher altitude of 620 m and sampling station is well surrounded by high trees. Daily sampling and monitoring do not take place due to lack of concern. Commercial and crowded areas like Dabholkar Corner and SBBC should have at least one sampling stations on 24 hours operational basis, may be a online continuous ambient air quality monitoring station with display of concentrations of important contributors is the need of the hour.
10. Majority of the roads in Kolhapur are two way in nature and always congested due to improper master plan by Urban Development authority. One-way roads shall serve the purpose of reducing air pollution from automobiles as well as

well being and safety of riders too. Use of parallel roads is always recommendable.

11. Public transportation like Kolhapur Municipal Transport (KMT) is not adequate and run on major roads in city. The frequencies of buses are low and passenger has to take the help of auto rickshaws and other private transport. This has increase of Auto rickshaws, which are polluting the city. Kerosene mixed fuels is used always leading to unburnt HCs and CO with SPM. Strengthening KMT shall benefit Kolhapur Municipal Corporation (KMC) for revenue generation as well as curb the problem of air pollution.

12. Many commuter private vehicles come from other nearby villages to Kolhapur for work and office. The frequencies of State Transport buses are too low and passenger has to wait for longer period. This has led to use of private vehicles like two wheelers, which often come and go in Kolhapur city. This is additional burden on traffic of Kolhapur City.

13. Unfortunately, Industrial MIDCs like Gokul Shirgaon and Shiroli are located on upstream of Kolhapur city. The city is always receiving the released air pollutants coming from these industries. The release of air pollutants from stack comes to city with wind direction facing towards city. The downstream of Kolhapur city is surrounded with higher mountain range of Sahyadri. The pollutants rebound and comes to Kolhapur city. The valley city like Kolhapur shall have air pollution disaster and hazard in near future if appropriate authorities do not take proper measures.

14. A finding of the present study includes chemical Characterization of trace elements associated with actual human exposure in urban areas. The study provides an integrated exposure assessment database for urban particulate matters characterization through outdoor monitoring for consideration in future Directives on air quality in India.

5.3 HIGHLIGHTS OF THE STUDY

1. Source Apportionment study, first time is carried out for tier II city like Kolhapur, Maharashtra, India.
2. US EPA PMF model is used since extensive source profiling based data not available.
3. Model validation is done through measurement of emissions from foundries and traffic which are major source and also soil metal analysis.
4. General suggestions for zoning of industries, traffic management and cause consequence study for health impact are suggested.
5. The present study was initiated in 2008 and monitoring was completed by 2010. The attempt was to characterize trace elements in SPM and quantification of contribution of each trace element to respective source.
6. Source apportionment studies worldwide have incorporated Receptor models like CMB, Unmix, PMF with respective to data availability. In India, CMB is used till date by CPCB, New Delhi for apportionment study at major metropolitan Tier I cities.
7. In present study, an attempt is made to incorporate PMF model for quantification of air quality at Kolhapur city, which is rapidly growing Tier II city. For the accurate estimation and quantification of contributions of trace elements, PMF was used along with CMB.
8. The project results may expect to be integrated with air quality management systems used by decision makers and city/regional planners in India for zoning policy.
9. Finally, the project will contribute with a scientific understanding of air pollution to zoning policy on air pollution and future Framework Directives.

5.4 FUTURE WORK

The present study was aimed at source apportionment and chemical characterization of trace elements in SPM at Kolhapur city. The following work can be initiated and incorporated with present study for better source apportionment at Tier II cities.

1. Sampling and monitoring of $PM_{2.5}$ as per New National Ambient Air Quality Standards (NAAQS) 2010.
2. Use of Cascade Impactor in sampling and monitoring for particle size distribution.
3. Specific trace elements like Pb and Cd to be addressed specially from automobile sources.
4. Generation of source profile data for point and area source.
5. Use of Chemical Mass Balance (CMB) along with PMF and Unmix.
6. Validation of results of trace elements with the results of trace elements found in Soil samples on and around the sampling location.
7. Inclusion of Urban and Air Quality Planners and decision makers in surce apportionment study.

ANNEXURES

ANNEXURE IA

NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)

United States Environmental Protection Agency

Pollutant	Type	Standard	Averaging Timea	Regulatory Citation
SO_2	Primary	0.14 ppm (365 µg/m3)	24-hour	40 CFR 50.4(b)
SO_2	Primary	0.030 ppm (80 µg/m³)	annual	40 CFR 50.4(a)
SO_2	Secondary	0.5 ppm (1,300 µg/m³)	3-hour	40 CFR 50.5(a)
PM_{10}	Primary and Secondary	150 µg/m³	24-hour	40 CFR 50.6(a)
$PM_{2.5}$	Primary and Secondary	35 µg/m³	24-hour	40 CFR 50.7(a)
$PM_{2.5}$	Primary and Secondary	15 µg/m³	annual	40 CFR 50.7(a)
CO	Primary	35 ppm (40 mg/m³)	1-hour	40 CFR 50.8(a)(2)
CO	Primary	9 ppm (10 mg/m³)	8-hour	40 CFR 50.8(a)(1)
O3	Primary and Secondary	0.12 ppm (235 µg/m³)	1-hourb	40 CFR 50.9(a)
O3	Primary and	0.075 ppm	8-hour	40 CFR 50.10(a)

	Secondary	(150 µg/m³)		
NO_2	Primary and Secondary	0.053 ppm (100 µg/m³)	annual	40 CFR 50.11(a) and (b)
Pb	Primary and Secondary	0.15 µg/m³	Rolling 3 months	40 CFR 50.12

(Source: NAAQS, EPA, USA as of October 2011)

- ^a **Each standard has its own criteria for how many times it may be exceeded, in some cases using a three year average.**
- ^b **As of June 15, 2005, the 1-hour ozone standard no longer applies to areas designated with respect to the 8-hour ozone standard (which includes most of the United States, except for portions of 10 states).**

ANNEXURE IB

NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)

Ministry of Environment and Forests, Government of India notification, 1994

Pollutant	**Time Weighted Average**	**Concentration in Ambient Air**		
		Industrial Area	Residential, Rural and other	Sensitive Area
Sulphur Dioxide (SO_2)	Annual 24 hours	80 $\mu g/m^3$ 120 $\mu g/m^3$	60 $\mu g/m^3$ 80 $\mu g/m^3$	15 $\mu g/m^3$ 30 $\mu g/m^3$
Oxides of Nitrogen (NO_2)	Annual 24 hours	80 $\mu g/m^3$ 120 $\mu g/m^3$	60 $\mu g/m^3$ 80 $\mu g/m^3$	15 $\mu g/m^3$ 30 $\mu g/m^3$
Suspended Particulate Matter (SPM)	Annual 24 hours	360 $\mu g/m^3$ 500 $\mu g/m^3$	140 $\mu g/m^3$ 200 $\mu g/m^3$	70 $\mu g/m^3$ 100 $\mu g/m^3$
Respirable ** Particulate Matter (RPM)	Annual 24 hours	120 $\mu g/m^3$ 150 $\mu g/m^3$	60 $\mu g/m^3$ 100 $\mu g/m^3$	50 $\mu g/m^3$ 75 $\mu g/m^3$
Lead (pb)	Annual 24 hours	1.0 $\mu g/m^3$ 1.5 $\mu g/m^3$	0.75 $\mu g/m^3$ 1.00 $\mu g/m^3$	0.50 $\mu g/m^3$ 0.75 $\mu g/m^3$
Carbon Monoxide(CO)	8 hours 1 hour	5.0 $\mu g/m^3$ 10.0 $\mu g/m^3$	2.0 $\mu g/m^3$ 4.0 $\mu g/m^3$	1.0 $\mu g/m^3$ 2.0 $\mu g/m^3$

**** Particle size less than 10** µm

REVISED NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS) 2009 NOTIFIED

The Ministry of Environment and Forests announced the notification of the Revised National Ambient Air Quality Standards 2009 in the official Gazette.

These ambient air quality standards/ limits which came after a gap of 15 years provide a legal framework for the control of air pollution and the protection of public health.

The previously existing National Air Ambient Air Quality Standards(NAAQS) were notified by the Central Pollution Control Board(CPCB in the year 1994 under the Air Act, 1981 for seven parameters i.e., Suspended Particulate Matter(SPM), Respirable Particulate Matter (RPM), Sulphur Dioxide(SO_2) ,Oxides of Nitrogen (NOx), Carbon Monoxide (CO), Ammonia (NH3) and Lead (Pb).The Central Government has thereafter also notified NAAQS for six parameters in the year 1996 under the Environment (Protection) Act,1986.

The review of the previous NAAQS and inclusion of new parameters was undertaken by the CPCB in association with the Indian Institute of Technology, Kanpur. The Proposal for revision in NAAQS was deliberated upon extensively and has been notified under the Environment (Protection) Act, 1986 on 16.11.2009 by the Ministry of Environment and Forests. The CPCB has initiated the process of harmonizing it’s notification under the Air Act, 1981 with the revised notification so as to ensure the efficient implementation of the new standards.

These revised Standards include initiatives that have been developed in consonance with global best practices and in keeping with the latest advancements in technology and research. Some of the salient features include:

1. Area classification based on land-use has been done away with so that industrial areas have to conform to the same standards as residential areas.
2. The standards shall be applicable uniformly with the exception of stringent standards for NO_2 and SO_2 in the Ecologically sensitive area.
3. The previous standards for residential area have been uniformly applied for fine particulate matter (PM_{10}), Carbon Monoxide and

Ammonia. More stringent limits for Lead, SO_2 and $N0_2$ have been prescribed even for residential areas.

4. Suspended particulate matter (SPM) as parameter has been replaced by fine particulate matter ($PM_{2.5}$) which is more relevant for public health.
5. Other new parameters, such as Ozone, Arsenic, Nickel, Benzene and Benzo (a) Pyrene (BaP) have been included for the first time under NAAQS based on CPCB/ IIT research, World Health Organisation guidelines and EU limits and practices.

Though Mercury has not been notified as part of these revised standards, the Ministry is conscious of the need to monitor the same. Research and development in standards setting and standardization of monitoring protocols for mercury is still in progress internationally. As a result, it may be noted that even the most progressive regimes in this regard, those of the member countries of the European Union, Have not included ‘mercury’ in their ambient air quality standards.

In furtherance of these Standards, the CPCB is in the process of creating a roadmap for the generation of maintenance of database, monitoring of required infrastructure and for the development of protocols. The ministry is also in the process of developing additional support systems of enforcement such as the National Environment Protection Authority (NEPA) and the National Green Tribunal (NGT) to ensure the effective enforcement of the standards.

ANNEXURE IC

AIR QUALITY IN KOLHAPUR CITY

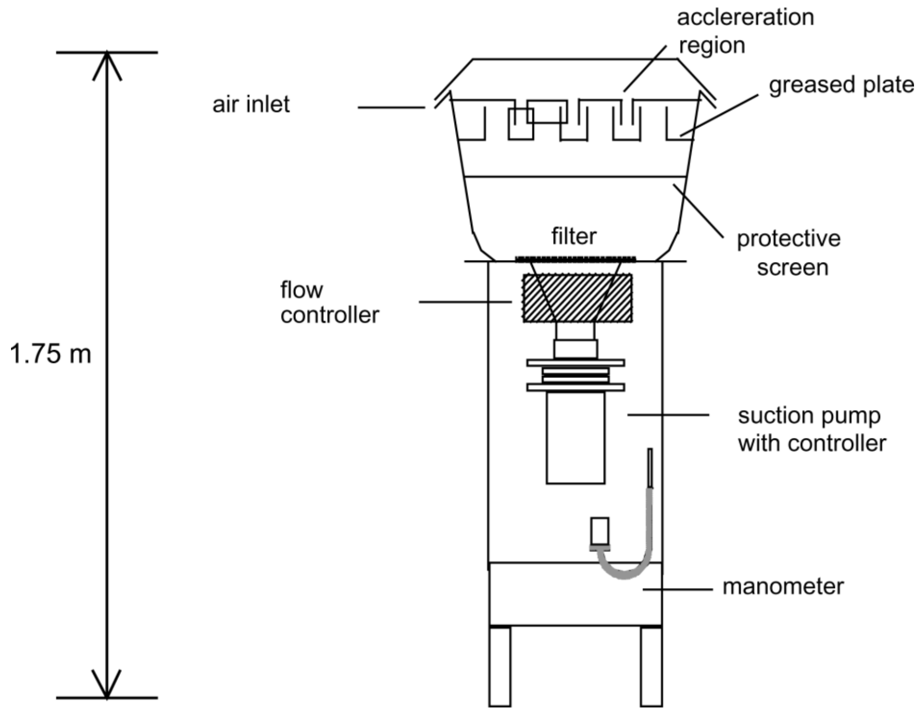
Months	**Dabholkar corner**				**Mahadwar road**				**Shivaji university campus**			
Parameter	**SO_2**	**NOx**	**RSPM**	**SPM**	**SO_2**	**NOx**	**RSPM**	**SPM**	**SO_2**	**NOx**	**RSPM**	**SPM**
Standards (CPCB)	80	80	100	200	80	80	100	200	80	80	100	200
Jan	11.53	25.31	119.0	259.2	8.59	12.34	99.18	215.8	4.69	6.30	45.8	101.3
Feb	13.3	32.80	122.8	272.2	8.82	13.44	79.36	198.6	6.21	8.04	55.6	130.8
March	20.57	40.78	104.8	361.6	15.62	24.71	114.72	247.3	10.93	13.21	62.0	130.5
April	19.68	41.55	105.0	342.8	16.47	27.22	110.40	211.3	10.12	13.39	60.5	130.5
May	24.67	43.20	107.0	331.9	17.64	28.96	174.77	212.7	11.33	14.13	56.6	125.9
June	19.77	36.80	77.08	219.3	12.46	21.88	115.92	142.6	10.20	13.33	45.8	100.9
July	15.17	31.55	15.17	23.36	9.46	17.36	16.47	119.9	6.95	11.78	47.9	101.2
August	10.36	15.79	59.16	123.3	6.43	9.97	56.31	117.2	4.17	5.66	40.1	83.11
Sept	10.51	15.72	74.56	159.3	6.37	9.69	57.33	227.3	5.03	7.26	49.8	105.4
October	14.48	22.90	108.5	273.2	11.21	15.16	100.6	227.3	7.21	11.10	68.0	143.1
November	17.27	23.27	114.2	310.0	11.78	17.05	103.5	250.9	6.95	11.78	67.2	145.3
December	16.79	24.60	106.2	316.0	12.15	17.64	91.63	228.7	8.55	12.76	67.7	147.4
Total	Min 10.36 Max 24.67	Min 15.72 Max 43.2	Min 15.17 Max 122.8	Min 23.36 Max 361.6	Min 6.37 Max 17.64	Min 9.69 Max 28.96	Min 16.47 Max 174.77	Min 117.2 Max 250.9	Min 4.17 Max 11.33	Min 5.66 Max 14.13	Min 40.1 Max 68	Min 83.11 Max 147.4

(Source: Maharashtra Pollution Control Board, Mumbai)

ANNEXURE II

HIGH VOLUME SAMPLER

Air-borne particulate matter is an ensemble of solid particles suspended and dispersed in air. The properties of these particles vary in terms of chemical composition, morphology (size/shape) optical parameters (color/light scattering), and electrical characteristics (charge, resistance). Particles, which in general are non spherical are classified in terms of their aerodynamic diameter. This is defined as the diameter of a sphere of density (1g/cm3 having a characteristic same as that of the particle in question.). In ambient air dust particles have size range from a few nanometers to hundreds of micrometer (μm). In ambient air SPM has bimodal mass distribution with respect to size whose shape depends on the predominant physical and chemical formation processes of particles.



PM_{10} and TSPM are measured by passing air at flow rate of about 1.1 m3/min through high efficiency cyclone which retains the dust particles greater than 10 micron size and allow only fines (less than 10 micron particles) to reach the glass microfiber filter where these particles are retained. The instrument provides instantaneous flow rate and the period of operation (on-time) for calculation of air volume passed through the filter. Amount of particulates collected is determined by measuring the change in weight of the cyclone cup and filter paper.

The passage of air entering in the cyclone is designed to prevent heavier settle able particles from reaching in the cyclone. It has following unique features for quality reliable results with user conveniences.

- Unique flow measurement system using orifice plate directly calibrated in M3/min. This is incorporated in filter holder casting which eliminates leakage
- While sampling and correct flow reading are obtained on provided manometer.
- Cabinet is anodized to withstand weathering effects. Thus unit can be operated in corrosive environment without any unwanted fears.

- A brushless and low noise pump is provided which reduces operation cost and
- Maintenance problems. Thus instrument can be operated in residential and
- Sensitive areas without hindrance.
- Manometer assembly has been shifted in top portion of the machine for better readability.
- MCB switch has been provided at the place of fuse and toggle switch for better safety and convenience.
- Pump is equipped with induction type motor which has capability to maintain its rpm at variable input voltage. Thus flow is not changing with change in input voltage.

Selection of Sampling Site

Monitoring site need to be 3-10m high from ground level. In present project where pollutants are expected from long distances through upper atmosphere. It is desirable to keep instrument at a height of about 8-10m. This shall result elimination of local activities contribution if any. To get a representative sample the sampler must not be positioned near a wall or other obstruction that would prevent free airflow. In excessively turbulent conditions or in the presence of strong surface winds or otherwise inclement weather, the sampling rate is likely to decrease rapidly and perhaps in a nonlinear fashion due to filter choking. If the sampler is operated continuously, day-to-day variations in the measurement are expected due to varying meteorological conditions and changing atmospheric phenomena, like wind speed and direction, dispersion, diffusion, etc. beside impact of emission sources.

Selection of Filter Medium

For most cases interest is limited to a gravimetric determination of the PM_{10} and total suspended particulate concentration. Glass Micro Fiber filters having low resistance to air flow, low affinity for moisture and 99% collection efficiency for particles of 0.3 microns or larger size are suitable for this purpose. However, where further analysis, of the particulates is to be attempted, to detect specific elements/radicals, care should be taken to choose special filter medium having a low background concentration of the substances of interest. For instance, special grades of Glass Microfiber filters like Whitman EPM2000 are available which have a controlled and a low known concentration of metals like Iron, Zinc, Cadmium, Lead, Arsenic, Nickel, etc.

Preparing the Filter

Prior to use, expose each filter to a light source and inspect for pinholes, particles and other imperfections. Filters with visible defects should not be used. A small brush is often used to remove stray particles adhering to the surface of new filters. Always handle filter papers from their edges and do not crease or fold the filter prior to use Filter papers, both blank and containing samples should be conditioned in a desiccators with active desiccant at 20 - 25°C, humidity below 50% R.H., for at least 16 hours prior to weighing. It is usual to put an identification number and date of sampling on the filters. Weigh the filters to the nearest milligram (accurate upto 0.1 mg for RDS filters and cup) and record the weight and filters identification number in data sheet Ensure keeping a perforated plastic bottle filled with active silica gel in weighing chamber for minimizing impact of moisture during weighing.

Installation of Filter paper

Install or remove filter paper only when the sampler is off. The numbered and the weighed filter paper are always kept with its rough side up. This increases the collection efficiency of the filter paper. The filter paper is placed in its proper position on the top of wire mesh. The sampler is started before putting back the top cover. This prevents the filter to shift from its place. As a result, any undesirable leakage from top is prevented. The top cover is not to be under tightened as it will give way to leakage and over tightening will damage the rubber gasket and filter. It is not very difficult to ascertain the extent to which the top cover is to be tightened but, one learns through practice only. A very light application of talcum powder on the rubber gasket prevents the filter from sticking to it.

Recording Correct Flow rates

Manometer Assembly for recording correct flow rate ensures zero level of the water in manometer tube. Always use distilled water for filling in the tube and every fortnightly water must be changed. Least count of manometer scale is 0.01 m3/min. Care is needed in taking reading always read lower meniscus of water level in the monometer tube. Manometer scale can be shifted up or down by loosening mounting screws of the scale to adjust zero level.

Rota meter Assembly

Ensure that no solids are deposited in the nozzle and tube of the Rota meter Float must move freely in the Rota meter tube. To record correct flow level of widest portion of float is recorded.

Time Totalizer

A time totalizer unit fitted in the machine uses a clock motor to drive a geared numerical display. The unit is wired so that it operates only when blower receives power. Hence its display indicates true time for which the sampler has sampled atmospheric air. It performs two important functions.

(i) It keeps a check on actual sampling time when instrument is operated.

(ii) It facilitates timely preventive maintenance.Time totalizer reading should be noted before and after each air sampling so that exact duration of sampling can be worked out.

ANNEXURE III

TRACE METALS EXTRACTION

(US EPA COMPENDIUM METHOD IO- 3.1)

The first step in the digestion is to prepare the containers ready for use. For this purpose the beakers were initially washed properly and then kept immersed in 0.25 % Nitric acid (HNO_3), for one day. Just before the digestion the beakers were taken out, washed again with tap water and then rinsed with double distilled water, in order to make the beakers free of contaminants and ready for further use.

The digestion mixture consists of a mixture of 3 ml Hydrochloric acid (HCl), 2 ml Nitric acid (HNO_3) and 1 ml Perchloric acid ($HClO_4$). The mixture was prepared by adding HCl, $HNO_{3,}$ and HClO4 in the ratio 3:2:1, respectively. The filter paper was reduced to small pieces were kept in each beaker and these beakers were covered by decontaminated watch glasses. These beakers were then kept on a hot plate at about 40-50 ^{0}C where they undergo decomposition. Initially, fumes may be observed, this is due to the burning of organic compounds present in the sample. If the fumes persist, it is suggested to turn off the hot plate for some time.

Proper temperature should be maintained during the digestion. If the temperature is low, then the digestion is very slow and improper while at high temperature the acid gets evaporated without digesting the sample completely.

The samples were digested till the black filter paper turns white and 1 -2 ml of acid was left in the beaker. The sample was not digested till evaporation, to avoid the loss of volatile trace metals. Finally the digested sample was extracted by filtration with double distilled water. The samples were made up to 25 ml by adding 0.25 % Nitric acid. These prepared samples were then used for trace metal determination using AAS.

ANNEXURE IV

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

In analytical chemistry, Atomic Absorption Spectroscopy (AAS) is a technique for determining the concentration of a particular metal element in a sample. The technique can be used to analyze the concentration of over 62 different metals in a solution.

Although atomic absorption spectroscopy dates to the nineteenth century, the modern form was largely developed during the 1950s by a team of Australian chemists. They were led by Alan Walsh and worked at the CSIRO (Commonwealth Science and Industry Research Organization) Division of Chemical Physics in Melbourne, Australia

Principles

The technique makes use of absorption spectrometry to assess the concentration of analyze in a sample. It relies therefore heavily on Beer-Lambert law.

In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals for an instant by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity.

As the quantity of energy (the power) put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured, it is possible, from Beer-Lambert law, to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured.

Instrumentation

In order to analyze a sample for its atomic constituents, it has to be atomized. The sample should then be illuminated by light. The light transmitted is finally measured by a detector. In order to reduce the effect of emission from the atomizer (e.g. the black body radiation) or the environment, a spectrometer is normally used between the atomizer and the detector.

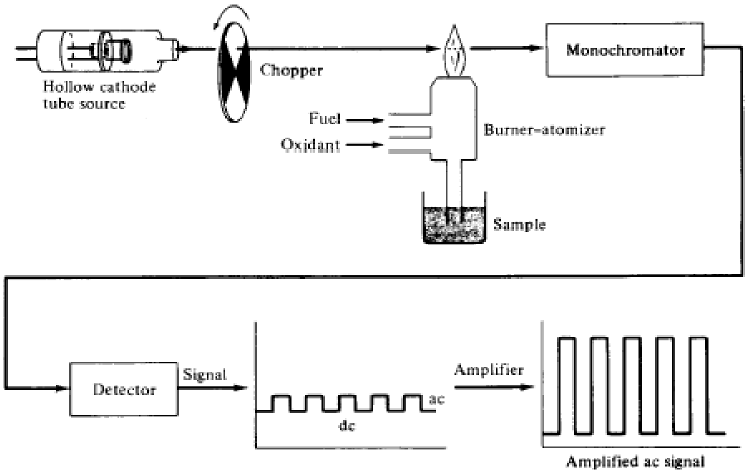


Figure: Working of AAS

Types of Atomizer

The technique typically makes use of a flame to atomize the sample, but other atomizers such as a graphite furnace or plasmas, primarily inductively coupled plasmas, are also used.

When a flame is used it is laterally long (usually 10 cm) and not deep. The height of the flame above the burner head can be controlled by adjusting the flow of the fuel mixture. A beam of light passes through this flame at its longest axis (the lateral axis) and hits a detector.

Analysis of liquids

A liquid sample is normally turned into an atomic gas in three steps:

1. Desolvation – the liquid solvent is evaporated, and the dry sample remains
2. Vaporization – the solid sample vaporizes to a gas
3. Atomization – the compounds making up the sample are broken into free atoms.

Radiation Sources

The radiation source chosen has a spectral width narrower than that of the atomic transitions.

Hollow cathode lamps

Hollow cathode lamps are the most common radiation source in atomic absorption spectroscopy. Inside the lamp, filled with argon or neon gas, is a cylindrical metal cathode containing the metal for excitation, and an anode. When a high voltage is applied across the anode and cathode, gas particles are ionized. As voltage is increased, gaseous ions acquire enough energy to eject metal atoms from the cathode. Some of these atoms are in excited states and emit light with the frequency characteristic to the metal. Many modern hollow cathode lamps are selective for several metals.

Diode lasers

Atomic absorption spectroscopy can also be performed by lasers, primarily diode lasers because of their good properties for laser absorption spectrometry. The technique is then either referred to as diode laser atomic absorption spectrometry

(DLAAS or DLAS), or, since wavelength modulation most often is employed, wavelength modulation absorption spectrometry.

Background Correction methods

The narrow bandwidth of hollow cathode lamps makes spectral overlap rare. That is, it is unlikely that an absorption line from one element will overlap with another. Molecular emission is much broader, so it is more likely that some molecular absorption band will overlap with an atomic line. This can result in artificially high absorption and an improperly high calculation for the concentration in the solution. Three methods are typically used to correct for this:

- Zeeman correction - A magnetic field is used to split the atomic line into two sidebands (see Zeeman Effect). These sidebands are close enough to the original wavelength to still overlap with molecular bands, but are far enough not to overlap with the atomic bands. The absorption in the presence and absence of a magnetic field can be compared, the difference being the atomic absorption of interest.
- Smith-Hieftje correction (invented by Stanley B. Smith and Gary M. Hieftje) - The hollow cathode lamp is pulsed with high current, causing a larger atom population and self-absorption during the pulses. This self-absorption causes a broadening of the line and a reduction of the line intensity at the original wavelength.
- Deuterium lamp correction - In this case, a separate source (a deuterium lamp) with broad emission is used to measure the background emission. The use of a separate lamp makes this method the least accurate, but its relative simplicity (and the fact that it is the oldest of the three) makes it the most commonly used method.

Working of AAS

Atomic absorption spectroscopy (AAS) is a widely used technique for determining a large number of metals. In the most common implementation of AAS, an aqueous sample containing the metal analyte is aspirated into an air-acetylene flame, causing evaporation of the solvent and vaporization of the free metal atoms. This process is called atomization. A line source (hollow cathode lamp) operating in the UV-visible spectral region is used to cause electronic excitation of the metal atoms, and the absorbance is measured with a conventional UV-visible dispersive spectrometer with photomultiplier detector.

The narrow spectral lines of atomic samples necessitate the use of a line source as well as a high-resolution monochromator. This helps to prevent interference from adjacent spectral lines of other atomic species present in the sample matrix. The availability of a spectrometer equipped with a lamp turret (allowing several line sources to be used in sequential fashion) will facilitate the measurement of multiple metals in the sample.

ANNEXURE V

SAMPLE ANALYSIS USING ATOMIC ABSORPTION SPECTROSCOPY

(US EPA Compendium Method IO- 3.2)

After gravimetric analysis, the acid digestion was carried out. Each exposed filter paper is cut into very small fragments and kept in a glass beaker of 100 ml capacity. Then 15 ml of mixture of oxidizing agents like HCl + HNO_3 + $HClO_4$ in the proportion (3:2:1) was poured into the digestion vessel and it is then placed over a hot plate and kept for about 1 hr at 40-50 ^{0}C. The residual is then filtered through filter paper and diluted as per requirement for the elemental analysis. The digested solutions were then analyzed by using the Atomic Absorption Spectroscopy (AAS) for Copper (Cu), Lead (Pb), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Manganese (Mn) and Iron (Fe).

The details of wavelength required for determinations of trace elements using AAS are given in the following table:

Wavelengths for AAS

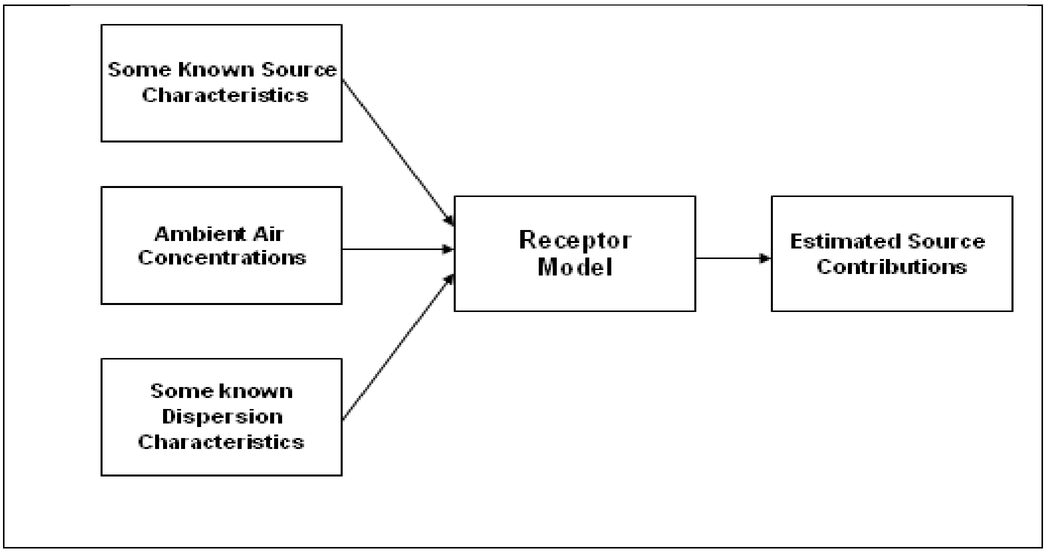
S. N.	Element	Wavelength nm	Working Range µg/ml	Sensitivity µg/ml
1	Ag	328.1	1.4-5.5	0.030
2	Al	396.2	25.0-110.0	0.550
3	As	193.7	32.0-190.0	0.640
4	Au	242.8	3.5-14.0	0.080
5	Ba	553.6	8.0-30.0	0.180
6	Be	234.9	1.0-5.0	0.015
7	Bi	223.1	9.0-36.0	0.200
8	Ca	422.7	1.0-4.0	0.020

9	Cd	228.8	0.2-1.8	0.009
10	Co	240.7	2.5-9.0	0.050
11	Cr	357.9	2.0-15.0	0.050
12	Cu	324.7	1.0-5.0	0.025
13	Fe	248.3	2.0-9.0	0.050
14	Hg	253.7	73-290	1.600
15	K	766.5	0.4-1.5	0.008
16	Li	670.8	1.0-4.0	0.020
17	Mg	285.2	0.1-0.4	0.003
18	Mn	279.5	1.0-3.6	0.020
19	Na	589.0	0.18-0.7	0.004
20	Ni	232.0	1.8-8.0	0.040
21	Pb	217.0	2.5-20.0	0.060
22	Pd	244.8	3.0-11.0	0.060
23	Sr	460.7	2.0-8.0	0.040
24	Yb	398.8	4.0-15.0	0.080
25	Zn	213.9	0.4-1.5	0.008

ANNEXURE VI

RECEPTOR MODELING

Receptor models are mathematical or statistical procedures for identifying and quantifying the sources of air pollutants at a receptor location. Receptor models use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. These models are therefore a natural complement to other air quality models and are used as part of State Implementation Plans (SIPs) for identifying sources contributing to air quality problems.



Framework for Receptor Modeling

In order to effectively manage air pollution problem, it is important to identify the major air pollution sources. After the obvious sources of aerosols have been controlled, there is still a need to identify the remaining sources so that efficient and effective air quality management strategies can be developed. Because the results of receptor models are based on the interpretation of actual measured ambient data, they offer a powerful advantage to the source attribution process.

The particle characteristics must be such that:

1. They are present in different proportions in different source emissions;

2. These proportions remain relatively constant for each source type;
3. Changes in these proportions between source and receptor are negligible or can be approximated.

Common types of Receptor Models include:

1. Chemical Mass Balance (CMB)
2. Principal Component Analysis (PCA, otherwise known as Factor Analysis)
3. Multiple Linear Regression (MLR)

Chemical mass balance is the fundamental receptor model, with all other approaches (including PCA and MLR) based on the use of the mass balance concept.

The United States Environmental Protection Agency (US EPA) has developed the Chemical Mass Balance (CMB) and UNMIX model as well as the Positive Matrix Factorization (PMF) method for use in air quality management. CMB fully apportions receptor concentrations to chemically distinct source-types depending upon the source profile database, while UNMIX and PMF internally generate source profiles from the ambient data.

A drawback of receptor models is that they can not be used to predict the impact of future sources. As well, they are limited spatially and temporally to the particular set of samples being analyzed.

Chemical Mass Balance (CMB)

The Chemical Mass Balance (CMB) air quality model is one of several receptor models that have been applied to air resources management. The chemical mass balance consists of a least squares solution to a set of linear equations which expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions. The source profile species abundances (i.e., the fractional amount of the species in the emissions from each source-type) and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to the CMB model.

The output consists of the amount contributed by each source-type to each chemical species. The model calculates values for the contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the importance of input data values in the solution and to calculate the uncertainties of the source contributions.

Miller *et al.* (1972) originally developed the chemical mass balance method. The basic assumption of this technique is that particles do not undergo any physical and chemical transformation during their transport from the release source.

Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices—factor contributions and factor profiles—which then need to be interpreted by an analyst as to what source types are represented using measured source profile information, wind direction analysis, and emission inventories. (Paatero and Tapper, 1994; Paatero, 1997).

Results are constrained so that no sample can have a negative source contribution. PMF allows each data point to be individually weighed. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. For example, data below detection can be retained for use in the model, with the associated uncertainty adjusted so these data points have less influence on the solution than measurements above the detection limit.

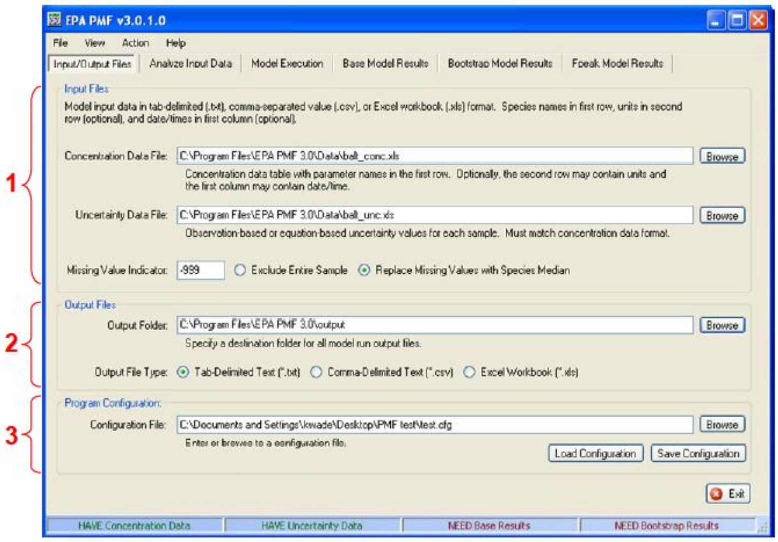
Variability in the PMF solution can be estimated using a bootstrapping technique, which is a re-sampling method in which “new” data sets are generated that are consistent with the original data. Each data set is decomposed into profile and contribution matrices, and the resulting profile and contribution matrices are compared with the base run (Eberly, 2005).

ANNEXURE VII

US EPA PMF MODELING

Each time the EPA PMF v3.0 program is started, a splash screen with information about the development of the software and various copyrights is displayed. The user must click the OK button or press the spacebar or Enter key to continue.

The first EPA PMF 3.0 screen and tab is the Input/Output Files screen as shown in Figure 3.5. On this screen, the user provides file location information and selects various specifications that will be used throughout the program. This screen has three sections: Input Files (Figure 3.5 - 1), Output Files (Figure 3.5 - 2), and Program Configuration (Figure 3.5 - 3), each of which is described in detail below. The status bar on the Input/Output Files screen indicates which section of the program has been completed. Before input into the parts of this screen, the status bar displays Need Concentration Data, Need Uncertainty Data, Need Base Results, and Need Bootstrap results in red. When a task is completed, Need is replaced with Have and the color changes to green. In the Figure 3.5 example, concentration and uncertainty files have been provided to the program, so the first two items on the status bar are green, but base runs and bootstrap runs have not been completed, so the last two items are red.



Input Files

Model input data in tab-delimited (.txt), comma-separated value (.csv), or Excel workbook (.xls) format. Species names in first row, units in second row (optional), and date/times in first column (optional).

Concentration Data File: C:\Program Files\EPA PMF 3.0\Data\balt_conc.xls

Concentration data table with parameter names in the first row. Optionally, the second row may contain units and the first column may contain date/time.

Uncertainty Data File: C:\Program Files\EPA PMF 3.0\Data\balt_unc.xls

Observation-based or equation-based uncertainty values for each sample. Must match concentration data format.

Missing Value Indicator: -999 ○ Exclude Entire Sample ● Replace Missing Values with Species Median

Output Files

Output Folder: C:\Program Files\EPA PMF 3.0\output

Specify a destination folder for all model run output files.

Output File Type: ● Tab-Delimited Text (*.txt) ○ Comma-Delimited Text (*.csv) ○ Excel Workbook (*.xls)

Program Configuration:

Configuration File: C:\Documents and Settings\kwade\Desktop\PMF test\test.cfg

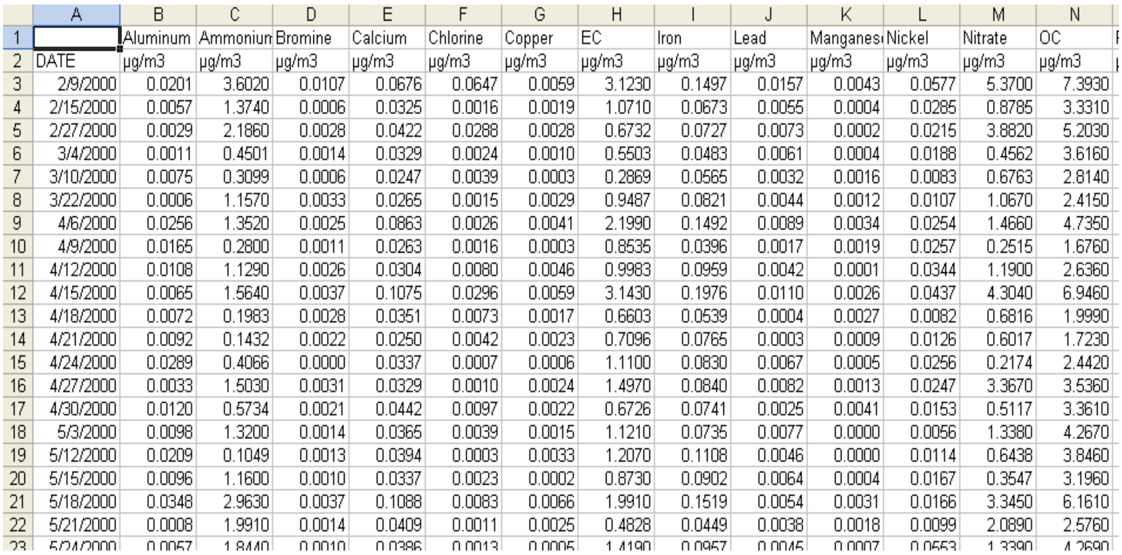
Enter or browse to a configuration file.

HAVE Concentration Data | HAVE Uncertainty Data | NEED Base Results | NEED Bootstrap Results

First EPA PMF 3.0 screen and Example Input/Output Files screen

Input files

Two input files are required by PMF: one containing concentration values and one containing either uncertainty values or parameters for calculating uncertainty. EPA PMF will accept tab delimited (.txt), comma-separated value (.csv), or MS Excel (.xls) files. Each file is loaded either by typing the path into the "data file" input boxes or browsing to the appropriate file. If the file includes more than one worksheet or named range, the user will be asked to select the one they want to use. The concentration file should contain parameters as columns and dates/samples as rows, with headers for each. All standard date and time conventions are accepted. Units can be included as a second heading row, but are not required. If units are supplied by the user, they will be used by the GUI for axes labels only and do not impact the model. The Baltimore example data set, included with EPA PMF v3.0 (balt_conc.xls and balt_unc.xls) is an example of input files containing units. Blank cells are not accepted; the user will be prompted to examine the data and try again. If values greater than 9000 or less than -900 are found in the data set, the program will give a warning message but will continue. If these values are not real or are missing value indicators, the user should fix the data file outside the GUI and reload the data sets.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1		Aluminum	Ammoniun	Bromine	Calcium	Chlorine	Copper	EC	Iron	Lead	Manganes	Nickel	Nitrate	OC
2	DATE	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3
3	2/9/2000	0.0201	3.6020	0.0107	0.0676	0.0647	0.0059	3.1230	0.1497	0.0157	0.0043	0.0577	5.3700	7.3930
4	2/15/2000	0.0057	1.3740	0.0006	0.0325	0.0016	0.0019	1.0710	0.0673	0.0055	0.0004	0.0285	0.8785	3.3310
5	2/27/2000	0.0029	2.1860	0.0028	0.0422	0.0288	0.0028	0.6732	0.0727	0.0073	0.0002	0.0215	3.8820	5.2030
6	3/4/2000	0.0011	0.4501	0.0014	0.0329	0.0024	0.0010	0.5503	0.0483	0.0061	0.0004	0.0188	0.4562	3.6160
7	3/10/2000	0.0075	0.3099	0.0006	0.0247	0.0039	0.0003	0.2869	0.0565	0.0032	0.0016	0.0083	0.6763	2.8140
8	3/22/2000	0.0006	1.1570	0.0033	0.0265	0.0015	0.0029	0.9487	0.0821	0.0044	0.0012	0.0107	1.0670	2.4150
9	4/6/2000	0.0256	1.3520	0.0025	0.0863	0.0026	0.0041	2.1990	0.1492	0.0089	0.0034	0.0254	1.4660	4.7350
10	4/9/2000	0.0165	0.2800	0.0011	0.0263	0.0016	0.0003	0.8535	0.0396	0.0017	0.0019	0.0257	0.2515	1.6760
11	4/12/2000	0.0108	1.1290	0.0026	0.0304	0.0080	0.0046	0.9983	0.0959	0.0042	0.0001	0.0344	1.1900	2.6360
12	4/15/2000	0.0065	1.5640	0.0037	0.1075	0.0296	0.0059	3.1430	0.1976	0.0110	0.0026	0.0437	4.3040	6.9460
13	4/18/2000	0.0072	0.1983	0.0028	0.0351	0.0073	0.0017	0.6603	0.0539	0.0004	0.0027	0.0082	0.6816	1.9990
14	4/21/2000	0.0092	0.1432	0.0022	0.0250	0.0042	0.0023	0.7096	0.0765	0.0003	0.0009	0.0126	0.6017	1.7230
15	4/24/2000	0.0289	0.4066	0.0000	0.0337	0.0007	0.0006	1.1100	0.0830	0.0067	0.0005	0.0256	0.2174	2.4420
16	4/27/2000	0.0033	1.5030	0.0031	0.0329	0.0010	0.0024	1.4970	0.0840	0.0082	0.0013	0.0247	3.3670	3.5360
17	4/30/2000	0.0120	0.5734	0.0021	0.0442	0.0097	0.0022	0.6726	0.0741	0.0025	0.0041	0.0153	0.5117	3.3610
18	5/3/2000	0.0098	1.3200	0.0014	0.0365	0.0039	0.0015	1.1210	0.0735	0.0077	0.0000	0.0056	1.3380	4.2670
19	5/12/2000	0.0209	0.1049	0.0013	0.0394	0.0003	0.0033	1.2070	0.1108	0.0046	0.0000	0.0114	0.6438	3.8460
20	5/15/2000	0.0096	1.1600	0.0010	0.0337	0.0023	0.0002	0.8730	0.0902	0.0064	0.0004	0.0167	0.3547	3.1960
21	5/18/2000	0.0348	2.9630	0.0037	0.1088	0.0083	0.0066	1.9910	0.1519	0.0054	0.0031	0.0166	3.3450	6.1610
22	5/21/2000	0.0008	1.9910	0.0014	0.0409	0.0011	0.0025	0.4828	0.0449	0.0038	0.0018	0.0099	2.0890	2.5760
23	5/24/2000	0.0057	1.8440	0.0010	0.0386	0.0013	0.0005	1.4190	0.0957	0.0045	0.0007	0.0553	1.3390	4.2690

Example formatting of input concentration file.

The user must also provide an uncertainty file to give the model an estimate of the confidence the user has in each value. The uncertainties provided should encompass errors such as sampling and analytical errors. For some data sets, the analytical laboratory or reporting agency provides an uncertainty estimate for each value. However, uncertainties are not always reported and, when they are not available, must be estimated by the user. A discussion of calculating uncertainties is provided in Reff et al. (2007). EPA PMF v3.0 accepts two types of uncertainty file: sample-specific and equation-based. The sample specific uncertainty file provides an estimate of the uncertainty for each sample of each species. It should have the same dimensions as the concentration file, however, the uncertainty file should not include units. If the concentration file contains a row of units, the uncertainty file will have one less row than the concentration file. The user will be notified if the column and row headers do not match, but the program will continue. If the headers are different due to naming conventions but actually have the same order, the user should proceed. If not, the user should correct the problem outside the GUI and reload the files. Negative values and zero are not permitted as uncertainties; EPA PMF will provide an error message and the user will have to remove these values outside EPA PMF and reload the uncertainty file. The equation-based uncertainty file provides species-specific parameters that EPA PMF v3.0 uses to calculate uncertainties for each sample. This file should have one column for each species, with species names as the column header (Figure 5-3). The first row under the species name is the detection limit; the second row is the error fraction. The error fraction should be the percent uncertainty x 100. Zeroes or negatives are not permitted for either the detection limit or the percent uncertainty. If the concentration is less than or equal to the method detection limit (MDL) provided, the uncertainty is calculated using the following equation (Polissar et al., 1998).

$$Unc = \frac{5}{6} \times MDL \tag{1-1}$$

If the concentration is greater than the MDL provided, the calculation is

$$Unc = \sqrt{(Error\ Fraction \times concentration)^2 + (MDL)^2} \tag{1-2}$$

The user can specify a “Missing Value Indicator” in the “Input Files” box on the **Input/Output Files** screen, which can be any numeric value. The user should use caution not to choose a numeric indicator that could potentially be a real concentration. The GUI will either remove the entire sample or replace the species concentration with the median concentration of that species and the uncertainty with four times the median concentration. For example, if the user specifies “-999” as the missing value indicator, and chooses to replace the species with the median, the GUI will find all instances of “-999” in the data file and replace them with the species-specific median. The GUI will also replace all associated uncertainty values with a high uncertainty of four times the species-specific median. If all samples of a species are missing, that species is automatically categorized as “bad” and excluded from further analysis. Whenever new input files are provided by the user, the GUI clears all output displays from previous runs. The user should take care to save all relevant graphics before providing new data sets to the GUI.

Output Files

The user defines the output directory (“Output Folder”) and chooses the EPA PMF output file types (“Output File Type” radio buttons): tab-delimited text, **.txt**; comma-separated variable, **.csv**; or MS Excel, **.xls** in “Output Files”. Five output files are automatically created by EPA PMF during base runs and are saved in the output folder selected by the user (if MS Excel output is designated by the user, the files are represented as separate tabs in ***_base.xls**):

- ***_diag** contains a record of the user inputs and model diagnostic information,
- ***_contrib** contains the contributions for each base run,

- ***_profile** contains the profiles for each base run,
- ***_resid** contains the residuals (regular and scaled by the uncertainty) for each base run, and
- ***_strength** contains the factor strength for each base run,

where * is the user-specified output file name prefix. Additional files are created and saved after bootstrapping (***_profile_boot**) and Fpeak (***_fpeak**) have been performed. The file, ***_profile_boot**, contains the number of bootstrap runs mapped to each base run, each bootstrap profile that was mapped to the base profile, and all bootstrapping statistics generated by the GUI. The file, ***_fpeak** contains the profiles and contributions of each fpeak run.

Configuration files

EPA PMF saves user preferences in a configuration file. The details saved include input files, output file location, qualifier, file type, species categorization, and all run specifications from the **Model Execution** screen. Previous model output is not saved in the configuration file. To save or load a configuration file, the user can click on “Browse” to browse to the correct path or type in a path and name. The user should then select “Load Configuration from File” to open a configuration or “Save Current Configuration to File” to save the current settings to a configuration file.

ANNEXURE VIII

SAMPLE CALCULATION FOR SPM CONCENTRATION

at Shahu Blood Bank Corner on 28th October 2008

$$\textbf{SPM concentrations in } \mu g/m^3 : = \frac{\textbf{Weight of particulate matter sampled, W}}{\textbf{Corrected Volume of air sample, V}}$$

1. Initial weight of the filter paper(W_1) : 5.005 gm
2. Final weight of the filter paper(W_2) : 5.690 gm
3. Sampling time(t) : 1440 min
4. Observed flow rate (Q) : 1000 lpm
5. Temperature (T) : 26 ^{0}C

Calculation of Weight of particulate matter sampled, W:

$$\begin{aligned} W &= w_2 - w_1 \\ &= 5.690 - 5.005 \\ &= 0.685 \text{ gm} \\ &= 0.685 \times 10^6 \ \mu g \end{aligned}$$

Calculation of Volume of air sampled at 30 °C,

$$\begin{aligned} \mathbf{V} &= \text{Observed flow rate X Sampling time} \\ &= 1000 \text{ X } 24 \text{ X } 60 \\ &= 1440000 \text{ Litres} \\ &= 1400.000 \text{ m}^3 \end{aligned}$$

Calculation of Corrected volume of air sampled at 25 ºC

According to Ideal gas law:

$$\frac{P_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

Assuming equal pressure, then $p_1 = p_2$

Therefore,

$$\frac{v_1}{T_1} = \frac{v_2}{T_2}$$

$$\frac{v_1}{(273 + 25)} = \frac{1400.000}{(273 + 26)}$$

$$V_1 = 1395.3177 \text{ m}^3$$

Corrected volume of air sampled at 25 ºC = 1395.3177 m^3

$$\textbf{SPM concentrations in } \mu g/m^3: = \frac{\textbf{Weight of particulate matter sampled, W}}{\textbf{Corrected Volume of air sample, V}}$$

$$\textbf{SPM concentrations in } \mu g/m^3: = \frac{0.685 \times 10^6 \mu g}{1395.3177 \text{ m}^3} = 490.92 \mu g/ \text{m}^3$$

ANNEXURE XI

CALCULATION OF SOURCE STRENGTH (gm/sec)

SPM concentrations from Vehicle Emission on 31/05/2010 between 10 am to 6 pm

Line Source Model

Application

- Motor vehicle travelling along a straight section of highway
- Agricultural burning along the edge of a field
- Line of industrial sources on the bank of a river

$$C(x) = (2q)/(\sqrt{2\pi}\,\sigma_z\,u)$$

Where,

C= Concentration of the pollutant (µg/m^3)

q = emissions per unit of distance along the line (gm/m-sec)

u = wind speed (m/sec)

σ_z = Vertical dispersion Parameter (m)

Assumption

- Infinite length source continuously emitting the pollution
- Ground level source
- Wind blowing perpendicular to the line source can be handled in principle as one dimensional dispersion from a point source

For wind perpendicular to line source:

$$c_{(z=0)} = \frac{2q}{\sqrt{2\pi}\,u\sigma_z}\exp -0.5\left(\frac{H}{\sigma_z}\right)^2$$

Where,

q = emission per unit time (gm/sec)

u = wind speed (m/sec)

σ_z = Vertical dispersion Parameter (m)

Case 1: when vehicle is in idle position

Category of Vehicle	Emission Factor (gm/km)	No. of Vehicle/8 hr	Speed of the Vehicle (assumed) km/hr	Vehicles/km	q(gm/hr)	gm/sec
2 wheeler	**0.05**	**1553**	**0.1**	**776.5**	**38.825**	**0.0013481**
3wheeler	**0.2**	**663**	**0.1**	**331.5**	**66.3**	**0.0023021**
4 wheeler	**0.03**	**813**	**0.1**	**406.5**	**12.195**	**0.0004234**
bus	**0.56**	**514**	**0.1**	**257**	**143.92**	**0.0049972**
					Total (1)	**0.0090708**

Case 2: when vehicle moves or accelerates as the signal goes green

Category of Vehicle	Emission Factor (gm/km)	No. of Vehicle/8 hr	Speed of the Vehicle (assumed) km/hr	Vehicles/km	q(gm/hr)	gm/sec
2 wheeler	**0.05**	**522**	**15**	**34.8**	**1.74**	**6.042E-05**
3wheeler	**0.2**	**222**	**15**	**14.8**	**2.96**	**0.0001028**
4 wheeler	**0.03**	**272**	**15**	**18.13**	**0.544**	**1.889E-05**
Bus	**0.56**	**171**	**15**	**11.4**	**6.384**	**0.0002217**
					Total (2)	**0.0004038**
					Total (1+2)	**0.0094746**

Modeling Results

Source Strength q (gm/sec)	Wind speed u (m/sec)	dz (m)	Distances (m)	concentration (gm/m^3)	concentration ($\mu g/m^3$)
0.0094746	2.1	10	100	0.000359499	**359.4991463**

ANNEXURE X

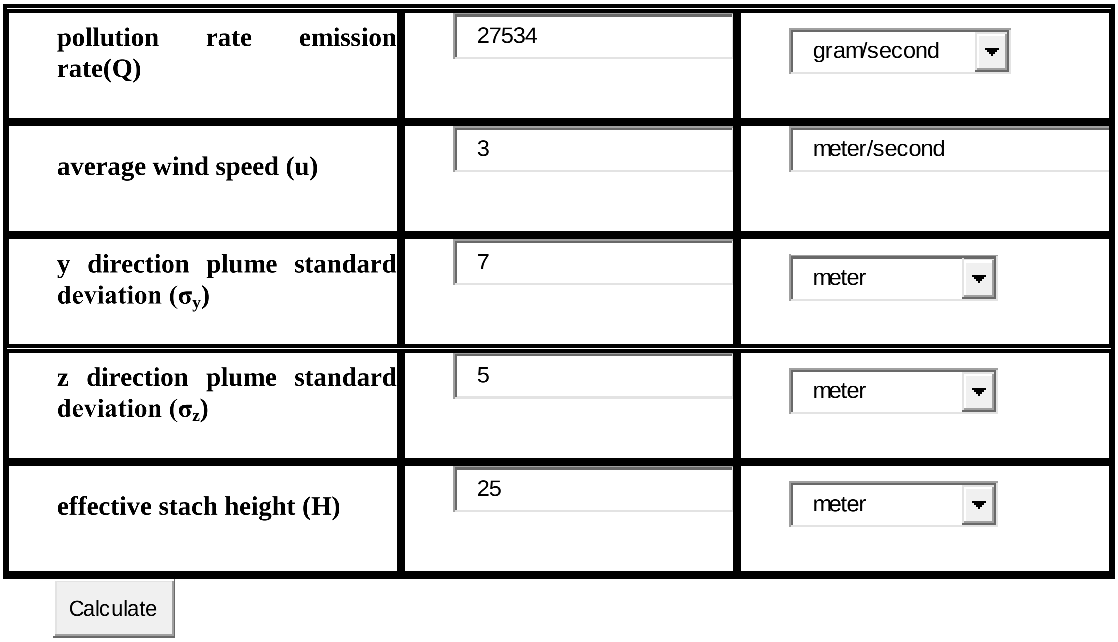
FOUNDRY EMISSIONS SOURCE STRENGTH CONCENTRATIONS AT SHIROLI MIDC

Source	**Emission factor(Ef)** **kg/1000 kg of iron produced**	**Number (N)**	**Source Strength (Q)** **gm/sec**
Cupola	6.9	20	26840
Induction Furnace	0.5	05	694
Total			27534

Contaminant concentration at ground level along the plume centerline.

$$C(x,0,0)=\frac{Q}{\pi u\sigma_y\sigma_z}e^{-\frac{H^2}{2\sigma_z^2}}$$

Inputs:



pollution rate emission rate(Q)	27534	gram/second
average wind speed (u)	3	meter/second
y direction plume standard deviation (σ_y)	7	meter
z direction plume standard deviation (σ_z)	5	meter
effective stach height (H)	25	meter

Conversions:

pollution rate emission rate(Q)	=	27534	gram/second	=	27534	gram/second
average wind speed (u)	=	3	meter/second	=	3	meter/second
y direction plume standard deviation (σ_y)	=	7	meter	=	7	meter
z direction plume standard deviation (σ_z)	=	5	meter	=	5	meter
effective stach height (H)	=	25	meter	=	25	meter

Solution:

contaminant concentration at ground level along the plume centerline (C)	=	**0.00031106354173807**	**gram/meter^3**

contaminant concentration at ground level along the plume centerline (C)	=	**311.06354173807**	**microgram/meter^3**

REFERENCES

Abu-Allaban, M., Gertler, A.W. and Lowenthal, D.H. (2002). “A Preliminary Apportionment of the Sources of Ambient PM10, PM2.5 and VOCs in Cairo.” *Atmos. Environ.* 36, 5549-5557.

Adams, H.S.., Nieuwenhuijsen, M.J. and Colvile, R.N. (2001); “Determinants of fine particle (PM2.5) personal exposure levels in transport microenvironments, London, UK.” *Atmospheric Environment*. 35 (27), 4557-4566.

Adgate, J.L., Willis, R.D., Buckley, T.J. Chow, J.C., Watson, J.G., Rhoads, G.G. and Lioy, P.J. (1998). “Chemical Mass Balance Source Apportionment of Lead in House Dust.” *Environ. Sci. Technol.* 32, 108-114.

Afroz, R., Hassan, M. N. and Ibrahim N. A. (2003). “Review of air pollution and health impacts in Malaysia.” *Environmental Research.* 92, 71–77.

Albergel, A. and F. Jasmin (1998). "3-D simulation of local-scale traffic pollution." *International Journal of Vehicle Design* 20(1-4): 79-87.

Ames, M.R. Gullu, G., Beal, J. and Olmez, I. (2000). “Receptor Modeling for Elemental Source Contributions to Fine Aerosols in New York.” *Journal of Air and Waste Management Association.* 50: 881-887.

Anderson, H. R. (1999). “Health Effects of Air Pollution Episodes.” *Air Pollution and Health.*461-482. doi:10.1016/B978-012352335-8/50096-X.

Anfossi, D., F. Desiato, et al. (1998). "TRANSALP 1989 experimental campaign - II. Simulation of a tracer experiment with Lagrangian particle models." *Atmospheric Environment* 32(7): 1157-1166.

Anju and Banerjee, D.K. (2003). “Heavy Metal Levels and Solid Phase Speciation in Street Dusts of Delhi, India.” *Environ. Pollut.* 123, 95–105.

Anttila, P., Paatero, P., Tapper, U., Tapper, U., Jarvinen, O. (1995).”Source identification of bulk wet deposition in Finland by positive matrix factorization.” *Atmos Environ*. 29(14), 1705–1718.

Ara, F., Iqbal, MZ. and Qureshi, MS. (1996), "Determination of heavy metals contamination of trees and soils due to vehicular emission in Karachi City". *Karachi University Journal of Science* 24:80-84.

Arditsoglou, A. and Samara, C. (2005). "Levels of Total Suspended Particulate Matter and Major Trace Elements in Kosovo: A Source Identification and Apportionment Study." *Chemosphere.* 59, 669-678.

Arimoto R, Duce R. A., Savoie D. L., Prospero J. M., Talbot R., Cullen J. D. (1996). "Relationships among aerosol constituents from Asia and the North Pacific during Pem-West A." *J Geophy Res*. 101, 2011–2023.

Arnfield, A. J., (1982), "An approach to the estimation of the surface radiative properties and radiation budgets of cities". *Phys. Geogr.,* 3, 97–122.

Artaxo, P., Andrade, F. and Maenhaut, W. (1990). "Trace Elements and Receptor Modeling of Aerosols in the Antarctic Peninsula." *Nuclear Inst Methods. Phy. Res.* B49, 383-387.

Azad, A.K. and Kitada, T. (1998). "Characteristics of the Air Pollution in the City of Dhaka, Bangladesh in Winter." *Atmos. Environ.* 32, 1991-2005.

Azimi S., Ludwig A., Thévenot D.R. and Colin J. L. (2003). "Trace metal determination in total atmospheric deposition in rural and urban areas." *Science of the Total Environment*. 308 (1-3), 247-254.

Azzi, M., G. M. Johnson, et al. (1992). "An introduction to the generic reaction set photochemical smog mechanism". *Proceedings of the 11th International Conference of the Clean Air Society of Australia & New Zealand,* Brisbane.

Bachmann K. (1982). "Separation of trace elements in solid samples by formation of volatile inorganic compounds." *Atlanta.* 29, 1-25.

Bais, A. F., C. S. Zerefos, et al. (1993). "Spectral measurements of solar UVB radiation and its relations to total ozone, SO_2 and clouds." *Journal of Geophysical Research* 98: 5199-5204.

Balachandran, S., Meena, B.R. and Khillare, P.S., (2000). “Particle Size Distribution and its Elemental Composition in the Ambient Air of Delhi.” *Environ. Int*. 26, 49–54.

Balczo, M., T. Farago, et al. (2005). “Modelling urban pollution dispersion by using MISKAM”. *Proceedings der Konferenz microCAD 2005*, Miskolc University.

Baldasano JM, Valera E, Jimenez P. (2003), “Air quality data from large cities”, *Sci Total Environ*. 20;307(1-3):141-65.

Barna, M. G. and N. R. Gimson (2002). "Dispersion modelling of a wintertime particulate pollution episode in Christchurch, New Zealand." *Atmospheric Environment* 36(21): 3531-3544.

Barrie, L.A. and Georgii, H.W. (1976). “An experimental investigation of the absorption of sulfur dioxide by water droplets containing heavy metal ions.” *Atmospheric Environment*. 10, 743-759.

Barth, M., McFadden, J.P., Sun, J., Wiedinmyer, C., Chuang, P., Collins, D., Hannigan, M., Karl, T., Kim, S-W., Lasher-Trapp, S., Levis, S., Litvak, M., Mahowald, N., Moore, K., Nandi, S., Nemitz, E., Nenes, A., Potosnak, M., Raymond, T.M., Smith, J., Still, C., Stroud, C. (2005). “Coupling between land ecosystems and the atmospheric hydrologic cycle through biogenic aerosol pathways.” *Am Meteorol Soc*. 86, 1738–1742.

Batterman, S.A., Dzubay, T.G.. amd Baumgardner R.E. (1988). “Development of Crustal Profiles for Receptor Modeling.” *Atmos. Environ.* 22, 1821-1828.

Beardsley, R., Bromberg, P.A., Costa, D.A., Devlin, R., Dockery, D.W., Frampton, M.W., Lambert, W., Samet, J.M., Speizer, F.E., (1997). “Smoke Alarm: Haze From Fires Might Promote Bacterial Growth.” *Sci. Am.* 24–25.

Beceiro-Gonazalez E., Andrade- Garda J.M., Serrano-Vela-Sco E., and Lopez-Mohia P. (1997). “Metals in the airborne particulate matter in LA Coruna (New Spain).” *Sci. Tot. Environ.* 196,131.

Beevers, S. D., Carslaw, D. C. (2005). “The impact of congestion charging on vehicle emissions in London.” *Atmospheric Environment.* 39, 1–5.

Begum, B.A., Biswas, S.K. and Hopke, P.K. (2006). “Temporal Variations and Spatial Distribution of Ambient PM2.2 and PM10 Concentrations in Dhaka, Bangladesh.” *Sci. Total Environ.* 358, 36-45.

Begum, B.A., Biswas, S.K., Hopke, P.K. and Cohen, D.D. (2006). “Multi-Element Analysis and Characterization of Atmospheric Particulate Pollution in Dhaka.” *Aerosol Air Qual. Res.* 6, 334-359.

Begum, B.A., Biswas, S.K., Kim, E., Hopke, P.K. and Khaliquzzaman, M. (2005). “Investigation of Sources of Atmospheric Aerosol at a Hot Spot Area in Dhaka, Bangladesh.” *J. Air Waste Manage. Assoc.* 55, 227-240.

Begum, B.A., Kim, E., Biswas, S.K. and Hopke, P.K. (2004). “Investigation of Sources of Atmospheric Aerosol at Urban and Semi-Urban Areas in Bangladesh.” *Atmos. Environ.* 38, 3025-3038.

Bellinger DC, Stiles KM, Needleman HL., (1992), “Low-level lead exposure, intelligence and academic achievement: a long-term follow-up study” *Pediatrics*. 90:855–861.

Benson, P. E. (1984). CALINE 4 – A Dispersion Model for Predicting Air Pollutant Concentrations near Roadways. *FHWA User Guide*. U. Trinity Consultants Inc.

Berkowicz, C. E., R. C. Easter, et al. (1989). "Theory and results from a quasi-steadystate precipitation-scavenging model." *Atmospheric Environment* 23: 1555-1571.

Berndt, T., O. Boege, et al. (2000). "Formation of new particles in the system H2SO4(SO3)/H2O/(NH3)-first results from a flow-tube study." *Journal of Aerosol Science* 31(Suppl. 1): S554-555.

Bhanuprasad, S.G., Venkataraman, C., Bhushan, M., (2008). “Positive matrix factorization and trajectory modeling for source identi.cation: a new look at Indian Ocean Experiment ship observations.” *Atmos. Environ.* 42, 4836–4852.

Bhave, P.V., Fergenson, D.P., Prather, K.A. and Cass, G.R. (2001). “Source Apportionment of Fine Particulate Matter by Clustering Single-particle Data: Tests of Receptor Model Accuracy.” *Environ. Sci. Technol.* 35, 2060-2072.

Biegalski, S.R., Landsberger, S. and Hoff, R.M. (1998). “Source-receptor Modeling Using Trace Metals in Aerosols Collected at Three Rural Canadian Great Lakes Sampling Stations.” *JAWMA.* 48, 227-237.

Billheimer, D. (2001). “Compositional Receptor Modeling.” *Environmetrics.* 2, 451-467.

Bilos C., Colombo J. C., Skorupka C. N., Rodriguez Presa, M. J. (2001). “Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina” *Environmental Pollution.* 111, 149-158.

Binkowski, F. S. and S. J. Roselle (2003). "Models-3 community multiscale air quality (CMAQ) model aerosol component - 1. Model description." *Journal of Geophysical Research-Atmospheres* 108(D6)

Binkowski, F. S. and U. Shankar (1995). "The Regional Particulate Matter Model .1. Model description and preliminary results." *Journal of Geophysical Research-Atmospheres* 100(D12): 26191-26209.

Biswas, S.K., Tarafdar, S.A., Islam, A., Khaliquzzaman, M., Tervahattu, H. and Kupiainen, K. (2003). “Impact of Unleaded Gasoline Introduction on the Concentration of Lead in the Air of Dhaka, Bangladesh.” *J. Air Waste Manage. Assoc.* 53, 1355-1362.

Brajer, V., Mead R.W., Xiao F. (2006). “Valuing the health impacts of air pollution in Hong Kong.” *Journal of Asian Economics.* 17, 85–102.

Brajer, V., Mead R.W., Xiao F., (2006). “Valuing the health impacts of air pollution in Hong Kong.” *Journal of Asian Economics*. 17, 85–102.

Bramfitt, B. L.; Benscoter, Arlan O. (2002). "The Iron Carbon Phase Diagram". Metallographer's guide: practice and procedures for irons and steels. *ASM International*. pp. 24–28.ISBN 978-0-87170-748-2.

Breed, C.A., Arocena, J.M. and Sutherland, D. (2002). “Possible Sources of PM10 in Prince George (Canada) as Revealed by Morphology and in Situ Chemical Composition of Particulate.” *Atmos. Environ.* 36, 1721–1731.

Briggs, G. (1973). "Internal memo as reported by F.A. Gifford Jr. in Turbulent Diffusion Typing Schemes: A Review." *Nuclear Safety* 17: 68-86.

Briggs, G. A. (1975). Plume Rise Predictions. Lectures on Air Pollution and Environmental Impact Analysis. D. A. Haugen. Boston, MA, *American Meteorology Society*: 59-111.

Briggs, G.A., (1968), "CONCAWE meeting: discussion of the comparative consequences of different plume rise formulas", Atmos. Envir., 2:228–232

Bytnerowicz A, Fenn M. E. (1996). “Nitrogen deposition in California forests—A review.” *Environ Pollut*. 92, 127–146.

Capaldo, K. P., C. Pilinis, et al. (2000). "A computationally efficient hybrid approach for dynamic gas/aerosol transfer in air quality models." *Atmospheric Environment* 34(21): 3617-3627.

Caputo, M., M. Gimenez, et al. (2003). "Intercomparison of atmospheric dispersion models." *Atmospheric Environment* 37(18): 2435-2449.

Carruthers, D. J., D. R. J. Holroy, et al. (1994). "Uk-Adms - a New Approach to Modeling Dispersion in the Earths Atmospheric Boundary-Layer." *Journal of Wind Engineering and Industrial Aerodynamics* 52(1-3): 139-153.

Carruthers, D. J., H. A. Edmunds, et al. (2000). "Use and validation of ADMS-Urban in contrasting urban and industrial locations." *International Journal of Environment and Pollution* 14(1-6): 364-374.

Carvalho, J. D., G. A. Degrazia, et al. (2002). "Lagrangian stochastic dispersion modelling for the simulation of the release of contaminants from tall and low sources." *Meteorologische Zeitschrift* 11(2): 89-97.

Celis, J.E., Morales, J.R., Zaror, C.A., Inzunza, J.C. (2004). “A study of the particulate matter PM10 composition in the atmosphere of Chillan, Chile.” *Chemosphere*. 54, 541–550.

Chakraborty, A. and Gupta, T. (2009). “Chemical Characterization of Submicron Aerosol in Kanpur Region: a Source Apportionment Study”; *International Journal of Environmental Science and Engineering*, 1:2.

Chameides, W. L., Hu H, Liu, S. C., Bergin, M., Zhou, X., Mearns, L.,Wang, G., Kiang, C.S., Saylor, R. D., Luo, C., Huang, Y., Steiner, A., Giorgi, F. (1999). “Case study of the effects of atmospheric aerosols and regional haze on agriculture: An opportunity to enhance crop yields in China through emission controls.” *Proc Nat Acad Sci*. 26, 3626–13633.

Chan, L.Y., Kwok, W.S. (2001). “Roadside suspended particulates at heavily trafficked urban sites of Hong-Kong: Seasonal variation and dependence on meteorological conditions.” *Atmospheric Environment.* 35, 3177-3182;

Chan, W. H., Thonassinin, F., and Loescher, B. (1983). “An evaluation of sorption properties of precipitation constituents on polythene surfaces.” *Atmospheric Environment.* 17, 1779-1785.

Chen, K.S., Lin, C.F. and Chou, Y.M. (2001). “Determination of Source Contributions to Ambient PM2.5 in Kaohsiung, Taiwan, using receptor model.” *JAWMA.* 51, 489-498.

Chen, L.W.A., Watson, J.G., Chow, J.C., Magliano, K.L. (2007). “Quantifying PM2.5 Source Contributions for the San Joaquin Valley with Multivariate Receptor Models.” *Environ. Sci. Technol.* 41, 2818-2826.

Cheng, M.D. and Hopke, P.K. (1989). “Identification of Markers for Chemical Mass Balance Receptor Model.” *Atmos. Environ.* 23, 1373-1384.

Chow, J. C., Watson, J. G., Lu, Z. Q., Lowenthal, D. H., Frazier, C. A., Solomon, P. A., Thuillier, R. H., Magliano, K., (1996). “Descriptive analysis of PM2.5 and PM10 at regionally representative locations during SJVAQS/AUSPEX.” *Atmos Environ.* 30(12), 2079–2112.

Chow, J.C. and Watson, J.G. (2002). “Review of PM2.5 and PM10 apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model.” *Energy Fuels.* 16, 222–260.

Christensen, W.F. (2004). “Chemical Mass Balance Analysis of Air Quality Data when Unknown Pollution Sources are Present.” *Atmos. Environ.* 38, 4305-4317.

Chueinta, W., Hopke, P.K. and Paatero, P. (2000). “Investigation of Source of Atmospheric Aerosol Oa Urban and Suburban Residential Areas in Thailand by Positive Matrix Factorization.” *Atmos. Environ.* 34, 3319-3329.

Clairborn, C., A. Mitra, et al. (1995). "Evaluation of Pm10 Emission Rates from Paved and Unpaved Roads Using Tracer Techniques." *Atmospheric Environment* 29(10): 1075-1089.

Conner Teri, L., Gary, A.N., Mathew, S.L. and Ronald, W. (2001). “Individual particle analysis of indoor, outdoor, and community samples from the 1998 Baltimore particulate matter study.” *Atmospheric Environment.* 35(23), 3935-3946.

Davidson C. I., Grimm T. A., and Nasta M. A. (1981). “Airborne Lead and other elements derived from local fires in the Himalayas” *Science.* 214, 1344-1346.

Decker, E.H., Elliott, S., Smith, F.A., Blake, D.R., Rowland, F.S. (2000). “Energy and material flow through the urban ecosystem.” *Annual Review of Energy and the Environment*. 25, 685–740.

Devraj T., Jan H., Hopke P. K. (2009). “Source Apportionment of Winter Submicron Prague Aerosols from Combined Particle Number Size Distribution and Gaseous Composition Data.” *Aerosol and Air Quality Research.* 9(2), 209-236.

Dockery, D. W., Pope, C. A., Xiping, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris Jr., B. G., and Speizer, F. E. (1993). “An association between air pollution and mortality in six US cities.” *New Engl. J. Med.* 329(24), 1753–1759.

Dockery, D.J. and Pope, C.A. (1994). “Acute Respiratory Effects of Particulate Air Pollution.” *Ann Rev Public Health*. 15, 107-132.

Donaldson, K., Li X Y, MacNee, W. (1998). “Ultrafine (nanometer) particle-mediated lung injury.” *J Aerosol Sci*. 29, 533–560.

Du, S. M. (2001). "A heuristic Lagrangian stochastic particle model of relative diffusion: model formulation and preliminary results." *Atmospheric Environment* 35(9): 1597-1607.

Dzubay, Thomas G. and Stevens, R. K. (1988). “A Composite Receptor Method Applied to Philadelphia Aerosol.” *Environmental Science and Technology*. 22 (1), 46-52.

Elbir, T. (2003). "Comparison of model predictions with the data of an urban air quality monitoring network in Izmir, Turkey." *Atmospheric Environment* 37(15): 2149-2157.

Engelbrecht, J.P., Swanepoel, L., Chow, J.C. and Watson, R.E. (2002). “The comparison of source contributions from residential coal and low-smoke fuels, using CMB modeling, in South Africa.” *Environ Sci. Pol.* 5, 2169-2185.

Fang G., Wu Y., Wen C., Huang S., and Rau J. (2006). “Ambient air particulate concentrations and metallic elements principal component analysis at Taichung Harbor (TH) and WuChi Traffic (WT) near Taiwan Street during 2004-2005.” *Journal of Hazardous Materials.* B137, 314-323.

Fenger, J. (1999). “Urban air quality.” *Atmospheric Environment*. 33, 4877-4900.

Fergussion, J.E. and Kim, N.D. (1991). “Trace Elements in Street and House Dust: Source and Speciation.” *Sci. Total Environ.* 100, 125-150.

Ferrero, E., D. Anfossi, et al. (2000). "Intercomparison of Lagrangian stochastic models based on two different PDFs." *International Journal of Environment and Pollution* 14(1-6): 225-234.

Fitzgerald, J. W., W. A. Hoppel, et al. (1998). "A One-Dimensional Sectional Model to Simulate Multicomponent Aerosol Dynamics in the Marine Boundary Layer. 1 Model Description." *Journal of Geophysical Research-Atmospheres* 103: 16085-16102.

Flament P., Deboudt K., and Puskaric E. (1996). “Changes in the lead content of Atmospheric aerosols above the eastern channel between 1982-83 and1994.” *Sci. Tot. Env.* 192,193;

Folinsbee et al. (1988), “Pulmonary function and symptom response after 6.6-hour exposure to 0.12 ppm ozone with moderate exercise”. *JAPCA* 38: 28-35.

Friedlander, S.K. (1973). “Chemical element balances and identification of air pollution sources.” *Environ. Sci. Technol.* 7, 235-40.

Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., Doherty, S. J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.-M., Lohmann, U., Russell, L. M., and Pschl, U. (2006). “Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change.” *Atmos. Chem. Phys.* 6, 2017–2038.

Gao, Y., Nelson, E. D., Field, M. P., Ding, Q., Li, H., Sherrell, R. M. (2002). “Characterization of atmospheric trace elements on PM2.5 particulate matter over the New York-New Jersey Harbor Estuary.” *Atmos Environ*. 36(6), 1077–1086.

Gariazzo, C., A. Pelliccioni, et al. (2004). "Evaluation of a Lagrangian particle model (SPRAY) to assess environmental impact of an industrial facility in complex terrain." *Water Air and Soil Pollution* 155(1-4): 137-158.

Gebhart, K.A., Kreidenweis, S.M., and Malm, W.C. (2001). “Back trajectory analysis of fine particulate matter measured at big bend national park in the historical database and 1996 scoping study.” *Science of the Total Environment*. 276,185-204.

Gery, M. W., G. Z. Whitten, et al. (1989). "A photochemical kinetics mechanism for urban and regional scale computer modeling." *Journal of Geophysical Research* 94: 12925-12956.

Gidhagen, L., C. Johansson, et al. (2003). "Model simulation of ultrafine particles inside a road tunnel." *Atmospheric Environment* 37: 2023-2036.

Gidhagen, L., C. Johansson, et al. (2004). "Simulation of NOx and ultrafine particles in a street canyon in Stockholm, Sweden." *Atmospheric Environment* 38(14): 2029-2044.

Gifford Jr., F. A. (1976). "Consequences of Effluent Releases." *Nuclear Safety* 17(1): 68-86.

Glover, G.E., Hopke, P.K., Vermette, S. J., Landsberger, S. and D'Auben, D. R. (1991). “Source Apportionment with Site Specific Source Profiles.” *J. Air Waste Manage. Assoc.* 41, 294-305.

Gordon, G.E. (1988). “Receptor Models.” *Environ. Sci. Technol.* 22, 1132-1142.

Greenberg, R.R., Zoller, W.H., and Gordan, G.E. (1978). “Composition and size distribution of particles released in refuse incineration” *Environmental Science and Technology.*

Gros, V., Sciare , J., Yu , T. (2007). “Air-quality measurements in megacities: Focus on gaseous organic and particulate pollutants and comparison between two contrasted cities, Paris and Beijing, C. R.” *Geoscience*. 339, 764–774.

Gupta, A. K., Karar, K., Srivastava, A., (2006). “Chemical Mass Balance Source Apportionment of PM10 and TSP in Residential and Industrial Sites of an Urban Region of Kolkata India.” *J. Hazard. Mater.* 142, 279–287.

Gurjar, B.R., Butler, T.M., Lawrence, M.G., Lelieveld, J. (2007). “Evaluation of emissions and air quality in megacities.” *Atmospheric Environment.* doi:10.1016/j.atmosenv.2007.10.048.

Gurjar, B.R., Lelieveld J. (2005). “New Directions: Megacities and global change.” *Atmospheric Environment*. 39 (2), 391-393.

Gurjar, B.R., van Aardenne J.A., Lelieveld J., Mohan M. (2004). “Emission estimates and trends (1990-2000) for megacity Delhi and implications.” *Atmospheric Environment*. 38 (33), 5663-5681.

Hall, D. J., A. M. Spanton, et al. (2002). "Evaluation of new generation atmospheric dispersion models." *International Journal of Environment and Pollution* 18(1):22-32.

Hamamci C., Gung-um B., Akba O., Erdogan S. (1997). “Lead in urban street dust in Diyarbakir, Turkey.” *Fresenius Environmental Bulletin.* 6, 430.

Hanna, S. R. (1982). Applications in Air Pollution Modeling. Atmospheric Turbulence and Air Pollution Modelling. *F. T. M. Nieuwstadt and H. Van Dop. Dordrecht*, Riedel.

Hanna, S. R., B. A. Egan, et al. (2001). "Evaluation of the ADMS, AERMOD, and ISC3 dispersion models with the OPTEX, Duke Forest, Kincaid, Indianapolis and Lovett field datasets." *International Journal of Environment and Pollution* 16(1-6): 301-314.

Harris, A.R. and Davidson, C.I. (2005). “The Role of Resuspended Soil in Lead Flows in the California South Coast Air Basin.” *Environ. Sci. Technol.* 39: 7410-7415.

Harrison, R. M., M. Jones, et al. (1999). "Measurements of the Physical Properties of Particles in the Urban Atmosphere." *Atmospheric Environment* 33: 309-321.

Harrison, R. M.; Tilling, R.; Romero, M. S. C.; Harrad, S. & Jarvis, K. (2003). A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment. *Atmospheric Environment*, 37, 2391-2402, 1352-2310

Harrison, R. N. and A. M. Jones (2005). "Multisite study of particle number concentrations in urban air." *Environmental Science & Technology* 39(16): 6063-6070.

Harvey, M.J., Fischer, G.W., Lechnier, I.S, Issac, P., Flower, N.E., and Dick, A.L. (1991). “Summer time aerosols measurements in the Ross sea region of Antarctica.” *Atmospheric Environment.* 25, 569-580.

Haus N., Zimmermann S., Wiegand J. and Sures B. (2007). “Occurrence of platinum and additional traffic related heavy metals in sediments and biota.” *Chemosphere*. 66 (4), 619-629.

Haus N., Zimmermann S., Wiegand J. and Sures B. (2007). “Occurrence of platinum and additional traffic related heavy metals in sediments and biota.” *Chemosphere*. 66 (4), 619-629.

He, K.B., Yang, F. M., Ma, Y. L., Zhang, Q., Yao, X. L., Chan, C. C., Cadle, S., Chan, T., Mulawa, P., (2001). “The characteristics of PM2.5 in Beijing, China.” *Atmos Environ.* 35(29), 4959–4970.

Hedberg, M., Gidhagen, L., Johansson, C. (2005). “Source contributions to PM10 and arsenic concentrations in Central Chile using positive matrix factorization.” *Atmos Environ.* 39(3), 549–561.

Henry, R.C. (2003). “Multivariate Receptor Modeling by N-Dimensional Edge Detection.” *Chemom. Intell. Lab. Sys.* 65, 179-189.

Heo I, Joo C, Cho J, Ha M, Han J, Kim VN., (2008), Lin28 mediates the terminal uridylation of let-7 precursor *MicroRNA. Mol Cell* 32:276–84.

Hidy, G.M. and Venkataraman, C. (1996). “The Chemical Mass Balance Method for Estimating Atmospheric Particle Sources in Southern California.” *Chem. Eng. Commun.* 151, 187-209.

Hitchins, J., L. Morawska, et al. (2000). "Concentrations of submicrometre particles from vehicle emissions near a major road." *Atmospheric Environment* 34: 51-64.

Ho, K.F., Lee, S.C., Chow, J.C. and Watson, J.G. (2003). “Characterization of PM10 and PM2.5 Source Profiles for Fugitive Dust in Hong Kong.” *Atmos. Environ.* 37, 1023-1032.

Holman, C. (1999). “Sources of Air Pollution”. *Air Pollution and Health.* 115-148.

Holman, C., (1999). “Sources of Air Pollution.” *Air Pollution and Health.* 115-148. doi:10.1016/B978-012352335-8/50083-1.

Holmes, N. S., L. Morawska, et al. (2005). "Spatial distribution of submicrometre particles and CO in an urban microscale environment." *Atmospheric Environment* 39(22): 3977-3988.

Hopke, P.K. (1991). “An Introduction to Receptor Modeling.” *Chemom. Intell. Lab. Syst.* 10, 21-43.

Hopke, P.K. (2003). “Recent Developments in Receptor Modeling.” *J. Chemometrics.* 17, 255-265.

Hopke, P.K., Begum, B.A., Biswas, S.K. (2005). “A Graphical Diagnostic Method for Assessing the Rotation in Factor Analytical Models of Atmospheric Pollution.” *Atmos. Environ.* 39, 193-201.

Hopke, P.K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P. and Cohen, D. (1997). “Characterization of the Gent Stacked Filter Unit PM10 Sampler.” *Aerosol Sci. Technol.* 27, 726-735.

Hopke, P.K.; Ito, K.; Mar, T.; Christensen, W.F.; Eatough, D.J.; Henry, R.C.; Kim, E.; Laden, F.; Lall, R.; Larson, T.V.; Liu, H.; Neas, L.; Pinto, J.; Stolzel, M.; Suh, H.; Paatero, P.; Thurston, G.D. (2006). “PM Source Apportionment and Health Effects: Intercomparison of Source Apportionment Results.” *J. Expo. Anal. Environ. Epidemiol.* 16, 275-286.

Huang, S., Arimoto, R. and Rahn, K.A. (2001). “Sources and source variations for aerosol at Mace Head, Ireland.” *Atmospheric Environment.* 35, 1421-1437.

Huang, S., Arimoto, R., Rahn, K. A., (1996). “Changes in atmospheric lead and other pollution elements at Bermuda.” *J Geophy Res.* 101, 21033–21040.

Huang, X. D., Olmez, I., Aras, N. K., Gordon, G. E. (1994). “Emissions of trace-elements from motor vehicles-potential marker elements and source composition profile.” *Atmos Environ.* 28(8), 1385–1391.

Huang, X.-F., Yu, J. Z., He, L.-Y., and Yuan, Z, (2006), Watersoluble organic carbon and oxalate in aerosols at a coastal urban site in China: Size distribution characteristics, sources, and formation mechanisms, *J. Geophys. Res.*, 111, D22212, doi:10.1029/2006jd007408

Hurley, P. J., A. Blockley, et al. (2001). "Verification of a prognostic meteorological and air pollution model for year-long predictions in the Kwinana industrial region of Western Australia." *Atmospheric Environment* 35(10): 1871-1880.

Hurley, P., P. Manins, et al. (2003). "Year-long, high-resolution, urban airshed modelling: verification of TAPM predictions of smog and particles in Melbourne, Australia." *Atmospheric Environment* 37(14): 1899-1910.

I. M. Ulbrich, M. R. Canagaratna, Q. Zhang, D. R. Worsnop, J. L. Jimenez, (2009), Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys*., 9, 2891-2918

Iqbal, MZ. and Rahmati, K. (1992), “Tolerance of Albizia lebbeck to Cu and Fe application.” *Ekologia (CSFR).* 11:427-430.

J.-B. Heo, P. K. Hopke, and S.-M. Yi, (2009), “Source apportionment of PM2.5 in Seoul, Korea”, *Atmos. Chem. Phys.*, 9, 4957–4971

J.R.McNeill. (2009) "Environmental History in the Americas: Two Great Invasions." *Nova Acta Leopoldina*, 98, 185-200.

Jacobson, M. Z. (1996). "Application of a sparse-matrix, vectorized gear-type code in a new air pollution modeling system." *Zeitschrift Fur Angewandte Mathematik Und Mechanik* 76: 333-336.

Jacobson, M. Z. (1997). "Development and application of a new air pollution modeling system .2. Aerosol module structure and design (vol 31, pg 131, 1997)." *Atmospheric Environment* 31(7): 1097-1097.

Jacobson, M. Z. (2001). "GATOR-GCMM: A global- through urban-scale air pollution and weather forecast model 1. Model design and treatment of subgrid soil, vegetation, roads, rooftops, water, sea ice, and snow." *Journal of Geophysical Research-Atmospheres* 106(D6): 5385-5401.

Jaffrezo, J.L., Aymoz, G., and Cozic, J. (2005). “Size distribution of EC and OC in the aerosol of Alpine valleys during summer and winter.” *Atmos. Chem. Phys*. 5, 2915–2925,

Jawarowski, Z., M. Bysiek and L. Kownacka. (1981). Flow of metals into the global atmosphere. *Geohimica et Cosmochimica Acta*, 45: 2185-2199

Jung, Y. R., W. G. Park, et al. (2003). "Pollution dispersion analysis using the puff model with numerical flow field data." *Mechanics Research Communications* 30(4): 277-286.

Kaasik, M. and V. Kimmel (2003). "Validation of the improved AEROPOL model against the Copenhagen data set." *International Journal of Environment and Pollution* 20(1-6): 114-120.

Kandlikar, M., Ramachandran, G. (2000). “The cause and consequence of particulate air pollution in urban India: A synthesis of the science.” *Annual Review of Energy and the Environment*. 25, 629–684.

Kandlikar, M., Ramachandran, G. (2000). “The cause and consequence of particulate air pollution in urban India: A synthesis of the science.” *Annual Review of Energy and the Environment*. 25, 629–684.

Kasahara, M., Choi, K. C., and Takahashi, K. (1990). “Source Contribution of Atmospheric Aerosols in Japan by Chemical Mass Balance Method.” *Atmospheric Environment*. 24A(3), 457- 466.

Kasperek K, Iyengar GV, Kiem J, Borberg H, Feinendegen LE (1979) Elemental composition of platelets. Part III. Determination of Ag, Au, Cd, Co, Cr, Cs, Mo, Rb, Sb and Se in normal human platelets by neutron activation analysis. *Clin Chem* 25:711–715

Ketzel, M., R. Berkowicz, et al. (2000). "Comparison of numerical street dispersion models with results from wind tunnel and field measurements." *Environmental Monitoring and Assessment* 65(1-2): 363-370.

Khemani, L.T., Naik, M.S., Momin, G.A., Kumar, R., Chatterjee, R.N., Singh, and Ramana Murty, B.V. (1985). “Trace Elements in the atmospheric Aerosols at Delhi, North India.” *J. Atmos. Chem.* 273–285.

Khillare, P.S., Balachandran, S. and Meena, B.R., (2004). “Spatial and Temporal Variation of Heavy Metals in Atmospheric Aerosol of Delhi.” *Environ. Monit. Assess.* 90, 1–21.

Kim Ki-Hyun., Kim Min-Young, Hong S.M., Youn Y.H., and Hwanget S.J. (2005). “The effects of wind speed on the relative relationships between different sized fractions of airborne particles.” *Chemosphere.* 59(7), 929-937.

Kim, E., Hopke, P.K. and Edgerton, E.S. (2003a). “Source Identification of Atlanta Aerosol by Positive Matrix Factorization.” *J. Air Waste Manage. Assoc.* 53, 731-739.

Kim, E., Larson, T.V., Hopke, P.K., Slaughter, C., Sheppardand L.E., Claiborne, C. (2003b). “Source Identification of PM2.5 in an Arid Northwest U.S. City by Positive Matrix Factorization.” *Atmos Research.* 66, 291-305.

Korhonen, H., K. E. J. Lehtinen, (2003). "Simulation of atmospheric nucleation mode: A comparison of nucleation models and size distribution representations." *Journal of Geophysical Research-Atmospheres* 108(D15)

Korhonen, H., K. E. J. Lehtinen, (2004). "Multicomponent aerosol dynamics model UHMA: model development and validation." *Atmospheric Chemistry and Physics* 4: 757-771.

Korhonen, P., M. Kulmala, (1999). "Ternary nucleation of H2SO4, NH3, and H2O in the atmosphere." *Journal of Geophysical Research-Atmospheres* 104(D21): 26349-26353.

Kowalcysk, E. A., J. R. Garratt, (1991). “A soil canopy scheme for use in a numerical model of the atmosphere - 1D stand alone model”. *C. D. o. A. Research, CSIRO.*

Kowalczyk, G.S., Gordon, G.E., and Rheingrover, S.W. (1982). “Identification of Atmospheric Particulate Sources in Washington D.C., Using Chemical Mass Balance.” *Environmental Science and Technology*. 16(2), 79-90.

Kuhn, M., P. J. H. Builtjes, (1998). "Intercomparison of the gas-phase chemistry in several chemistry and transport models." *Atmospheric Environment* 32(4):693-709.

Kukkonen, J., L. Partenan, (2003). "Evaluation of the OSPM model combined with an urban background model against the data measured in 1997 in Runeberg Street, Helsinki." *Atmospheric Environment* 37(8): 1101-1112.

Kusik, C. L. and H. P. Meissner (1978). "Electrolyte activity coefficients in inorganic processing." AIChE Symp. Series 173(14-20).

Laden F, Neas LM, Dockery DW, Schwartz J (2000). “Association of fine particulate matter from different sources with daily mortality in six U.S. cities”. *Environ Health Perspect* 108(10):941-7.

Lanz V. A., Alfarra, M. R. Baltensperger, U. Buchmann, B. Hueglin, C. and Prevot, A. S. H. (2007) “Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra.” *Atmos. Chem. Phys.*7, 1503–1522.

Lawrence, M.G., Butler, T.M., Steinkamp, J., Gurjar, B.R., Lelieveld, J., (2007). “Regional pollution potentials of megacities and other major population centers.” *Atmospheric Chemistry and Physics.* 7, 3969–3987.

Lee D.S., Garland J.A., Fox A.A. (1994). “Atmospheric Concentrations of trace elements in the urban areas of the United Kingdom.” *Atmospheric Environment*. 28, 2691-2713.

Lee, E., Chan, C. K., Paatero, P., (1999). “Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong.” *Atmos Environ.* 33(19), 3201–3212.

Lee, J. H. and Hopke, P. K. (2006). “Apportioning sources of PM2.5 in St. Louis, MO using speciation trends network data.” *Atmos. Environ.* 40, SUP2, S360–S377.

Lelieveld, J., Dentener, F.J. (2000). “What controls tropospheric ozone?” *Journal of Geophysical Research*. 105(D3), 3531–3551.

Li, Z., Hopke, P. K., Husain, L., Qureshi, S., Dutkiewicz, V. A., Schwab, J. J., Drewnick, F., Demerjian, K. L. (2004). “Sources of fine particle composition in New York city.” *Atmos Environ.* 38(38), 6521–6529.

Linkov, I.; Loney, D.; Cormier, S.; Satterstrom, F.K.; Bridges, T. (2009). “Weight-of-evidence evaluation in environmental assessment: Review of qualitative and quantitative approaches.” *Sci. Total Environ.*407(19), 5199-5205.

Liu, X., Feng, Y., Jia, H., Zhang, Y., Ma, Q. and Shao, Y. (1998). “Source Apportionment of Qingdao Atmospheric Aerosol with A chemical Mass Balance Method.” *Res. Environ. Sci.* 11, 51-54.

Lohmeyer, A. (2001). Comparison of the procedures of different modellers for air pollutant concentrations prediction in a street canyon-The Podbielski Street exercise, http://www.lohmeyer.de/podbi/.Lu, R., R. P. Turco, et al. (1997). "An integrated air pollution modeling system for urban and regional scales .1. Structure and performance." *Journal of Geophysical Research-Atmospheres* 102(D5): 6063-6079.

Lowenthal, D.H.; Watson, J.G.; Koracin, D.; Chen, L.-W.A.; DuBois, D.; Vellore, R.; Kumar, N.; Knipping, E.M.; Wheeler, N.; Craig, K.; Reid, S. (2010). “Evaluation of regional scale receptor modeling.” *J. Air Waste Manage. Assoc.* 60(1), 26-42.

Lu, H. C. (2002). “The Statistical Characters of PM10 concentrations in Taiwan area.” *Atmospheric Environment*. 36(3), 491-502.

Luhar, A. K. and P. J. Hurley (2003). "Evaluation of TAPM, a prognostic meteorological and air pollution model, using urban and rural point-source data." *Atmospheric Enivironment* 37: 2795-2810.

Luhar, A. K. and R. Patil (1989). "A General Finite Line Source Model for Vehicular Pollution Dispersion." *Atmospheric Environment* 23: 555-562.

Lurmann, F. W., A. S. Wexler, (1997). "Modelling urban and regional aerosols .2. Application to California's South Coast Air Basin." *Atmospheric Environment* 31(17): 2695-2715.

Mage, D., Ozolins, G., Peterson, P., Webster, A., Orthofer, R., Vandeveerd, V., Gwynne, M., (1996). “Urban air pollution in megacities of the world.” *Atmospheric Environment.* 30, 681-686.

Makela, J. M., I. K. Koponen, (2000). "One-year data of submicron size modes of tropospheric background aerosol in Southern Finland." *Journal of Aerosol Science* 31(5): 595-611.

Malm, W.C.; Sisler, J.F.; Huffman, D.; Eldred, R.A.; Cahill, T.A. (1994). “Spatial and Seasonal Trends in Particle Concentration and Optical Extinction in the United States.” *J. Geophys. Res.* 99, 1347-1370.

Manoli, E., Voutsa, D., and Samara, C. (2002). Chemical Characterization and Source Identification/Apportionment of Fine and Coarse Air Particles in Thessaloniki, Greece. *Atmos. Environ.* 36: 949–961.

Maricq, M.M., Chase, R.E., Xu, N. and Laing, P.M. (2002). “The Effects of the Catalytic Converter and Fuel Sulfur Level on Motor Vehicle Particulate Matter Emissions: Light Duty Diesel Vehicles.” *Environ. Sci. Technol.* 36, 283-289.

Mayer, H. (1999). “Air pollution in cities.” *Atmospheric Environment*. 33 , 4029-4037.

Mayer, M., Wang, C., Webster, M., Prinn, R.G. (2000). “Linking local air pollution to global chemistry and climate.” *Journal of Geophysical Research.* 105, 22869–22896.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M.C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T.F., Murphy, D.M., O’Dowd, C.D., Snider, J.R., Weingartner, E. (2005). “The effect of physical and chemical aerosol properties on warm cloud droplet activation.” *Atmos Chem Phys Discuss*. 5, 8507–8647.

McMurray, P. H. and S. K. Frielander (1979). "New particle formation in the presence of an aerosol." *Atmospheric Environment* 13: 1635-1651.

McRae, G. J., W. R. Goodin, (1982). "Development of a second-generation mathematical model for urban air pollution." *Atmospheric Environment* 16:679-696.

Mehdizadeh, F. and H. S. Rifai (2004). "Modeling point source plumes at high altitudes using a modified Gaussian model." *Atmospheric Environment* 38(6):821-831.

Mehra, A., Farago, M. E. and Banerjee, D. K., (1998). "Impact of Fly Ash from Coal-Fired Power Stations in Delhi, with Particular Reference to Metal Contamination." *Environ Monit Assess.* 50, 15 – 35.

Meng, Z. Y., D. Dabdub, (1998). "Size-resolved and chemically resolved model of atmospheric aerosol dynamics." *Journal of Geophysical Research-Atmospheres* 103(D3): 3419-3435.

Mensink, C., A. Colles, (2003). "Integrated air quality modelling for the assessment of air quality in streets against the council directives." *Atmospheric Environment* 37(37): 5177-5184.

Metzger, S., F. Dentener, (2002). "Gas/aerosol partitioning: 1. A computationally efficient model." *Journal of Geophysical Research- Atmospheres* 107(D16): 10102.

Middlebrook, A.M.; Murphy, D.M.; Lee, S.H.; Thompson, D.S.; Prather, K.A.; Wenzel, R.J.; Liu, D.Y.; Phares, D.J.; Rhoads, K.P.; Wexler, A.S.; Johnston, M.V.; Jimenez, J.L.; Jayne, J.T.; Worsnop, D.R.; Yourshaw, I.; Seinfeld, J.H.; Flagan, R.C. (2003). "A comparison of particle mass spectrometers during the 1999 Atlanta Supersite Project." *J. Geophys. Res.*108(D7):SOS 12-1-SOS 12-13.

Mighuel, E., Llamass, J.F., Chacon, E., Berg, T., Larssens, Royset, O. and Vadset, M. (1997). "Origin and Patterns of distribution of trace elements in street dust: unleaded petrol and urban lead." *Atmospheric Environment*. 31, 2733.

Milford, J. B. and Davidson, C.I. (1985). "The sizes of particulate trace elements in the atmosphere." *APCA Journal*. 35, 1249-1260.

Miller, M.S., Friedlander, S.K., and Hidy, G.M. (1972). "A Chemical Element Balance for the Pasadena Aerosol." *Journal of Colloid and Interface Science*. 39(1), 165-176.

Mirjana, T., Branislava, Đ. S., Slavica, R., Zoran, M., Velibor, N. (2006). "Physico-Chemical Characterization of PM10 and PM2.5 in the Belgrade Urban Area." *Acta Chim. Slov.* 53, 401–405.

Mohan, M., Kandya A. (2007). "An Analysis of the Annual and Seasonal Trends of Air Quality Index of Delhi." *Environ Monit Assess*. 131, 267–277.

Molina, L. T., Kolb, C. E., Foy, B. de., Lamb, B. K., Brune, W. H., Jimenez, J. L., and Molina, M. J. (2007). "Air quality in North America's most populous city – overview of MCMA-2003 Campaign." *Atmos. Chem. Phys. Discuss.* 7, 3113–3177.

Molina, L.T. (2007). "MILAGRO Measurement Campaign over Mexico City Metropolitan Area." *Geophysical Research Abstracts*. 9, 11662.

Molina, L.T., Molina M.J., Slott R., Kolb C.E., Gbor P.K., Meng F., Singh R., Galvez O., Sloan J.J., Anderson W., Tang X.Y., Shao M., Zhu T., Zhang Y.H., Hu M., Gurjar B.R.,. Artaxo P, Oyola P., Gramsch E., Hidalgo P., Gertler A. (2004). "Air Quality in Selected Megacities: Critical Review." *J. Air & Waste Manage. Assoc.* 55

Molina, M.J., Molina, L.T. (2004). "Megacities and atmospheric pollution." *Journal of The Air & Waste Management Association*. 54(6), 644-680.

Monkkonen, P., Uma, R. Srinivasan, D., Koponen, I.K., Lehtinen, K.E.J., Hameri, K., Suresh, R., Sharma, V.P. and Kulmala, M. (2004). "Relationship and Variations of Aerosol Number and PM10 Mass Concentrations in a Highly Polluted Urban Environment - New Delhi, India." *Atmos. Environ.* 38: 425–433.

Monn, C., A. Fuchs, (1997). "Particulate Matter less than 10 µm (PM10) and Fine Particles less than 2.5 µm (PM2.5): Relationship between Indoor and Outdoor and Personal Concentrations." *The Science of the Total Environment* 208: 15-21.

Moon, D., A. Albergel, (1997). "The use of the MERCURE CFD code to deal with an air pollution problem due to building wake effects." Journal of Wind Engineering and Industrial Aerodynamics 67-8: 781-791.

Morales, J.A., Pirela, D. and Duran, J. (1996). “Determination of the Levels of Na, K, Ca, Mg, Fe, Zn and Cu in Aerosols of the Western Venezuelan Savannah Region.” *Sci. Total Environ.* 180, 155-164.

Morselli L., Olivieri P., Brusori B. and Passarini F. (2003). “Soluble and insoluble fractions of heavy metals inwet and dry atmospheric depositions in Bologna, Italy.” *Environmental Pollution*. 124 (3), 457-469.

Mosher, B. W., R. A. Duce, (1987), “A global atmospheric selenium budget”, J.*Geophys. Res*., 92, 13,289- 13,298,

Nanni, A., G. M. Riva, (1996). "Particle model simulation of pollutants dispersion from a line source in complex terrain." *Science of the Total Environment* 190: 301-309.

Napari, I., M. Noppel, et al. (2002). "An improved model for ternary nucleation of sulfuric acid-ammonia-water." Journal of Chemical Physics 116(10): 4221-4227.

Narin, I., Soylak, M., and Dogen, M. (1997). “Traffic pollution in Nigde-Turkey: Investigation of trace element contents of soil samples.” *Fresenius Environmental Bulletin*, 6,749.

Nenes, A., S. N. Pandis, (1998). "ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols." *Aquatic Geochemistry* 4(1): 123-152.

Nenes, A., S. N. Pandis, 1999). "Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models." Atmospheric *Environment* 33(10): 1553-1560.

Nriagy J.O. and Pacyna J.M. (1988). “Quantitative assessment of worldwide contamination of air, water and soils by trace metals.” *Nature*. 333 (6169), 134-139.

Oettl, D., J. Kukkonen, (2001). "Evaluation of a Gaussian and a Lagrangian model against a roadside data set, with emphasis on low wind speed conditions." *Atmospheric Environment* 35(12): 2123-2132.

Oettl, D., P. J. Sturm, (2003). "Dispersion from road tunnel portals:comparison of two different modelling approaches." *Atmospheric Environment* 37(37): 5165-5175.

Oettl, D., P. J. Sturm, (2005). "Evaluation of GRAL for the pollutant dispersion from a city street tunnel portal at depressed level." *Environmental Modelling & Software* 20: 499-504.

Oke, T. R., H. A. Cleugh, (1987), “Urban heat storage derived as energy balance residuals. *Bound.-Layer Meteor.*, 39, 233–245.

O'Neill, S. M. and B. K. Lamb (2005). "Intercomparison of the community multiscale air quality model and CALGRID using process analysis." *Environmental Science & Technology* 39(15): 5742-5753.

Paatero, P. (1997). “Least squares formulation of robust non-negative factor analysis.” *Chemometrics and Intelligent Laboratory Systems*. 37, 23-35.

Paatero, P. (1999). A Table-driven Least Squares Program for Solving Multilinear Problems, Including th N-Way Parallel Factor Analysis Model. *J. Comput. Graph. Stat.* 8: 854-888.

Paatero, P. and Tapper, U. (1993). “Analysis of Different Methods of Factor Analysis as Least square Fit Problem.” *Atmos. Environ.* 18, 183-194.

Paatero, P., Tapper, U. (1994).” Positive matrix factorization: a nonnegative factor model with optimal utilization of error estimates of data values.” *Environmetrics*. 5, 111–126.

Paatero, P.; Hopke, P.K.; Song, X.H.; Ramadan, Z. (2002). “Understanding and Controlling Rotations in Factor Analytical Models.” *Chemom. Intell. Lab. Sys.* 60, 253-264.

Pacyna J.M. and Pacyna E.G. (2001). “An assessment of global and regional emissions of trace metals to theatmosphere from anthropogenic sources worldwide.” *Environmental Reviews.* 9 (4), 269-298.

Pai, P., K. Vijayaraghavan, (2000). "Particulate matter modeling in the Los Angeles basin using SAQM-AERO." *Journal of the Air & Waste Management Association* 50(1): 32-42.

Pandis, S., L. M. Russell, (1994). "The Relationship Between DMS Flux and CCN Concentration in Remote Marine Regions." *Journal of Geophysical Research-Atmospheres* 99: 16945-16957.

Patel, V. C. and A. Kumar (1998). "Evaluation of three air dispersion models: ISCST2, ISCLT2, and SCREEN2 for mercury emissions in an urban area." *Environmental Monitoring and Assessment* 53(2): 259-277.

Peerboom JW Copius, (1985), “Science Total Environ”, The Science of the total environment, Mar 15;42(1-2):1-27.

Pekney, N.J., Davidson, C.I., Robinson, A., Zshou, L., Hopke, P.K., Eatough, D., Rogge, W.F. (2006). “Major source categories for PM2.5 in Pittsburgh using PMF and UNMIX.” *Aerosol Sci. Technol.* 40, 910–924.

Peterson, P.J. and Williams, W.P. (1999), New indicator approaches for effective urban air quality management, *Environmental Science and Pollution Research* 6(4): 225-232.

Physick, W. L. and J. R. Garratt (1995). "Incorporation of a High-Roughness Lower Boundary into a Mesoscale Model for Studies of Dry Deposition over Complex Terrain." *Boundary-Layer Meteorology* 74(1-2): 55-71.

Pielke, R. A., W. R. Cotton, (1992). "A Comprehensive Meteorological Modeling System - Rams." *Meteorology and Atmospheric Physics* 49(1-4):69-91.

Pilinis, C. (1990). "Derivation and numerical solution of the species mass distribution equations for multicomponent particulate systems." *Atmospheric Environment* Part a-General Topics 24: 1923-1928.

Pilinis, C. and J. H. Seinfeld (1988). "Development and Evaluation of an Eulerian Photochemical Gas-Aerosol Model." *Atmospheric Environment* 22(9`): 1985-2001.

Pilinis, C., K. P. Capaldo, (2000). "MADM - A new multicomponent aerosol dynamics model." *Aerosol Science and Technology* 32(5): 482-502.

Pirjola, L., M. Kulmala, (1999). "Formation of sulphuric acid aerosols and cloud condensation nuclei: An expression for significant nucleation and model comparison." Journal of Aerosol Science 30(8): 1079-1094.

Pitzer, K. S. and J. J. Kim (1974). "Thermodynamics of electrolytes - IV.Activity and osmotic coefficients for mixed electrolytes." *Journal of American Chemical Society* 96: 5701-5707.

Pleim, J., A. Venkatram, et al. (1984). The Dry Deposition Model. Volume 4 ADOM/TADAP Model Development Program. Rexdale, Ontario, Canada,Ontario Ministry of the Environment.

Pohjola, M., Kousa, A., Aarnio, P., Koskentalo, T., Kukkonen, J., Härkönen, J. and Karppinen, A.: (2000), ‘Meteorological interpretation of measured urban PM2.5 and PM10 concentrations in the Helsinki Metropolitan Area’, in J. W. S. Longhurst, C. A. Brebbia and H. Power (eds), *Air Pollution VIII*, Wessex Institute of Technology Press, Southampton, U.K., pp. 689–698.

Pohjola, M., L. Pirjola, (2003). "Modelling of the influence of aerosol processes for the dispersion of vehicular exhaust plumes in street environment." *Atmospheric Environment* 37(3): 339-351.

Pope CA III, Thun MJ, Namboodiri M, (1995), “Particulate air pollution as a predictor of mortality in a prospective study of U.S. adults”. *Am J Respir Crit Care Med* 151:669–674.

Pope, C.A. (2000). “Epidemiology of Fine Particulate Air Pollution and Human Health: Biologic Mechanisms and Who's at Risk.” *Environ. Health Perspect.* 108, 713-723.

Prendej, M. M., Egido, M., Tomas, C., Seco, J., Calvo, A., and Romero, H. (1995). “Source assessment of articulate air pollutants measured at the southwest European coast, Correlation between solar radiation and total suspended particulate matter in Santigo, Chile.” *Atmospheric Environment.* 29, 1543-1551.

R A. Goyer (1993), Environ Health Perspect. April; 100: 177–187. PMCID: PMC1519587

Ramadan, Z.; Song, X.H.; Hopke, P.K. (2000). “Identification of sources of Phoenix aerosol by positive matrix factorization.” *J. Air Waste Manage. Assoc.* 50(8), 1308-1320.

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D. (2001). “Aerosols, climate, and the hydrological cycle.” *Science*. 294, 2119–2124.

Rannik, U., P. Aalto, (2003). "Interpretation of aerosol particle fluxes over a pine forest: Dry deposition and random errors." Journal of Geophysical Research-Atmospheres 108(D17)

Ravindra, K., Wauters, E., Tyagi, S. K., Mor, S., and Grieken, R. V. (2006). “Assessment of air quality after the implementation of compressed natural gas (cng) as fuel in public transport in Delhi, India.” *Environmental Monitoring and Assessment.* 115, 405–417.

Raza, S. S., R. Avila, (2001). "A 3-D Lagrangian stochastic model for the mesoscale atmospheric dispersion applications." *Nuclear Engineering and Design* 208(1): 15-28.

Reff, A.; Eberly, S.I.; Bhave, P.V. (2007).“Receptor Modeling of Ambient Particulate Matter Data Using Positive Matrix Factorization: Review of Existing Methods.” *J. Air & Waste Manage. Assoc.*57, 146-154.

Riddle, A., D. Carruthers, (2004). "Comparisons between FLUENT and ADMS for atmospheric dispersion modelling." Atmospheric Environment 38(7):1029-1038.

Rinehart, L.R.; Fujita, E.M.; Chow, J.C.; Magliano, K.L.; Zielinska, B. (2006). “Spatial distribution of PM2.5 associated organic compounds in central California.” *Atmos. Environ.* 40(2), 290-303.

Rizzo, M. J., Scheff, P. A., (2007). “Fine particulate source apportionment using data from the USEPA speciation trends network in Chicago, Illinois: Comparison of two source apportionment models.” *Atmos Environ*. 41(29), 6276–6288.

Roorda-Knape, M. C., N. A. H. Janssen, (1998). "Air Pollution from Traffic in City Districts near Major Motorways." *Atmospheric Environment* 32: 1921-1930.

Rossi G, Vigotti MA, Zanobetti A, Repetto F, Giannelle V, Schwartz J. (1999), “Air pollution and cause specific mortality in Milan, Italy, 1980–1989”. *Arch Environ Health* 1999;54:158–164.

Russell, A. G., R. A. Winner, (1993). "Mathematical modeling and control of the dry deposition flux of nitrogen-containing air pollutants." *Environmental Science & Technology* 27(2772-2782).

Saffmann, P. G. and J. S. Turner (1956). "On the collision of drops in turbulent clouds." *Journal of Fluid Mechanics* 1: 16-30.

Salam, A., Bauer, H., Kassin, K., Ullah, S.M. and Puxbaum, H. (2003). “Aerosol Chemical Characteristics of a Mega-City in Southeast Asia (Dhaka, Bangladesh).” *Atmos. Environ.* 37, 2517-2528.

Salma, I., Ocskay, R., Raes, N. and Maenhaut, W. (2005). “Fine Structure of Mass Size Distributions in an Urban Environment.” *Atmos Environ.* 39, 5363-5374.

Samara, C. (2005). "Chemical Mass Balance Source Apportionment of TSP in a Lignite Burning Area of Western Macedonia, Greece." *Atmos. Environ.* 39, 6430–6443.

Samara, C., Kouimtzis, T., Tsitouridou, R., Kanias, G.. and Simeonov, V. (2003). "Chemical Mass Balance Source Apportionment of PM10 in an Industrialized Urban Area of Northern Greece." *Atmos. Environ.* 37, 41–54.

Samet JM, Dominici F, Zeger SL, Schwartz J, Dockery DW. (2005), "The National Morbidity, Mortality, and Air Pollution Study. Part I: Methods and methodologic issues". *Res Rep Health Eff Inst*. 75-84.

Sansoni B., and Pandey V. K. (1983)."Ashing in trace analysis of biological materials; Analytical techniques for heavy metals in biological fluids." *Elsevier*. 91- 13.

Saxena, P., A. B. Hudischewskyi, (1986). "A comparative study of equilibrium approaches ti the chemical characterization of secondary aerosols." *Atmospheric Environment* 20(1471-1483).

Schack Jr, C. J., S. E. Pratsinis, (1985). "A general correlation for deposition of suspended particles from turbulent gases to completely rough surfaces." *Atmospheric Environment* 19: 953-960.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A. and Cass, G.R. (1996). "Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers." *Atmos. Environ.* 30, 3837–3855.

Scholorling M. (2000). "Urban transport and its compliance with future air quality standards." *Sixth International Conference on Urban Transport and the Environment for the 21st Century* .July 26–28, Cambridge, UK.

Schulman, L. L. and J. S. Scire (1993). "Building Downwash Screening Modeling for the Downwind Recirculation Cavity." *Journal of the Air & Waste Management Associatio*n 43(8): 1122-1127.

Schulman, L. L., D. G. Strimaitis, (2000). "Development and evaluation of the PRIME plume rise and building downwash model." *Journal of Air and Waste Management Association* 50: 378-390.

Schwartz, J. (2001). “Is There Harvesting in the Association of Airborne Particles with Daily Deaths and Hospital Admissions.” *Epidemiology*. 12, 55-61.

Schwartz, J., Laden, F., and Zanobetti, A. (2002). “The concentration response relation between PM2.5 and daily deaths.” *Environ. Health Persp.* 110(10), 1025–1029.

Scoullos, M. J. (2001). Mercury, Cadmium, Lead: Handbook for Sustainable Heavy Metals Policy and Regulation. Springer. pp. 104–116. ISBN 978-1-4020-0224-3.

Senaratne, I. and Shooter, D. (2004), Elemental composition in source identification of brown haze in Auckland, New Zealand. *Atmos. Environ.* 38, 3049-3059.

Sharan, M., A. K. Yadav, (1996). "Plume dispersion simulation in low-wind conditions using coupled plume segment and Gaussian puff approaches." *Journal of Applied Meteorology* 35(10): 1625-1631.

Sharma, V.K. and Patil, R.S. (1992). “Size Distribution of Atmospheric Aerosols and Their Source Identification Using Factor Analysis in Bombay, India.” *Atmos. Environ.* 26, 135-141.

Sharma, V.K., Patil, R.S. (1994). “Chemical mass balance model for source apportionment of aerosols in Bombay.” *Environmental Monitoring and Assessment*. 29: 75-88.

Simpson, D. (1992). "Long-period modelling of photochemical oxidants in Europe. Model calculation for July 1985." *Atmospheric Environment* 26A: 1609-1634.

Singh, R. B., A. H. Huber, (2003). "Development of a Microscale Emission Factor Model for Particulate Matter for Predicting Real-Time Motor Vehicle Emissions." *Journal of Air and Waste Management Association* 53(10): 1204-1217.

Sivacoumar, R. and K. Thanasekaran (2001). "Comparison and performance evaluation of models used for vehicular pollution prediction." *Journal of Environmental Engineering-Asce* 127(6): 524-530.

Slinn, S. A. and W. G. N. Slinn (1980). "Predictions for particle deposition on natural waters." *Atmospheric Environment* 24: 1013-1016.

Snyder, W. H., R. S. Thompson, (1985). "The structure of the strongly stratified flow over hills: Dividing streamline concept." *Journal of Fluid Mechanics* 152(249-288).

Sokhi, R., B. Fisher, (1998). Modelling of Air Quality around Roads. *Proc of 5th Int. Conf. On Harmonisation with Atmospheric Dispersion Modelling for Regulatory Purposes, Greece.*

Song, X.H, Polissar, A.V. and Hopke, P.K. (2001). “Source of fine particle composition in the Northeastern US.” *Atmos. Environ.* 35: 5277–5286.

Song, Y. Tang, X.Y., Zhang Y.H., Hu M., Fang C., Zen L.M. and Wang W. (2002). “Effects on fine particles by the continued high temperature weather in Beijing.” *Environ. Sci.* 23: 33–36.

Song, Y., Tang, X. Y., Xie, S. D., Zhang, Y. H., Wei, Y. J., Zhang, M. S. (2007). “Source apportionment of PM2.5 in Beijing in 2004.” *J Hazard Mater*. 146(1-2): 124–130.

Song, Y., Tang, X.Y., Xie, S.D., Zhang, Y.H. and Wei,Y.J. (2005). “Source Apportionment of $PM_{2.5}$ in Beijing in 2004.” *J. Hazard. Mater.* 146: 124–130.

Sriramachari S., (2004), “The Bhopal gas tragedy: An environmental disaster”. *Curr Sci*. 86:905–20.

Srivastava, A. (2004). “Source Apportionment of Ambient VOCs in Mumbai City.” *Atmos. Environ.* 38, 6829–6843.

Srivastava, A. and Jain, V.K. (2003). “Relationships between Indoor and Outdoor Air Quality in Delhi.” *Indoor Built Environ.* 12, 159-165.

Srivastava, A. and Jain, V.K. (2005). “A Study to Characterize the Influence of Outdoor TSPM and Associated Metals on the Indoor Environments in Delhi.” *J. Environ Sci Eng.* 47, 222-231.

Srivastava, A. and Jain, V.K. (2007). “A Study to Characterize the Suspended Particulate Matters in an Indoor Environment in Delhi, India.” *Build Environ.* 42, 2046–2052.

Srivastava, A. and Jain, V.K. (2007). “Seasonal trends in coarse and fine particle sources in Delhi by the chemical mass balance receptor model.” *J. Hazard. Material.* 144 (1-2), 283-291.

Srivastava, A. and Jain, V.K. (2007). “Size distribution and source identification of total suspended particulate matter and associated heavy metals in the urban atmosphere of Delhi.” *Chemosphere*. 68, 579-589.

Srivastava, A. and Jain, V.K. (2008). “Source apportionment of suspended particulate matters in a clean area of Delhi: a note.” *Transport. Res. D.* 13(1), 59-63.

Srivastava, A. Sengupta, B. and Dutta, S.A. (2005). “Source Apportionment of Ambient VOCs in Delhi City.” *Sci. Total. Environ.* 343, 207– 220.

Stern, R. and R. J. Yamartino (2001). "Development and first evaluation of microcalgrid: a 3-D, urban-canopy-scale photochemical model." *Atmospheric Environment* 35: S149-S165.

Stockwell, W. R., D. Middleton, (1990). "The second-generation Regional Acid Deposition Model chemical mechanism for regional air quality modeling." *Journal of Geophysical Research-Atmospheres* 95: 16343-16367.

Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., and Cooper, O. (2003). “A backward modeling study of intercontinental pollution transport using aircraft measurements.” *Journal of Geophysical Research*. 108 (D12), 4370.

Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., and Cooper, O. (2003). “A backward modeling study of intercontinental pollution transport using aircraft measurements.” *Journal of Geophysical Research.* 108 (D12), 4370.

Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., and Cooper, O. (2003). “A backward modeling study of intercontinental pollution transport using aircraft measurements.” *Journal of Geophysical Research.* 108 (D12), 4370.

Sun, Y. L., Zhuang, G. S., Wang, Y., Han, L. H., Guo, J. H., Dan M. (2004). “The air-borne particulate pollution in Beijingconcentration, composition, distribution and sources.” *Atmos Environ.* 38(35), 5991–6004.

Sun, Y. L., Zhuang, G. S., Zhang, W. J., Wang, Y., Zhuang, Y. H., (2006). “Characteristics and sources of lead pollution after phasing out leaded gasoline in Beijing.” *Atmos Environ.* 40(16):2973–2985.

Sutherland R.A. and Tolosa C.A. (2000). “Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii.” *Environmental Pollution*. 110 (3), 483-495.

Takeda, A. (2003). "Manganese action in brain function". *Brain Research Reviews* 41 (1): 79–87. doi:10.1016/S0165-0173(02)00234-5. PMID 12505649.

Thomson, D. J. (1987). "Criteria for selection of stochastic models of particle trajectories in turbulent flows." *Journal of Fluid Mechanics* 180: 529-556.

Thomson, D. J. and A. J. Manning (2001). "Along-wind dispersion in light wind conditions." *Boundary-Layer Meteorology* 98(2): 341-358.

Tsuang, B. J. (2003). "Quantification on the source/receptor relationship of primary pollutants and secondary aerosols by a Gaussian plume trajectory model: Part I theory." *Atmospheric Environment* 37(28): 3981-3991.

Tsyro, S. G. (2005). "To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM10 and PM2.5?" *Atmospheric Chemistry and Physics* 5: 515-532.

Turnlund J. R. (1998). "Human whole-body copper metabolism". *Am. J. Clin. Nutr* 67 (5 Suppl): 960S–964S. PMID 9587136

Utell, M. (1997). “Smoke Alarm: Haze From Fires Might Promote Bacterial Growth.” *Sci. Am.* 24–25

Valvanidis, A., Salika, A., and Theodopoulou, A. (2000). “Generation of hydroxyl radicals by urban suspended particulate air metter: The role of iron ions.” *Atmospheric Environment*. 34, 2379-2386.

Van Borm, W.A., Adams, F.C., and Maenhaut, W. (1990). “Receptor modeling of the Antwerp Aerosols.” *Atmospheric Environment Part B, Urban Atmosphere*. 24 (3), 419-435.

Van Dingenen, R., F. Raes, (2004). "A European aerosol phenomenology-1:physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe." *Atmospheric Environment* 38(16): 2561-2577.

Vardoulakis, S., B. E. A. Fisher, (2003). "Modelling air quality in street canyons: a review." *Atmospheric Environment* 37(2): 155-182.

Vega, E. García, I. Apam, D., Ruíz, M.E. and Barbiaux M. (1997). “Application of a Chemical Mass Balance Receptor Model to Respirable Particulate Matter in Mexico City.” *JAWMA.* 47, 524-529.

Vehkamaki, H., M. Kulmala, (2002). "An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions." *Journal of Geophysical Research-Atmospheres* 107(D22):

Venkatesan, R., R. Mathiyarasu, (2002). "A study of atmospheric dispersion of radionuclides at a coastal site using a modified Gaussian model and a mesoscale sea breeze model." *Atmospheric Environment* 36(18): 2933-2942.

Venkatram, A. and J. Pleim (1999). "The electrical analogy does not apply to modeling dry deposition of particles." *Atmospheric Environment* 33(18): 3075-3076.

Venkatram, A., P. Karamchandani, (1997). "The development of a model to examine source-receptor relationships for visibility on the Colorado Plateau." *Journal of the Air & Waste Management Association* 47(3): 286-301.

Vignati, E., R. Berkowicz, (1999). "Transformation of size distributions of emitted particles in streets." *The Science of the Total Environment* 235: 37-49.

Villasenor, R., C. Claiborn, (2001). "Mesoscale modeling of wintertime particulate matter episodes in eastern Washington, USA." *Atmospheric Environment* 35(36): 6479-6491.

Villasenor, R., M. Magdaleno, (2003). "An air quality emission inventory of offshore operations for the exploration and production of petroleum by the Mexican oil industry." *Atmospheric Environment* 37(26): 3713-3729.

Villasenor, R., M. T. Lopez-Villegas, (2003). "A mesoscale modeling study of wind blown dust on the Mexico City Basin." *Atmospheric Environment* 37(18): 2451-2462.

Vincent, John B. (2010). "Chromium: Celebrating 50 years as an essential element?". *DaltonTransactions* 39 (16):3787–4.doi:10.1039/B920480F. PMID 20372701

Wang, Y., Zhuang, G. S., Tang, A. H., Yuan, H., Sun, Y. L., Cheng, S., Zheng, A. H. (2005). “The ion chemistry and the source of PM2.5 aerosol in Beijing.” *Atmos Environ.* 39(21), 3771– 3784.

Ward N.I. (1990). “Multielement contamination of British motorway environments.” *Science of the Total Environment*. 93, 393-401.

Watson J. G. (2002). “Visibility: Science and regulation.” *J Air Waste Management Association.* 52, 628–713.

Watson, J. G., Chow, J.C., Lu, Z., Fujita, E.M., Lowenthal, D.H. and Lawson, D.R. (1994). “Chemical Mass Balance Source Apportionment of PM10 During the Southern California Air Quality Study.” *Aerosol Sci. Technol.,* 21, 1-36.

Watson, J.G. and Chow, J.C. (2001). “PM2.5 Chemical Source Profiles for Vehicular Exhaust, Vegetation Burning, Geological Materials and Coal Burning in Northwestern Colorado during 1995.” *Chemosphere.* 43, 1141-1151.

Watson, J.G. and Chow, J.C. (2001). “Source Characterization of Major Emission Source in the Imperial and Maxicali Valleys along the US/Mexico Boarder.” *Sci. Total Environ.* 276, 33-47.

Watson, J.G.; Chen, L.-W.A.; Chow, J.C.; Lowenthal, D.H.; Doraiswamy, P. (2008). “Source Apportionment: Findings from the U.S. Supersite Program.” *J. Air & Waste Manage. Assoc.* 58, 265-288.

Watson, J.G.; Cooper, J.A.; Hunzicker, J.J. (1984). “The Effective Variance Weighting for Least Squares Calculations Applied to the Mass Balance Receptor Model.” *Atmos. Environ.*18, 1347-1355.

Wesely, M. L. (1989). "Parameterization of surface resistance to gaseous dry deposition in regional scale numerical models." *Atmospheric Environment* 23:1293-1304.

Wesely, M. L. and B. B. Hicks (1977). "Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation." *Journal of Air Pollution Control Association* 27: 1110-1116.

Wexler, A. S., F. W. Lurmann, (1994). "Modeling Urban and Regional Aerosols .1. Model Development." *Atmospheric Environment* 28(3): 531-546.

Willis, G. E. and J. W. Deardorff (1981). "A Laboratory study of dispersion in the middle of the convectively mixed layer." Atmospheric Environment 15: 109-117.

Wilson, W. E.., Judith, C., Chow, Claiborn, C., Fusheng, W., Engelbrecht, J., Watson, J. G. (2002). Monitoring of Particulate matter outdoors." *Chemosphere*. 49(9), 1009-1043.

Wolff, G.T., Korsog, P.E., Kelly, N.A. and Fermam, M.A. (1985). "Relationships between Fine Particulte Species, Gaseous Pollutants and Meteorological Parameters in Detroit19." *Atmos. Environ.* 19, 1341-1349.

Yao, X. H., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P. (2002). "The water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China." *Atmos Environ.* 36(26), 4223– 4234.

Yao, X., Lau, A. P. S., Fang, M., Chan, C. K., Hu, M. (2003). "Size distribution and formation of ionic species in atmospheric particulate pollutants in Beijing, China." *Atmos Environ.* 37(21), 2991–3000.

Yogesh Sathe, Atul Ayare, G. Srinikethan, (2011), "Application of US EPA PMF model to Source Apportionment of trace elements in Atmospheric aerosols at Kolhapur, Maharashtra (india), *Journal of Environmental Research And Development* Vol. 5 No. 3

Young, T.M., Heeraman, D.A., Sirin, G. and Ashbaugh, L.L. (2002). "Resuspension of Soil as a Source of Airborne Lead near Industrial Facilities and Highways." *Environ. Sci. Technol.* 36, 2484-2490.

Yruela, Y. (2005), "Copper in plants". *Brazilian Journal of Plant Physiology*. 17:145-156.

Yu Song, Yuanhang Zhang, Shaodong Xie, Limin Zeng, Mei Zhengc, Lynn G. Salmon, Min Shao, Sjaak Slanina, (2006), "Source apportionment of PM2.5 in Beijing by positive matrix factorization", *Atmospheric Environment* 40, 1526–1537

Yuan, H., Wang, Y., Zhuang, G. S. (2003). “The simultaneous determinationof organic acid, MSA with the inorganic anions in aerosol and rain-water by ion chromatography.” *J. Instru Anal*. 6, 11–14.

Zhang, W., Guo, J. H., Sun, Y. L., Yuan, H., Zhuang, G. S., Zhuang, Y. H., Hao, Z. P. (2007). “Sources apportionment for urban PM2.5 and PM10 in Beijing area.” *Chin Sci Bullet.* 52(5), 608–615.

Zhang, Y., B. Pun, et al. (2004). "Development and application of the model of aerosol dynamics, reaction, ionization, and dissolution (MADRID)." *Journal of Geophysical Research-Atmospheres* 109(D1):

Zhao, W. X., Hopke, P. K., (2004). “Source apportionment for ambient particles in the San Gorgonio wilderness.” *Atmos Environ.* 38(35), 5901–5910.

Zhao, W. X., Hopke, P. K., (2006). “Source identification for fine aerosols in Mammoth Cave National Park.” *Atmos Res.* 80(4), 309–322.

Zheng, M., Salmon, L.G. Schauer, J.J., Zeng, L., Kiang, C.S., Zhang, Y. and Cass, G.R. (2005). “Seasonal Trends in PM2.5 Source Contributions in Beijing, China.” *Atmos. Environ.* 39, 3967–4166.

Zhu, Y., W. C. Hinds, (2002a). "Concentration and Size Distribution of Ultrafine Particles Near a Major Highway*." Journal of Air and Waste Management Association* 52: 1032-1042.

Zhu, Y., W. C. Hinds, (2002b). "Study of ultrafine particles near a major highway with heavy-duty diesel traffic." *Atmospheric Environment* 36: 4323-4335.

Zhuang, G. S., Guo, J. H., Yuan, H., Zhao, C. Y. (2001). “The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment.” *Chin Sci Bullet.* 46(11)895–901.

REPORTS

Akhter, S., Islam, M.A., Hossain, A.M.S., Quadir, S.M.A., Khan, A.H., Begum, B.A., Khaliquzzaman, M. and Swapan, K.B. (2004). “Air Quality Monitoring Program in Bangladesh: Trends analysis of Criteria Pollutants and Source Apportionment of Particulate Matter in Dhaka, Bangladesh.” Clean Air Initiative (Asia),

Alcamo J., “Transboundary air pollution in central Europe and Eastern Europe.” In J. Alcamo (Ed.) Coping with crisis in Eastern Europe’s environment. IIASA. Book, Parthenon Publishing Group,Carnforth, 1992, pp. 87-101.

Anderson, M.K. and Brookman, E.T., Preliminary Analyses at a PM10 Sampling Site Using a Combined Source Apportionment Approach. Prepared by TRC Environmental Consultants, East Hartford, CT, 1995.

Andrease M.O.; Future Climate of the World, Edited by A. Henderson-Sellers, Elsevier, NewYork; 1995

Bakshi S. K., Chawla K. P., Khandekar R. N., and Radh Raghunath; Cd and Hypertension in Health and Disease, Ashish Publishing House, New Delhi; 173 – 174

Beck B. D. and Brain J. D. (1982) Prediction of the pulmonary toxicity of respirable combustion products from residential wood and coal stoves. In Residential *Wood and Coal Combustion,* pp. 264-280. Air Pollution Control Association, Louisville, Kentucky.

BJEPB (Beijing Municipal Environmental Protection Bureau), 2008. Environmental Situation

Bowen HJM (1966) Trace elements in biochemistry. Academic. Press, London New York. 3. Gibbs RD (1974) Chemotaxonomy of flowering plants, vol 1.

Burt, E. W. (1977). Valley Model User's Guide. U. S. E. P. Agency, U.S. Environmental Protection Agency, Research Triangle Park, NC. 57

California Air Resources Board; Findings of the Scientific Review Panel on the Report on Diesel Exhaust as adopted at the Panelís 22 April 1998 Meeting.

Carruthers, D. J., J. C. R. Hunt, et al. (1988). Computational model of airflow over hills. FLOWSTAR I. Proc. Of Envirosoft., Springer Verlag. Carter, W. P. L. (2000). Implementation of the SAPRC-99 Chemical Mechanism into the models-3 framework,

Chemical Mass Balance Receptor Model Version 8 (CMB8), User Manual, US EPA Research Triangle Park, NC, Desert Research Institute, Reno, N.V., 1997.

Chowdhury, Z., Zheng, M. and Russell, A. (2003). "Source Apportionment of the Ambient Fine Particles in Mumbai, Delhi and Kolkata, Georgia Institute of Technology, World Bank Report (ESMAP, 281/04).

Cornille, Philippe and Maenhuat, Willy: 1990, 'Sources and Characteristics of the Atmospheric Aerosol near Damascus, Syria', Atmospheric Environment 24A (5), 1083-1093.

CPCB, (2010): "Conceptual Guidelines and Common Methodology for Air Quality Monitoring, Emission Inventory & Source Apportionment Studies for Indian Cities"

Dockery D. W., Pope C. A. III, Xu X., Spengler J. D., Ware J. H., Fay M. E., Ferris B. G. Jr. and Speizer F. E. (1993) An association between air pollution and mortality in si;U.S. cities. New Enaland *J.* Med. 329. 175>1759.

Draxler, R.R., and Hess, G.D., (1998). "Description of the HYSPLIT_4 Modeling System. NOAATechnical Memorandum ERL ARL-224, Air Resources Laboratory, Silver Spring, MD, August 1998.

Drew, H.M. (1975). Metal-Based Lubricant Compositions. Noyes Data Corporation, NJ.466

Dursbeck, F., Erlandsson, L. and Weaver, C., 2001. Status of Implementation of CNG as a Fuel for Urban Buses in Delhi: Findings – Conclusions – Recommendations, Report done for Centre for Science and Environment, New Delhi, May 23.

Eberly S. (2005) EPA PMF 1.1 user's guide. Prepared by the U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, NC, June.

Economic Survey of Delhi: 2003–04. Government of National Capital Territory of Delhi, 6th Level, B-Wing, Delhi Secretariat, I. P. Estate, New Delhi, India.

Ellis, K., C. McHugh, (2001). "Comparison of ADMS-Roads, Caline4 and UK DMRB Model Predictions for Roads." 7th International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes.

EPA Manual, (1983). Methods of Chemical Analysis of Water and Wastes. US Environmental Protection Agency,Cincinnati, OH.

EPA-450/4-85-002: 1984, 'Receptor Model Source Composition Library', United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, U.S.A.EPA-450/4-87-010: 1987, 'Protocol for Applying and Validating the CMB Model', United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, U.S.A.

Esty, D.C., Srebotnjak, T., Kim, C.H., Levy, M.A., de Sherbinin, A., Anderson, B. (2006). "Environmental Performance Index." Yale Center for Environmental Law and Policy. 301 Prospect Street, New Haven, CT 06511, USA.

Gadi, R., Singh, N., Sarkar, A.K. and Parashar, D.C. (2000). Mass Size Distribution and Chemical Composition of Aerosols at New Delhi. In Pollution in Urban Environment, K. Siddappa, S. Sadasivan, V.N. Sastri, K.P. Eappen, R.K. Somashekar, and N. Manamohan Rao, Eds. Bangalore University, Bangalore, p.

30-32Government of India, White Paper on Pollution in Delhi with an Action Plan, Ministry of Environment and Forests, Paryavaran Bhawan, New Delhi, 2001.

Henry, R.C. (1997) History and Fundamentals of Multivariate Air Quality Receptor Models.

Henry, R.C. (2002) Multivariate Receptor Modeling by N-dimensional Edge detection. Journal of Chemometrics and Intelligent Laboratory Systems, (submitted).

Henry, R.C.; Kim, B.M. (1989). A Factor Analysis Receptor Model with Explicit Physical Constraints. In Transactions, Receptor Models in Air Resources Management; Watson, J.G., Ed.; A&WMA: Pittsburgh, PA,; pp 214-225.

Hopke, P.K. (1985). Receptor Modeling in Environmental Chemistry, John Wiley & Sons Inc.; New York.

Hosker, R. P. (1984). Flow and Diffusion Near Obstacles. Atmospheric Science and Power Production. D. Randerson. Washington, D.C., U.S. Department of Energy.

Houck J.E., Chow J.C., Watson J.H., Simons C.A., Pritchett L.C., Houlet J.M. and Frazier C.A., Determination of particle size distribution and chemical composition of particulate matter from selected under agreement no. A6-175-32 for California Air Resource Board, by OMNI Environmental Services Inc., Beaverton and Desert Research Institute, Reno NV; 1989

IPCC, 2001. Climate change 2001. In: Houghton JT, Ding Y, Griggs DJ, Noguer M, van der Linden PJ, Dai X, Maskell K, Johnson CA, editors. The scientific basis, contribution of working group I to the Third Assessment Report of the Intergovernmental Panel on climate change. New York: Cambridge University Press.

J. Alcamo, Transboundary air pollution in central Europe and Eastern Europe, In J. Alcamo (Ed.)Coping with crisis in Eastern Europe's environment. IIASA. Book, Parthenon Publishing Group,Carnforth, 1992, pp. 87-101.

J. H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics—From Air Pollution to Climate Change, John Wiley & Sons, Inc., New York, 1998.

Katz, M., (1977). Methods of Air Sampling and Analysis. 2nd Ed. APHA.

King JC, Keen CL., (1999), Zinc. In: Shils ME, Olson JA, Shike M, Ross AC, eds. Modern Nutrition in Health and Disease, 9th ed. Philadelphia: Lea & Febiger,

Kumar, P. and Bhattacharya, S., 1999. When wealth is not health. Down to Earth 7, 33.

Li, R. Q., Zheng, L. M., Zhu, G. R., (1990). Innermongolia Lakes and the Environmental Changes. Beijing: Beijing Normal University Press.

Liu Y, Peter H D, 2002. Anthropogenic aerosols: Indirect warming effect from dispersion forcing. Nature, 419: 580–581.

Lyenger G. V., and Sansoni B.; Elemental analysis of biological materials-Current problems and techniques with special reference to trace elements; Technical Report Series No. 197, IAEA, Vienna, 73-101.

Malinowski, E. R.: Factor analysis in chemistry, John Wiley and Sons, Inc, 2002.

Malm, W.C.; Pitchford, M.L.; Scruggs, M.; Sisler, J.F.; Ames, R.G.; Copeland, S.; Gebhart, K.A.; Day, D.E. Spatial and Seasonal Patterns and Temporal Variability of Haze and Its Constituents in the United States: IMPROVE Report III; Cooperative Institute for Research in the Atmosphere; Colorado State University: Fort Collins, CO, 2000.

Markert B. (1993). "Instrumental analysis of plants." In B. Markert (Ed.), Plants as biomonitors. Indicators for heavy metals in terrestrial environment, Wiley, VCH, 1993, pp. 65-103.

Maykut, N.N., Lewtas, J. And Larson, T.V. (2001). Source apportionment of PM2.5 and carbon in Seattle using Chemical Mass Balance and Positive Matrix Factorization. Regional Haze and Global Radiation Balance – Aerosol Measurements and Models: Closure, Reconciliation and Evaluation, Speciality Conference, Bend, Oregon

MEP (Ministry of Environmetal Protection), 1996. Ambient air quality standard GB 3095-1996. http://www.envir.gov.cn/law/airql.htm.

Mertz, W., (1987), Trace elements in human and animal nutrition. New York: Academic Press, p. 225-240. .

Ministry of Health (1654) Mortality and Morbidity during the London Fog of December, 1952. Reports on Public Health and Medical Subjects No. 95, Her Majesty's Stationary Office, London.

Ministry of Health (1654) Mortality and Morbidity during the London Fog of December, 1952. Reports on Public Health and Medical Subjects No. 95, Her Majesty's Stationary Office, London.

MoEF. (2002). Agenda 21: An Assessment. Prepared by Tata Energy Research Institute on Behalf of Ministry of Environment and Forests, Government of India, New Delhi.

Morawska, L. (2003). Motor vehicle emissions as source of indoor particles. Indoor Environment. L. Morawska and T. Salthammer. Weinheim, Wiley-VCH.XVII: 297-319.

National Acid Precipitation Assessment Program. 1991. 1990 Integrated Assessment Report. In.Washington, DC20503: The U.S. National Acid Precipitation Assessment Program, Office of the Director.

National Air Quality and Emissions Trends Report, 1999; EPA 454/R-01-004; U.S. Environmental Protection Agency, Research Triangle Park, NC, 2002; available at http://www.epa.gov/air/aqtmd99 (accessed 2009).

New Scientist Magazine, “How Big Can Cities Get?" 17 June 2006, page 41.

NRC. 1996. Aerosol radiative forcing and climate change; Washington, DC: Council: National Academy Press.

Nriagu J.O.; A Global assessment of natural sources of atmospheric trace metals, Nature, 338, 47-49; 1989

Pacyna J M, 1986. Toxic Metals in the Atmosphere. New York: Willey.

Pacyna JM; Emission factors of the atmospheric elements, Toxic metals in the Atmosphere; Advances in Environmental Science and Technology, 17, John Wiley and Sons Inc. New York; 1986

Pasquill, F. (1961). "The Estimation of the Dispersion of Windborne Material." *Meteorology Magazine* 90(1063): 33-40.

Pauling, Linus (1947). General Chemistry. W.H. Freeman. ISBN 978-0-486-65622-9.

Pirjola, L. and M. Kulmala (2001). "Development of particle size and composition distributions with a novel aerosol dynamics model." Tellus Series B-Chemical and Physical Meteorology 53(4): 491-509.

Pruppacher, H. R. and J. D. Klett (1997). Microphysics of Clouds and Precipitation, Springer.

Raiswell, R.W., Brimblecombe, P, Dent, D.L. Liss, P.S. (1980). Environmental chemistry. Edward Arnold, London.

Santra, S.C. (2004). Environmental Science. New Central Book Agency (P) Ltd., Kolkata, India. First Published in 2001. ISBN: 81-7381-404X.

Sarath Guttikunda, (2009), Urban Particulate Pollution Source Apportionment - Part 1. Definition, Methodology, and Resources;

Sarath Guttikunda, “Urban Particulate Pollution Source Apportionment”; www.sim-air.org; June, 2009

Scholorling M. (2000). “Urban transport and its compliance with future air quality standards.” *Sixth International Conference on Urban Transport and the Environment for the 21st Century* .July 26–28, Cambridge, UK.

Schwartz J. and Dockery D. W. (1992) Increased mortality in Philadelphia associated with daily air pollution concentrations. *Amer. Rev.* Respir. Disease 145, 600-604.

Scire, J. S. and R. J. Yamartino (1989). CALGRID; A Mesoscale Photochemical Grid Model Volume II: User's Guide, University of Iowa.

Seinfeld J H, Pandis S N, 1998. Atmospheric chemistry and physics from air pollution to climate change. New York: Wiley. 649–655.

Seinfeld, J. H. and S. Pandis (1998). Atmospheric Chemistry and Physics from Air Pollution to Climate Change. New York, Wiley.

Senaratne, I. (1999). “An investigation of hydrocarbon compounds and metals in the Christchurch atmosphere, and their sources.” *M. Sc. Thesis in Environmental Science*. University of Canterbury, Christchurch, New Zealand.

Senaratne, I. (2003). “Chemical characterization of airborne particulate matter in New Zealand cities.” *Ph. D. thesis*, The University of Auckland.

Smith K. R., Apte M. G., Ma Y., Wongsekiartitar W. and Kulkarni A. (1994) Air pollution and the energy ladder in Asian cities. Energy Int. *J.* 19, 587-591.

Speciate 3.2, USEPA (2002). Particulate Matter (PM) speciation data system. USEPA, QAQPS Research Triangle Park, North Carolina.

Stevens, J. (1996). Applied Multivariate Statistics for the Behavioral Sciences (3rd ed.). Mahwah, Erlbaum, NJ.

Sun Y L, 2005. Physicochemical characterizations of airborne particulate matter in the typical regions of China and its impact on regional environment. Doctoral thesis, Beijing Normal University, China.

Tsyro, S. G. (2003). Model performance for particulate matter. In: EMEP Status report 1/2003. Transboundary acidification, eutrophication and ground ozone level, Part II: Unified EMEP model performance. EMEP/MSC-W & MSC-E Status report 1/2003 Part II. N. M. Institute. Oslo.

Turner, D. B. (1970). Workbook of Atmospheric Dispersion Estimates.

U.S. Environmental Protection Agency, Research Triangle Park, NC, http://www.epa.gov/ttn/scram/guidance/guide/final-03-pm-rh-guidance.pdf.

U.S.EPA (1987). Protocol for reconciling differences among receptor and dispersion models. Report Number EPA-450/4-87-008; prepared by Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC,

U.S.EPA (2007). Guidance on the use of models and other analyses for demonstrating attainment of air quality goals for ozone, PM2.5, and regional haze. Report Number EPA -454/B-07-002; prepared by

UN (1989) Prospects of *World Urbanization* 1988. Population Studies Go. lli, New York.

UN (1989) Prospects of *World Urbanization* 1988. Population Studies Go. lli, New York.

UNEP/WHO (19881 Assessment of *Urban Air Oualitv*. United Nations invironment Piogramme and_Worid Health Organization, Nairobi.

UNEP/WHO (1993). City air quality trends, Vol. 2. WHO PEP/93 26, UNE93 26P GEMS 93.A.2, Genf.

UNEP/WHO, 1993. City air quality trends, Vol. 2. WHO PEP/93 26, UNE93 26P GEMS 93.A.2, Genf. UNEP/WHO, 1993. City air quality trends, Vol. 2. WHO PEP/93 26, UNE93 26P GEMS 93.A.2, Genf. Utell, M., 1997. Smoke Alarm: Haze From Fires Might Promote Bacterial Growth. Sci. Am. 24–25

US EPA (1998). A Comparison of Calpuff Modeling Results to Two Tracer Field Experiments, http://www.epa.gov/scram001/7thconf/calpuff/tracer.pdf.

US EPA Positive Matrix Factorization (PMF) 3.0: Fundamentals & User Guide, 2007-08

US EPA: Compendium Method IO-2.1; "Sampling Of Ambient Air For Total Suspended Particulate Matter (SPM) And PM_{10} Using High Volume (HVS) Sampler"; Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, June 1999

US EPA: Compendium Method IO-3.2; "Determination Of Metals In Ambient Particulate Matter Using Atomic Absorption (AA) Spectroscopy"; Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, June 1999

USEPA (1994) The Concise Guide to AIRS AQS (May, 1994). OfEce of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

USEPA (1994) The Concise Guide to AIRS AQS (May, 1994). OfEce of Air Quality Planning and Standards. Research Triangle Park, North Carolina.

USEPA (1995). Screen3 Model User's Guide. U. EPA. Research Triangle Park, North Carolina, http://www.epa.gov/scram001/userg/screen/screen3d.pdf.

USEPA, (1997). Compendium Method TO-14A, EPA/625/R-96/ 010b.

Venkatram, A. (2003). Validation of Concentrations estimated from air dispersion modeling for source-receptor distances of less than 100 meters. Sacramento, California, California Air Resources Board, Research Division.

W. C. Hinds, Aerosol Technology—Properties, Behaviour, and Measurement of Airborne Particles, second ed., JohnWiley & Sons, Inc., New York, 1998.

Watson, J.G. (1979). “Chemical element balance receptor model methodology for assessing the sources of fine and total suspended particulate matter in Portland, Oregon.” Oregon Graduate Center.

Watson, J.G. (1984). “Overview of Receptor Model Principles.” *J. Air Poll. Control Assoc.* 34, 619-623.

Watson, J.G. (2004). Protocol for applying and validating the CMB model for PM2.5 and VOC. Report Number EPA-451/R-04-001; prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC,

Watson, J.G., Chow, J.C. and Pace, T.G. (1991). “Chemical Mass Balance Receptor Modeling for Air Quality Management.” Hopke, P.K. editor. Elsevier Press, New York, NY, 1991, p. 83-116.

Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B., Nguyen, Q.T., Meyer, E.L. and Pace, T.G. (1990). Receptor Model Technical Series, Vol. III, CMB7 User's Manual, http://www.epa.gov/ttn/chief/software.htmlUS Environmental Protection Agency, Report EPA-450/4-90-004, January.

Watson, J.G., Robinson, N.F., Lewis, C.W., Coulter, C.T., Chow, J.C., Fijita, E.M., Lowenthal, D.H., Conner, T.L., Henry, R.C. and Willis, R.D. (1997). Chemical Mass Balance Receptor Model Version 8 (CMB). User Manual, Prepared for US EPA Research Triangle Park, NC, Desert Research Institute, Reno, N.V.USEPA, (2001). CMB8 User Manual, EAP-454/R-01-XXX.

Watson, J.G.; Chow, J.C. (2005). Receptor models. In Air Quality Modeling - Theories, Methodologies, Computational Techniques, and Available Databases and Software. Vol. II - Advanced Topics, Zannetti, P., Ed.; Air and Waste Management Association and the EnviroComp Institute: Pittsburgh, PA, 455-501.

Watson, J.G.; Chow, J.C. (2007). Receptor models for source apportionment of suspended particles. In Introduction to Environmental Forensics, 2nd Edition, 2;Murphy, B., Morrison, R., Eds.; Academic Press: New York, NY, 279-316.

Watson, J.G.; Chow, J.C.; Chen, L.; Wang, X.L.; Merrifield, T.A.; Fine, P.M.; Barker, K. (2011). Measurement system evaluation for upwind/downwind sampling of fugitive dust emissions. AAQR, 11(4):331-350. doi: 10.4209/aaqr.2011.03.0028. http://aaqr.org/.

Watson, J.G.; Chow, J.C.; Wang, X.L.; Kohl, S.D. (2010). "Emission characterization plans for the Athabasca Oil Sands Region. In Proceedings, 103rd Annual Meeting of the Air & Waste Management Association, Tropp, R. J., Legge, A. H., Eds.; Air & Waste Management Association: Pittsburgh, PA, 1-6.

Watson, John G.: 1988, 'Transactions Receptor Models in Air Resources Management', An International Specialty Conference Sponsored by Air and Waste Management Association, San Francisco,California.

WH@PEP (1992) Urban A& Pollution Monitoring-Report of a Meeting of UNEP/WHO Government-Designated Experts, Geneva, 5-8 November 1991. WHO/PEP/92.2, UNEPIGEMSP2.A.1, World Health Organization, Geneva.

WH@PEP (1992) Urban A& Pollution Monitoring-Report of a Meeting of UNEP/WHO Government-Designated Experts, Geneva, 5-8 November 1991. WHO/PEP/92.2, UNEPIGEMSP2.A.1, World Health Organization, Geneva.

WHO (1987). "Air quality guidelines for Europe" World Health Organization Regional Office for Europe, WHO Regional Publications, European Series, No. 23.

WHO (1977) *Air Monitoring Programme* Design for *Urban and Industrial Areas.* WHO Offset Publication No. 33, WHO, Geneva.

WHO (1980) *Analysing and Interpreting Air Monitoring Data.* WHO Offs& Publication No. 511 WHO, Geneva.

WHO (1982) Estimatina *Human Exposure to Air Pollution.*WHO O&et Publicaiion No. 69,'WHO, Geneva.

WHO (1982) Estimatina *Human Exposure to Air Pollution.*WHO O&et Publicaiion No. 69,‘WHO, Geneva.

WHO (1987). Air Quality Guidelines for Europe. Copenhagen, WHO Regional Office for Europe, 1987 (WHO Regional Publications, European Series, No. 23).

WHO (1995) Interpretation of WHO Air Quality Guidelines. Report of an Expert Working Group, WHO/EOS/95, Geneva (in press).

WHO (2000). “Air quality guidelines for Europe (2nd ed.).” World Health Organization Regional Office for Europe. WHO Regional Publications, European Series, No. 91.

WHO/ECOTOX (1992) In Motor *Vehicle Air Pollution-Public Health Impact* and *Control* Measures, WHO/PEP/*92.4* (edited by Gage D. T. and Zali 0.). World Health Organization and ECOTOX. Geneva.

WHO/UNEP (1992) *Urban Air Pollution in* Megacities of *the World.* World Health Organization, United Nations Environment Programme, Blackwell, Oxford.

Wiederkehr, P., Yoon, S.-J., 1998. Air quality indicators. In: Fenger, J., Hertel, O., Palmgren, F. (Eds.), Urban Air Pollution, European Aspects. Kluwer Academic Publishers, Dordrecht, pp. 403-418.

Wiederkehr, P., Yoon, S.-J., 1998. Air quality indicators. In: Fenger, J., Hertel, O., Palmgren, F. (Eds.), Urban Air Pollution, European Aspects. Kluwer Academic Publishers, Dordrecht, pp. 403-418.

World Health Organization (WHO); Air Quality Management: Air Quality Guidelines, WHO, Geneva, 1999.

Xie S D, Liu Z, 2007. Source apportionment of inhalable particles in Beijing. In: Proceeding of Research on the Formation and Control Technology of Particles from Combustion Sources. 179–195.

Xu X, 1993). Research on the Mineral Compositions of Chinese Salt Lakes. Beijing: Science Press.

Yadav, S. and Rajamani, V. (2006). Air Quality and Trace Metal Chemistry

Yamartino, R. J., J. S. Scire, (1989). CALGRID: A Mesoscale Photochemical Grid Model. Volume I: Model Formulation Document. Sacramento, CA, California Air Resources Board.

Zhu L, Wang J, Du Y, Xu Q., "Research on PAHs fingerprints of vehicle discharges." Department of Environmental Science, Zhejiang University, China, Huan Jing Ke Xue, 2008 May; 24(3):26-9.

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National Institute of Technology Karnataka (Former REC), Surathkal, India
Thesis: Source Apportionment and Chemical Characterization of Trace Elements in Suspended Particulate Matter at Kolhapur City

07/1998-10/2000 **M.E. Civil Engineering (Specialization: Environmental Engineering)**
Walchand College of Engineering, Sangli, Maharashtra, India
Thesis: Ambient Air Quality Index (AQI) for Kolhapur City

07/1994-06/1996 **M.B.A. (Specialization: Marketing and Finance)**
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Thesis: Open Office Layout System for Ghatge Patil Transports Limited, Kolhapur

07/1988-06/1993 **B.E. Environmental Engineering (Specialized course in Civil Engineering)**
KIT's College of Engineering, Kolhapur, Maharashtra, India
Thesis: A Characterization study of Sugar Industry Waste

RESEARCH EXPERIENCE

04/2005-03/2007 **Monbukagakusho (Japanese Government) Research Student**
Graduate School of Life and Environmental Science, University of Tsukuba, Japan
Research: Numerical Simulation of Dispersion of Aerosols from Mobile Sources in South Asia

04/2005-03/2006 **Research Assistant**
Terrestrial Environmental Research Centre, Japan
Research Projects participated:

- Large Scale Atmospheric and Air Pollution Modeling and Simulation
- Urban Air Pollution Management and Control
- Meteorological data Analysis and Instrumentation, Modeling & Simulation
- Gewex Asian Monsoon Experiment (GAME)
- Air Pollution Data Analysis, Emission Inventory and Project management
- Urban Transportation Planning and Artificial Intelligence

TEACHING EXPERIENCE

05/2014- Present **Principal Advisor (Environment and Climate Change)**
Fresco Advisory of Atmospheric Pollution, Pune, Maharashtra, India

01/2014-04/2014 **Associate Professor in Civil Engineering**
GSM College of Engineering, Pune, Maharashtra, India

02/2006-12/2013 **Associate Professor in Environmental Engineering**
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07/2009-06/2011 **Visiting Professor in M.Tech in Environmental Engineering**
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07/2009-06/2011 **Visiting Professor in Industrial Safety, Health, Environment**
Shivaji University, Kolhapur, Maharashtra, India

07/2003-04/2005 **Visiting Professor in M.Tech in Environmental Engineering**
KLE's College of Engineering and Technology, Belgaum, Karnataka, India
Visveshwaraiyya Technological University, Belgaum, Karnataka, India

02/2001- 02/2006 **Senior Lecturer in Environmental Engineering**
KIT's College of Engineering, Kolhapur, Maharashtra, India

02/1996- 02/2001 **Lecturer in Civil & Environmental Engineering**
KIT's College of Engineering, Kolhapur, Maharashtra, India

ACHIEVEMENTS

2013	**Certified Faculty Member** International Accreditation Organization (IAO), Texas, USA
2013	**Post Graduate Teacher in Environmental Engineering** Shivaji University, Kolhapur, Maharashtra, India
2013	**Functional Area Expert in Air Quality and Air Pollution Modeling** Quality Council of India-NABET, New Delhi, India
2011	**International Award for Excellence in Climate Change** Common Ground Publishing, USA
2005	**Monbukagakusho Research Scholarship** MEXT, Government of Japan
2004	**Recommended for Monbukagakusho Scholarship** Ministry of Higher Education, Government of India

GRANTS/FUNDED PROJECTS

2011-2013	**Principal Investigator,** City Sanitation Plan Kolhapur Municipal Corporation, Maharashtra, India Funds Received: Rs. 4.0 Lakhs for DPR
2011-2013	**Principal Investigator, MODROBS of Air Pollution Laboratory** All India Council for Technical Education, New Delhi, India Funds Received: Rs. 5.0 Lakhs
2009-2010	**Principal Investigator, R&D for PhD Research and Dissertation** All India Council for Technical Education, New Delhi, India Funds Received: Rs. 6.0 Lakhs
1999-2002	**Co-Investigator,** World Bank Environmental Management Capacity Building (EMCaB), Mumbai, Maharashtra, India Funds Received: Rs. 9.1 Lakhs for DPR
1997-1999	**Co-Investigator, MODROBS of Surveying Laboratory** All India Council for Technical Education, New Delhi, India Funds Received: Rs. 7.0 Lakhs

GUEST LECTURES

12/2012	**Eminent Speaker, Carbon Credits: Incentive for an Industry** **National Workshop on Recent Trends in Monitoring, Control and Abatement of Air Pollution** National Institute of Technology Karnataka, Surathkal, India
02/2012	**Session Chairman, EHS in Manufacturing Industry** **National Conference on Lean and Green Manufacturing** KIT's College of Engineering, Kolhapur, Maharashtra, India
12/2010	**Eminent Speaker, Global Warming-India Perspective** The Institution of Engineers, Kolkata, Kolhapur Division, Maharashtra, India
02/2008	**Session Chairman, Climate Change** **National Conference on Environmental Engineering and Management** TKIET, Warnanagar, Kolhapur, Maharashtra, India
03/2003	**Session Chairman, Advances in Environmental Engineering** **National seminar on Geo-Environmental Hazards – Future Perspective** J. T. Mahajan College of Engineering, Faizpur, Dist. Jalgaon, Maharashtra, India

PROFESSIONAL AFFILATIONS

2014-Present	**Principal Advisor** Fresco Advisory of Atmospheric Pollution, Pune, Maharashtra, India
2013-Present	**Certified faculty Member** International Accreditation Organization, USA
2010-Present	**Environmental Expert** Grass Root Creations Private Limited, New Delhi, India
2010-Present	**Expert Advisor and Functional Area Expert in AQ and AP** Equinox Environments (I) Pvt. Ltd., Kolhapur, Maharashtra, India
2007-Present	**Environmental Expert** The Institute of Science of Success, Kolhapur, Maharashtra, India
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1996-2010	**Environmental Expert** AB Consultants, Kolhapur, Maharashtra, India

SELECTED PUBLICATIONS

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- **Atul Ayare**, Priya Gurav, (2011), “Health Assessment of Pb and CD through Source Apportionment of Atmospheric Aerosols in Kolhapur City”, International Journal of Climate Change: impacts and responses, ISSN 1835-7156, Vol. 3
- **Atul Ayare**, Yogesh Sathe, G. Srinikethan, (2011), “Application of US EPA PMF model to Source Apportionment of Trace Elements in Atmospheric Aerosols at Kolhapur City”, International Journal Of Environmental Research and Development, Vol. 5, Issue 3
- **Atul Ayare**, G. Srinikethan, (2010), “Source Apportionment and Chemical Characterization of Trace Elements in Aerosols at Kolhapur City”, International Journal of Climate Change: impacts and responses, USA, ISSN 1835-7156, Vol. 2
- **Atul Ayare**, Arti Soni, Manisha Ganeshan, (2009), “Design of a CO2 Capture system for a foundry”, International Journal of Climate Change: impacts and responses, USA, ISSN 1835-7156, Vol. 1