

**STUDIES ON CARBONACEOUS AEROSOL AND WATER SOLUBLE IONIC SPECIES EMITTED FROM RESIDENTIAL BIOMASS BURNING OF ANDHRA PRADESH, INDIA**

**A**

***Dissertation***

Submitted in partial fulfilment of the requirements  
For the award of degree of

**Master of Technology**

**(Environmental Science and Technology)**

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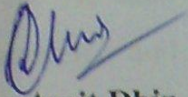
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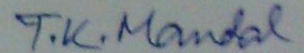
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## CERTIFICATE

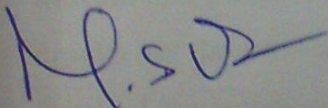
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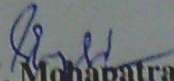
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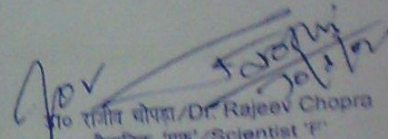
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## **DECLARATION**

I, the undersigned hereby declare that the research work presented in the M.Tech project entitled “**Studies on carbonaceous aerosol and water soluble ionic species emitted from residential biomass burning of Andhra Pradesh, India**” has been carried out under the guidance of Dr. T. K. Mandal, Scientist National physical Laboratory, New Delhi. Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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**List of abbreviation:**

AIDS	Acquired immunity deficiency syndrome
BC	Black carbon
CCN	Cloud condensation nuclei
DST	Department of Science & Technology
EC	Elemental carbon
IMPROVE	Interagency Monitoring of Protected Visual Environments
INDOEX	Indian Ocean Experiment-Intensive Field Phase
LPG	Liquid Petroleum Gas
NMHC	Non-methane hydrocarbons
OC	Organic carbon
PAHs	Polycyclic aromatic hydrocarbons
PM	Particulate Matter
RSPM	Respirable suspended particulate matter
TSP	Total suspended particulate
WHO	World Health Organization

## **Abstract:**

Biomass is widely used as energy source in rural households in India. Biomass burning is the burning of living and dead vegetation. Ninety percent of all biomass-burning events are thought to be human initiated. Human induced fires are used for a variety of “applications” such as agricultural expansion, deforestation, weed and residue burning, and harvesting practices. Natural fires are grassland and forest fires mainly induced by lightning. It is estimated that 8700 Tg of dry matter/year are burnt each year in total. Emissions from biomass burning include a wide range of gaseous compounds and particles that contribute significantly to the tropospheric budgets on local, regional, and even global scales. The emission of CO, CH<sub>4</sub> and VOC affect the oxidation capacity of the troposphere by reacting with OH radicals, and emissions of nitric oxide and VOC lead to the formation of ozone and other photo oxidants. For a large number of compounds biomass burning is one of the largest single sources in the troposphere, especially in the tropics. Biomass burning emissions play an important role in the biogeochemical cycles of carbon and nitrogen. Following the first systematic investigations on fire emissions in laboratory experiments in the 1960's, the last 20 years saw an increasing number in studies on biomass-burning emissions in various ecosystems. Recently, our knowledge of the emissions of gaseous compounds in the troposphere from fires has increased considerably. This report focuses on the review of emission factor and emission rates of Particulate matter, Cation, Anion, Organic carbon and Elemental carbon containing compounds. We discuss the implications of our results on such studies. The last decade has seen tremendous advances in atmospheric aerosol particle research that is often performed in the context of climate and global change science. Biomass burning, one of the largest sources of accumulation mode particles globally, have been closely studied for its radiative, geochemical, and dynamic impacts. These studies have taken many forms including laboratory burns, in situ experiments. Budget estimate for carbonaceous aerosols including black carbon (BC) and organic carbon, emitted from the combustion of various fuels, is very important for regional climate studies. Emission factors for carbonaceous aerosols from bio-fuels was determined in a controlled combustion study. The emission factors thus obtained along with those available for other fossil fuels consumed in different sectors have been applied to assess the budget for carbonaceous aerosols from India.

Finally, we compare total emissions from a variety of residential end-use technologies and estimate their effect on the radiative balance, with the implication that improvements could lead to a cleaner atmosphere on scales that are much larger than typically considered.

**Keywords:** aerosol, trace gases, combustion, biomass burning, human health.

Biomass, a renewable energy source, is biological material from living, or recently living organisms, such as wood, crop residue, (hydrogen) gas, and alcohol fuels. Biomass is commonly plant matter grown to generate energy or produce heat. Biomass is a very term used to describe material of recent biological origin that can be used either as a source of energy or for its chemical components. Biomass, in ecology, is the mass of living biological organisms in a given area or ecosystem at a given time. Biomass can refer to species biomass, which is the mass of one or more species, or to community biomass, which is the mass of all species in the community. It can include microorganisms, plants or animals <sup>{1}</sup>. The mass can be expressed as the average mass per unit area, or as the total mass in the community. Harvesting biomass such as crops, trees or dung and using it to generate energy such as heat, electricity or motion, is bio-energy. Presently, the biomass source contributes 14% of global energy and 38% of energy in developing countries <sup>{2}</sup>.

Biomass burning is the burning of living and dead vegetation. It includes the human-initiated burning of vegetation for clearing of land and land-use change as well as natural, lightning-induced fires. Biomass open burning practices include a large variety of combustion activities including post-harvest burning of agricultural fields, residential wood burning for heating and cooking, and wildfires. These activities are considered to be potential source of toxic releases. Scientists estimates that humans are responsible for about 90% of biomass burning (anthropogenic) with only a small percentage of natural fires contributing to the total amount of vegetation burned (NASA, earth observatory). In India, biomass fuels accounted 93% of total biomass consumption (577 Million tonne/yr), with forest fires contributing only 7%. This is in contradiction of global patterns, where forest fires are the primary and biofuels a negligible contributor. The bio-fuel mix varied across different regions, with a national average of 56: 21: 23% for fuel wood, crop waste and dung-cake, respectively <sup>{3}</sup>

Biomass is a major source of energy in developing countries, particularly India, where most of the energy requirement in the rural sector is met by biomass fuels. Biomass fuels are often burned under primitive and inefficient conditions by about half the world's population as the major source of domestic energy as amongst the available types of renewable energy, biomass is unique in its ability to provide solid, liquid and gaseous fuels which can be

stored and transported<sup>{4}</sup>. In South Asia, all types of biomass fuels like fuel-wood, agricultural residues and animal waste are used. Domestic bio-fuel burning accounts for 42% of the total biomass burnt in India <sup>{5}</sup>. In South-East Asia, biomass is the major source of energy nearly accounting for 33% of the country's energy usage reaching levels as high as 75-90%. Fuel wood is mostly used for cooking and heating purposes <sup>{6}</sup>. The choice of biomass fuel depends on availability, local customs and season <sup>{7}</sup>.

Biomass burning has both short and long term impacts on the environment. Recognising the significance of bio-fuel combustion to green-house gas emissions is an important step in the development of a solution to the problem of traditional fuel use<sup>{8}</sup> and to the more general question of finding appropriate energy resources for a vast and rapidly changing world.

The increasing consumptions of fossil fuels and biomass fuels increase the emissions of carbonaceous aerosols, which affect the air quality and regional climate. This increase is more significant in the tropics due to increasing population and changing standard of living. Biomass is a major source of energy in developing countries, particularly India, where most of the energy requirement in the rural sector is met by biomass fuels. Although the per capita usage of the bio-fuels is declining, as they are being substituted by more efficient commercial energy sources, but with the increase in population, the total consumption of biomass fuels is still showing an increasing trend<sup>{9}</sup>. Nearly 20 wt (percent) % of total suspended particulate matter and up to 80 wt% of fine particles in the atmosphere are carbonaceous species in polluted suburban and industrialized areas <sup>{10}</sup>.

Biomass burning has attracted the attention of people globally due to its contribution to air pollution issues and the effects of these emissions on human health. Quantitative information on biomass burning is necessary to understand the source and sinks of the atmospheric trace gases and aerosols. Biomass burning releases large amounts of particulates (solid carbon combustion particles), aerosols, un-burnt carbon and gases, including greenhouse gases, carbon dioxide, methane, and nitrous oxide. In addition, biomass burning is a source of chemically active gases, including carbon monoxide, non-methane hydrocarbons, and nitric oxide<sup>{11}</sup>. The biomass burning smoke contributes about three quarters of the aerosol burden in the regional haze while other sources like fossil fuel burning contributes the rest<sup>{12}</sup>. The dark component of these carbonaceous aerosols often referred to as soot or black carbon (BC) is actually a mixture of graphite-like particles and light-absorbing organic matter<sup>{12}</sup>. The chemical composition of aerosols play a major role with respect to their effect and alters fast and frequently due to new particle formation, scavenging of particles and chemical reactions.

Burning of bio-fuels, emit many trace substances which are reactants in atmospheric chemistry and soot particulate matter that decreases visibility and have significant health implications on humans, animals & vegetation linked to morbidity and mortality <sup>{13, 14, 15, 16}</sup> .such as on atmospheric chemistry and radiation budget <sup>{17}</sup> and even on acidification of clouds, rain and fog <sup>{18}</sup> .

The impact on the radiation balance of the earth occurs both directly, by absorbing and scattering incoming solar radiation; and indirectly, by acting as cloud condensation nuclei (CCN) and also by altering the clouds microphysical processes on a mesoscale <sup>{19, 20}</sup> .Studies suggest that biomass burning has increased on a global scale over the last 100 years, and computer calculations indicate that a hotter Earth resulting from global warming will lead to more frequent and larger fires. Biomass burning particulates impact climate and can also affect human health when they are inhaled, causing respiratory problems. (NASA , earth observatory).

Biomass burning is also a major source of ambient particulate matter with aerodynamic diameter less than 2.5  $\mu\text{m}$  (PM2.5) and has significant impacts on human health <sup>{21}</sup> regional and global air quality<sup>{22}</sup> and climate <sup>{23,24}</sup> . Water-soluble potassium ( $\text{K}^+$ ) has been used extensively as an inorganic tracer to apportion biomass burning contributions to ambient aerosol <sup>{25,26,27,28,29}</sup> .Organic compounds are the largest component produced from fires and there are specific compounds found 20 to be exclusively emitted from biomass burning. The most commonly used organic tracer is levoglucosan, a sugar anhydride produced during the combustion of cellulose <sup>{30,31,32,33}</sup> .

Biomass burning includes the burning of the world's vegetation--forests, savannas, and agricultural lands--to clear the land and change its use. Only in the past decade have researchers realized the important contributions of biomass burning to the global budgets of many radiatively and chemically active gases-carbon dioxide, methane, nitric oxide, tropospheric ozone, methyl chloride--and elemental carbon particulates<sup>{10}</sup> .

A better characterization of emission is needed to improve the understanding of overlapping benefits for emission reduction strategies. The improved characterization of emission will help in two ways: by quantifying the most efficient strategies for improving both global warming and health related problems and by identifying sources that are under reported or missing.

Limited study has been done in India, to evaluate the impact of biomass fuel burning on ambient air quality and chemical characteristics of aerosol. South of India is of the major source of trace gases and aerosols due to usage of biomass fuel as energy. The present study was being carried out across the southern India. Southern India is one of the major contributor of trace gases and aerosols due to usage of biomass fuel as energy is a major environmental concern. These pollutants affect the ambient air quality as well as climate of the region.

The major goal of this research is to study the effects of biomass fuel burning on ambient air quality and chemistry of atmosphere.

The aim of this study is to provide an emission factor inventory for southern India Plains that resolves the spatial and temporal variations. Emissions from the household burning of biomass fuels strongly influence the air quality in India. Furthermore, the concentration of climatic active trace species in the atmosphere is considerably changed by these emissions in particular years. The inventory is applied to estimate the effects of aerosols emitted from the burning of biomass fuels on the regional air quality and human health. This study focuses on the air pollution caused by particulate matter emissions which are of primary relevance for public health and hence, contribute to Climate Change.

## 2.1 BIOMASS AND BIOMASS ENERGY

Biomass materials are used since millennia for meeting myriad human needs including energy. Main sources of biomass energy are wood, crop residue and animal waste. Until the middle of 19th century, biomass dominated the global energy supply with a seventy percent share<sup>{34}</sup>. Among the biomass energy sources, wood fuels are the most prominent. With rapid increase in fossil fuel use, the share of biomass in total energy declined steadily through substitution by coal in the nineteenth century and later by refined oil and gas during the twentieth century. Despite its declining share in energy, global consumption of wood energy has continued to grow. During 1974 to 1994, global wood consumption for energy grew annually by over 2 percent rate. Presently, the biomass sources contribute 14% of global energy and 38% of energy in developing countries<sup>{2}</sup>. Globally, the energy content of biomass residues in agriculture based industries annually is estimated at 56 exajoules, nearly a quarter of global primary energy use of 230 exajoules<sup>{35}</sup>.

Wood is a form of biomass, and as such can be understood as an energy resource in the context of biomass energy. Biomass fuels include any organic matter that is available on a renewable basis including forest residues, wood product residues, agricultural field residues and processing wastes, animal wastes, agricultural and woody crops grown for fuels. Implicit in this definition is the need not only for the organic energy resource itself, but also for an ongoing feedstock management plan in order to make the renewable aspect a reality. Biomass fuels produce very low emissions, generate relatively few acid rain- and smog-causing particles, and have a minimal impact on the environment when converted to energy correctly. In addition, all share the characteristic that they can be regenerated relatively quickly to provide a reliable energy feedstock over time. Biomass energy can be derived from almost any configuration of organic components of flora and fauna. Petroleum and coal are also organically derived fuels, but they are derived from fossilized flora and fauna of earlier eras, and consequently are not renewable (in a practical timeframe for our civilization). Biomass feedstocks are not homogenous, and their physical characteristics vary widely. They may have high moisture content like some animal wastes, or low moisture content like wheat straw; or, any one kind of biomass—like wood can be green (newly cut from live specimens) and high in moisture, or dried and lower in moisture. The single most

important characteristic of biomass feedstock, from the perspective of energy production, is their moisture content. Biomass heating values are determined by their moisture content, but are consistently lower in energy density than coal or petroleum, which often limits the distance over which biomass can be transported economically. Wood is the most commonly used biomass resource. Wood can be used in solid form or processed and pelletized for use for residential, institutional, and commercial heating. Modern technologies enable us to extract more energy per unit volume of wood; future technologies will allow wood residues to be processed into a syn-gas for internal combustion engines, fuel cells, or natural gas power plants. Finally, more advanced technologies can generate a variety of liquid fuels from cellulosic materials found in wood.

Biomass energy accounts for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in developing countries <sup>{36}</sup>. In South Asia, all types of biomass fuels like fuel-wood, agricultural residues and animal waste are used. Domestic bio-fuel burning accounts for 42% of the total biomass burnt in India <sup>{5}</sup>. Biomass burning is an important source of trace gas emissions, aerosols, un-burnt carbon and has important effect on atmospheric chemistry and radiation budget <sup>{24}</sup>.

### **2.1.1 Biomass Energy in The Asia-Pacific Region**

Biomass remains the primary energy source in the developing countries in Asia. Share of biomass in energy varies - from a very high over three quarters in percent in Nepal Laos, Bhutan, Cambodia, Sri Lanka and Myanmar; nearly half in Vietnam, Pakistan and Philippines; nearly a third in India and Indonesia, to a low 10 percent in China and 7 percent in Malaysia . In the wake of rapid industrialization and marketization during past two decades, the higher penetration of commercial fossil fuels in most Asian developing nations has caused decline in the share of biomass energy. The absolute consumption of biomass energy has however risen unabatedly during past two decades, growing at an annual rate of over 2 percent. Various factors like rising population and shortages or unaffordability of commercial fuels in rural and traditional sectors have sustained the growing biomass use. The increasing pressure on existing forests has already lead to considerable deforestation. Despite policy interventions by many Asian governments, the deforestation in tropics far exceeded afforestation (by a ratio of 8.5:1) during the 1980's .The deforestation and land degradation has made tropical Asian forests the net emitters of atmospheric CO<sup>2</sup> <sup>{37}</sup> which is a major supporter of Global Warming.

**Table 1.1 People relying on biomass resources as their primary fuel for cooking, 2004**

	Total population		Rural		Urban	
	%	million	%	Million	%	Million
Sub-Saharan African	76	575	93	413	58	162
North Africa	3	4	6	4	.2	.2
India	69	740	87	663	25	77
China	37	480	55	428	10	52
Indonesia	72	156	95	110	45	46
Rest of Asia	65	489	93	455	35	92
Brazil	13	23	53	16	5	8
Rest of Latin America	23	60	62	59	9	25
<b>Total</b>	<b>52</b>	<b>2528</b>	<b>83</b>	<b>2417</b>	<b>23</b>	<b>461</b>

Sources: IEA analysis based on the latest available national census and survey data, including the 2001 Population and Household Census of Botswana; the 2003 Demographic and Health Survey of Nigeria; the National Bureau of Statistics of Tanzania, 2000/01; the 2001 Census of India; Energy Statistics for Indonesia, 2006; the Bangladesh Bureau of Statistics, 2005; the National Statistical Office Thailand, 2000; ORC Macro (2006); WHO (2006).

### 2.1.2 BIOMASS ENERGY IN INDIA

Biomass has been a key player in energy generation even in the past. Due to the dominance of coal and petroleum products in the industrial age there was a fall in biomass usage. Anyway, in India, though the energy scenario in India today indicates a growing dependence on the conventional forms of energy, about 32% of the total primary energy use is still using biomass and more than 70% of the country's population depends upon it for its energy needs. This section provides status of and trends in India Biomass Energy. Biomass contributes over a third of primary energy in India. Biomass fuels are predominantly used in rural households for cooking and water heating, as well as by traditional and artisan industries. Biomass delivers most energy for the domestic use (rural - 90% and urban - 40%) in India <sup>{38}</sup>. Wood fuels contribute 56 percent of total biomass energy <sup>{39}</sup>. Supply-side estimates <sup>{40}</sup> of biomass energy are reported as: fuelwood for domestic sector- 218.5 million tons (dry), crop residue-

96 million tons (estimate for 1985), and cattle dung cake- 37 million tons. A recent study <sup>{41}</sup> estimates demand in India for fuelwood at 201 million tons (Table 1). Biomass fuels used in India account for about one third of the total fuel used in the country, being the most important fuel used in over 90% of the rural households and about 15% of the urban households.

**.Table 1.2: Fuelwood Demand in India in 1996**

Consumption of Fuelwood	Consumption of Fuelwood(M t)
1. Household	
(a) Forested Rural	78
(b) Non Forested Rural	74
(c) Urban Areas	10
Sub Total	162
2. Cottage Industry	25
3. Rituals	4
4. Hotels etc.	10
Total	201

Source: Rai and Chakrabarti, 1996

## **2.2 CONSTRAINTS ASSOCIATED WITH TRADITIONAL BIOMASS ENERGY USAGE**

The biomass energy consumption is primarily limited to meet cooking needs of households and traditional industries and services in rural areas. The major problem with the traditional biomass use is the social costs associated with excessive pollution. The incomplete combustion of biomass in traditional stoves releases pollutants like carbon monoxide, methane, nitrogen oxides, benzene, formaldehyde, benzo(a)pyrene, aromatics and respirable particulate matter. These pollutants cause considerable damage to health, especially of women and children who are exposed to indoor pollution for long duration <sup>{42,43,44}</sup>. The twin problems of traditional biomass use are the energy inefficiency and excessive pollution.

Exploitation of abundant biomass resources from common lands sustained the traditional biomass consumption since millennia. Increasing pressure from growing population, growing

energy needs from rural industry and commerce and penetration of logistics infrastructure into remote biomass rich areas have now led to an unsustainable exploitation of biomass. Three main problems associated with the traditional biomass are inefficient combustion technologies, environmental hazards from indoor pollution and unsustainable harvesting practices.

### **2.3 AEROSOLS AND EMISSIONS OF TRACE GASES**

Aerosol science studies the properties of particles suspended in air or other gases, or even in vacuum, and the behaviour of collections of such particles. A collection of aerosol particles is referred to as an aerosol; although the particles may be suspended in some other gaseous medium, not just air. The term cosmosol is used for a collection of particles suspended in vacuum. Although attempts to give a strict definition of aerosol have appeared from time to time, to date no commonly acceptable and concise definition of an aerosol exists. In my opinion, it is better not to make any attempts in this direction, especially because intuitively it is clear what an aerosol is. For example, it is clear that birds or airplanes are not aerosol particles. On the other hand, smoke from cigarettes, fumes from chimneys, dust raised by the wind, and so on, is aerosols. Hence, there are some essential features that allow us to distinguish between aerosols and other objects suspended in the gas phase. There are at least two such features: (i) aerosol particles can exist beyond the aerosol for a sufficiently long time; and (ii) an aerosol can be described in terms of the concentration of aerosol particles, or, better, the concentration field. From this point of view, it is clear why birds are not aerosols. Interestingly, clouds are also not aerosols! Of course, we can introduce the concentration of cloud droplets. But if we isolate a cloud particle, it will immediately evaporate. The cloud creates a specially designed environment inside it – the humidity and the temperature fields – the conditions in which a water droplet does not evaporate during a long time. Aerosols are divided into two classes, namely primary aerosols and secondary aerosols, according to the mechanisms of their origination. Primary aerosol particles result, for example, from fragmentation processes or combustion, and appear in the carrier gas as already well-shaped objects. Of course, their shape can change because of a number of physico-chemical processes such as humidification, gas–particle reactions, coagulation, and so on. Secondary aerosol particles appear in the carrier gas from ‘‘nothing’’ as a result of gas-

to-particle conversion. For example, such aerosols regularly form in the Earth's atmosphere and play a key role in a number of global processes such as the formation of clouds <sup>{60}</sup>.

Secondary aerosols are solid or liquid particles created in the atmosphere through gas-to-particle conversion which involves chemical or physical transformation of precursor gases <sup>{61}</sup>.

Anthropogenic aerosols are composed of inorganic species such as sulphate, nitrate, ammonium, and trace metals, carbonaceous material consisting principally of organic species and black carbon <sup>{49}</sup>.

Aerosols emitted during biomass burning are predominantly in the form of submicrometer, accumulation mode particles (smoke)<sup>{62}</sup>. These can affect the earth's albedo, as well as decrease local and regional visibility, because of their light-scattering properties <sup>{63}</sup>. Tropospheric aerosols and their radiative effects pose a large uncertainty in the evaluation of climate change from anthropogenic modification of the composition of the atmosphere <sup>{64,65}</sup>. Aerosol radiative effects depend upon aerosol concentration and optical properties, which in turn are governed by their chemical composition and size distribution. Size distribution and chemical composition are fundamental aerosol properties relevant to study the climate impacts. Experimental studies of aerosol size and chemical characteristics, along with optical and radiative measurements, are needed to validate and refine calculations of optical and radiative effects. The potential for aerosols to act as cloud condensation nuclei (CCN), and participate in indirect radiative forcing <sup>{66}</sup> is also governed by their size and chemical characteristics.

In addition, smoke aerosols can act as efficient cloud condensation nuclei (CCN), which modify the cloud droplet size distribution and, hence, the reflectivity of <sup>{67,68}</sup>. On a global scale, these combined direct and indirect radiative effects are estimated to be responsible for a net radiative forcing that is comparable to that from sulfate aerosol <sup>{69}</sup>. The chemical composition and sources of atmospheric aerosols have been studied for different parts of the world. Atmospheric aerosol particles originate from a variety of natural and anthropogenic sources.

Generally the aerosols contain carbonaceous aerosols, sulfate aerosols and metal species. About 70% of the mass of particulates related is fine carbon-containing particles. Carbonaceous aerosols include both black carbon (BC) and organic carbon (OC). BC is often

used interchangeably with elemental carbon (EC), while OC is usually a mixture of various organic compounds, some of which are carcinogenic and mutagenic, such as polycyclic aromatic hydrocarbons (PAHs). High concentrations of BC and OC in the atmosphere pose a great concern for air quality and human health. BC and OC also have important implications for global climate change. BC primarily absorbs solar radiation and has a warming effect on the atmosphere. For this reason, BC has been proposed as the second most important global warming compound after CO<sub>2</sub>. In contrast, OC scatters solar radiation and has a cooling effect on the atmosphere<sup>{79}</sup>. Carbonaceous aerosols consist of fine particles, mostly less than 1 micrometer (µm) in diameter, which are usually classified as black carbon (BC), essentially but not identically the same as elemental carbon (EC)<sup>{71}</sup>, and organic carbon (OC), in which the carbon is bonded to other elements. Anthropogenic aerosols are believed to affect climate in several ways. These primarily scatter and cool the earth's surface and the dark absorbing component are present they also may heat the air in which they are suspended. Role of aerosols in modifying the earth's climate has been known for many years. BC has been proposed as possibly the second most important greenhouse species after CO<sub>2</sub>] with a positive net radiative forcing of as much as 0.5 W/m<sup>2</sup>.<sup>{72}</sup> BC emissions from biomass combustion are 0.25 Tg/yr and account for 71 % of the total BC emissions from India, with most of the balance from diesel vehicles<sup>{73}</sup>. Largest contributors to BC emissions are fuel-wood and crop waste accounting 72% of BC emissions from biomass combustion.

### **2.3.1. Characteristics of ambient aerosols:**

Awareness of air pollution has led to numerous studies on the chemical composition of ambient aerosols and determination of pollution sources. Most of the earlier studies reported from Peninsular India focused on the physical characteristics of aerosols<sup>{86,87,88}</sup> and except for a few studies conducted at urban sites in northern<sup>{89,90}</sup> not much studies have been carried out on the chemical composition of aerosols at the interior locations over the peninsular India. The chemical characterization of aerosols play an important role with respect to their effect and alters fast and frequently due to new particle formation, scavenging of particles, chemical reactions and removal by deposition. Aerosol deposits on land downwind of the cities and on agricultural and potentially sensitive ecosystems modify the chemical and radiative properties<sup>{91}</sup> of the downwind atmosphere and alter regional cloud precipitation<sup>{92}</sup> depending upon their number, composition and size distribution. Several

investigators have studied the chemical composition and mass size distribution of atmospheric aerosols both in India <sup>{93,94,95, 96}</sup> and abroad <sup>{101,102}</sup>. In Agra, a few sporadic measurements have been made <sup>{97,98}</sup> in which chemical compositions of particulate matter has been reported. Atmospheric aerosols consist of complex mixtures of inorganic and organic components. The organic fraction of the aerosols generally contributes 30-60% of the total fine particulate matter (PM) in the atmosphere <sup>{103}</sup>. Nearly 20 wt% of total suspended particulate matter and upto 80 wt% of fine particles in the atmosphere are carbonaceous species in polluted suburban and industrialized areas <sup>{9}</sup>. In another study, levels of carbon in RSPM (PM<sub>10</sub>) were studied by and the results indicated that total carbon (TC) and black carbon (BC) mass concentration were as high as 341 μg/m<sup>3</sup> and 216 μg/m<sup>3</sup> respectively. The ability of carbonaceous aerosols to modify local meteorology and climatology in regions where emissions are high like China and India, has been postulated <sup>{103}</sup> Black Carbon (BC) is thought to be the second largest contributor to global excess radiative forcing after CO<sub>2</sub> <sup>{104}</sup>. Urban areas have always been known to be a major source of particulate pollution <sup>{105}</sup> which is expected to continue to increase due to increase in world population growth and increasing industrialization and energy use especially in developing countries <sup>{106}</sup>. Particulate Matter (PM) is the general term used for a mixture of solid particles and liquid droplets found in the air and are produced by a wide variety of natural and manmade source <sup>{107}</sup>. In the past 20 years, the composition and sources of PM<sub>10</sub> aerosols in various environments have been studied by various scientists <sup>{108,109}</sup>. Some of the characterization studies carried out in India are mainly with respect to TSP, PM<sub>10</sub> and size distribution of aerosols. Instead of monitoring total suspended particles (TSP, D<sub>p</sub> < 100 μm) levels, which are widely acknowledged not to be important from the point of view of public health impact, smaller particles such as PM<sub>10</sub>(, D<sub>p</sub> < 100 μm) and PM<sub>2.5</sub> (D<sub>p</sub> < 2.5 μm) should be monitored regularly. The study of size fractionated aerosols in Agra reported that 52% of the particles were smaller than 2 μm <sup>{97}</sup> whereas in Delhi it was found to be 68% of the PM<sub>10</sub> mass <sup>{110}</sup>. Comparison of PM<sub>2.5</sub> values recorded at various places in India indicates that it constituted about one half of PM<sub>10</sub>. PM<sub>10</sub> aerosols in Mumbai during the INDOEX-IFP (The Intensive Field Phase of Indian Ocean Experiment) contains significant amount of carbonaceous 30%, ionic 20% and trace metals 4% <sup>{111}</sup>. The particulates consist of variety of inorganic and organic components. Experience in India as well as in some other countries has indicated that in atmosphere about 70-80% of particulate matter is inorganic in nature and remaining 20-30% is organic fraction <sup>{112}</sup>

So it becomes necessary to study the characteristics of ambient aerosols over mega cities. The main anthropogenic sources of these particles are direct emissions from transportation, domestic coal and bio-fuels burning as well as by industrial emissions <sup>{113}</sup>. Aerosols can also be transported for a long distance through regional and global wind circulation patterns <sup>{114}</sup>. Emission inventory models suggest that bio-fuel burning accounts for 50 to 90% of emissions, whereas the elemental composition of ambient aerosols points to fossil fuel combustion. These constraints show that both biomass combustion and fossil fuel combustion should be targeted to mitigate climate effects and thus to improve air quality <sup>{115}</sup>.

#### **2. 4. Biomass burning**

Biomass burning emissions are a significant, global source of trace gas and aerosol species in the atmosphere and affect climate, visibility and human health <sup>{45, 46, 47}</sup>. Bio-fuels burning emit many trace substances which are reactants in atmospheric chemistry and soot particulate matter that decreases visibility and have significant health implications on humans, animals and vegetation. The biomass burning smoke contribute about three quarters of the aerosol burden in the regional haze while other sources like fossil fuel burning contribute the rest <sup>{11}</sup>.

With the formation of green house and chemically active gases as direct combustion products and a longer-term enhancement of biogenic emissions of gases, biomass burning may be a significant driver for global change in atmosphere and climate. The chemical composition of aerosols play a major role with respect to their effect and alters fast and frequently due to new particle formation, scavenging of particles and chemical reactions. The chemical composition and sources of atmospheric aerosols have been studied for different parts of the world. Atmospheric aerosol particles originate from a variety of natural and anthropogenic sources. A major source of anthropogenic aerosol is biomass burning. When emitted in particulate form, they are referred to as primary aerosols and when nucleated in the atmosphere from gaseous precursor, then referred to as secondary aerosols <sup>{49}</sup>. Anthropogenic aerosols are composed of inorganic species such as sulphate, nitrate, ammonium, and trace metals, carbonaceous material consisting principally of organic species and black carbon <sup>{50}</sup>. The emissions from biomass burning represent a large perturbation to global atmospheric chemistry, especially in the tropics, where most biomass burning emissions are produced <sup>{51}</sup>.

The ignition, evolution and behaviour of a biomass fire and its emissions depend on many factors which are ultimately controlled by the environment. Local climate is extremely

important in the determination of the amount and characteristics of the biomass available. For a given type of biomass, the local weather, including temperature, precipitation, humidity and wind, controls the conditions required for the fire ignition and maintenance. Biomass burning can be described in four basic stages: ignition, flaming, smoldering and extinction <sup>{52}</sup>. The flaming stage is a pyrolytic process, with elevated temperatures as high as 1800 K, that acts to break apart the biomass molecules and decompose compounds of high molecular weight mostly into lower molecular-weight species, but also producing soot and tar along with the principle product. Nitrogen oxides, hydrocarbons and an abundance of aerosol particles are also emitted during the flaming stage. CO and other compounds characterized by incomplete oxidation as well as aerosol particles are emitted primarily during the smoldering phase at temperatures typically below 1000 K<sup>{54}</sup>. The amount of water in the biomass is one of the most important biomass burning control factors and can determine which stage, flaming or smoldering, will be more significant and defines the ratio between the emitted CO and CO<sub>2</sub>.

Biomass burning is estimated to contribute 39 ±6% to the carbon monoxide (CO) globally emitted and more than 20% to the nitric oxides (NO<sub>x</sub>), non-methane hydrocarbons (NMHC) and methyl chloride (CH<sub>3</sub>Cl) emissions<sup>{54}</sup>. To the global emissions of elemental carbon (EC) and particulate organic carbon (POC), biomass burning contributes even 63 ±9% and 91 ±10%, respectively <sup>{55}</sup>.The emitted trace gases affect the oxidizing capacity of the atmosphere and lead to the photo-chemical production of ozone in the troposphere <sup>{56}</sup>.In the stratosphere, the halogen compounds contribute to ozone depletion<sup>{57}</sup>. Aerosols emitted during biomass burning events may influence climate directly by reflecting solar radiation back into space. Furthermore, aerosols act as cloud condensation nuclei (CCN), and may thus affect climate indirectly by modifying cloud microphysics and sunlight reflectance <sup>{58,59}</sup>.

#### **2.4.1 Characteristics of aerosols emitted from biomass burning**

Biomass combustion results in severe indoor air pollution, especially particulate matter (PM). The problem of air pollution is aggravated in the developing countries because wood biomass and agricultural residue are the primary sources of household fuel for cooking, heating and lighting in these countries<sup>{74}</sup>. A major global source of anthropogenic aerosol is biomass burning. Anthropogenic aerosols are composed of inorganic species such as sulphate, nitrate, ammonium and trace metals, carbonaceous material consisting principally of organic species and black carbon <sup>{49}</sup>. Aerosols containing black carbon are emitted primarily in the tropical

and subtropical regions of the world, accounting for the release of almost 100 million tons of smoke aerosols into the atmosphere as a result of biomass burning. Once released to the atmosphere, biomass smoke is mixed with the particulate matter emitted from many other natural and anthropogenic sources, in many cases becoming difficult to recognize and quantify<sup>{75}</sup>.

Incomplete combustion of fossil fuels or bio-fuels produces soot in the form of elemental or black carbon, and numerous organic carbon (OC) species<sup>{76}</sup>. Particulate organic carbon from biomass burning accounts for over one-third of the organic carbon aerosol released globally<sup>{54}</sup>. Different types of soot contain different amounts of BC, the blacker soot. Fossil fuel and biofuel soot are blacker than soot from biomass burning (e.g., forest fires and wood fuel), which is generally more of a brownish colour. The composition of aerosols over India is different from that over Europe and the USA as it has an abundance of BC<sup>{77,78}</sup>. Using the BC data onboard Rown H. Brown ship,<sup>{79}</sup> have found that the carbonaceous aerosols outflow from India is normally originated from biomass/ biofuels burning (74-79%). Since the mean residence time of BC aerosols in the atmosphere is about 6 days, they can be transported upto a few thousand km from their source. So the observed concentrations at a given location are likely the sum of local emissions plus a component transported from distant sources<sup>{81}</sup>. The BC particles are frequently small enough ( $< 1 \mu\text{m}$ ) to be readily inhaled, where they have a certain probability of getting deposited in the lungs or other airways. Thus the study of BC is very crucial.

In India, biomass combustion is a major source of carbonaceous aerosol emissions, accounting 71% and 76% of the total BC and OM emissions. It was estimated that Asian BC emissions in 2000 were 2.5 Tg, of which China generated 1.1 Tg and India 0.6 Tg<sup>{81}</sup> estimated BC emissions in India to be 600 Gg<sup>{82}</sup> estimated Indian BC emissions to be 380 Gg for 1998–99. However,<sup>{78}</sup> expressed that BC emissions could be considerably higher, possibly as high as 2–3 Tg, based on atmospheric measurements taken during INDOEX, especially the observed BC/CO ratios.

Thus it is now recognised that aerosols and sulphur dioxide (precursor gas to sulphate aerosol) play an important role in regional and global climate change, with some aerosol constituents (e.g. sulphate, organic matter (OM) and mineral matter) resulting in cooling and others (e.g. black carbon (BC)) in warming of Earth's atmosphere<sup>{92,93,94}</sup>.

#### **2.4.2 Tracers from biomass burning**

Biomass burning is also a major source of ambient PM<sub>2.5</sub> (particulate matter with aerodynamic diameter less than 2.5 µm) and has significant impacts on human health<sup>{21}</sup> regional and global air quality<sup>{22}</sup> and climate<sup>{23,24}</sup>. Numerous studies have attempted to assess the impact of biomass burning on local and regional PM<sub>2.5</sub> concentrations. A number of chemical species have been used as particle-phase biomass burning emission tracers. Water-soluble potassium (K<sup>+</sup>) has been used extensively as an inorganic tracer to apportion biomass burning contributions to ambient aerosol<sup>{25, 26, 27, 28}</sup>. K<sup>+</sup> is not an ideal tracer as it has other sources, such as sea salt and soil dust<sup>{116,117}</sup>. Attempts have been made to eliminate these sources by calculating non-sea-salt non-dust K<sup>+</sup><sup>{31,118}</sup> but this requires knowledge of the source characteristics and an assumption that they are invariant among different locations and seasons. Organic compounds are the largest component produced from fires and there are specific compounds found to be exclusively emitted from biomass burning. The most commonly used organic tracer is levoglucosan, a sugar anhydride produced during the combustion of cellulose<sup>{30,31,32,33}</sup>.

## **2.5 Health hazards by emissions**

The World Health Organization (WHO) estimates that 1.5 million premature deaths per year are directly attributable to indoor air pollution from the use of solid fuels. 8 That is more than 4 000 deaths per day, more than half of them children under five years of age. More than 85% of these deaths (about 1.3 million people) are due to biomass use, the rest due to coal. This means that indoor air pollution associated with biomass use is directly responsible for more deaths than malaria, almost as many as tuberculosis and almost half as many as AIDS<sup>{119}</sup>. Just as the extent of dependence on polluting fuels and inefficient stoves varies widely around the world, so does the death toll due to indoor smoke. Fuelwood, roots, agricultural residues and animal dung all produce high emissions of carbon monoxide, hydrocarbons and particulate matter<sup>{43}</sup>. Hydrocarbon emissions are highest from the burning of dung for fuel, while particulate emissions are highest from agricultural residues. Women and children suffer most from indoor air pollution because they are traditionally responsible for cooking and other household chores, which involve spending hours by the cooking fire exposed to smoke. Young children are particularly susceptible to disease, which accounts for their predominance in the statistics for premature deaths due to the use of biomass for cooking.

There is a limited study has been done in India to evaluate the impact of biomass fuel burning on ambient air quality and chemical characteristics of aerosol. Southern India is of the major source of trace gases and aerosols due to usage of biomass fuel as energy.

This study was conducted in order to determine the chemical properties of aerosols emitted from biomass fuel burning and to estimate the contribution of biomass burning aerosols to ambient air quality.

### **3.1 Study Area**

#### **3.1.1 Site description and collection of bio-fuel samples**

Biomass-fuel samples used for this study were already collected by Radio and Atmospheric Sciences Division of National Physical Laboratory, New-Delhi-110012 for an ongoing DST-project entitled “Evaluation of emission factors and budget of gases and particulate matter of relevance to climate change emitted by fuels particularly biomass used in India by rural sectors and small scale industries.”

Biomass fuel/fuel wood samples were collected at district level by visiting various rural places of southern India of Andhra Pradesh . Two villages were chosen (sites) of two different subdivisions in each district to get the representative data for each district. Survey of the village was conducted by using semi-structured interviews. Questionnaire was developed to collect information of crop yield in that area, type of biomass fuels used as energy and their percentage, percentage of Chulha and LPG used for cooking, approximate percentage of service holders, cultivators and self employed etc. Household biomass fuels were categorized into three different types: residues of all agricultural crops as agricultural biomass (crop residue), all types of wood used as fuelwood and faeces of domestic animals used as energy under dung cakes. These samples were analyzed for the present study to determine the chemical properties of aerosols emitted from biomass fuel/fuelwood burning. 52 biomass fuel samples from Andhra Pradesh were analysed. Fig 2.1 shows the map of India with Andhra Pradesh.



Fig. 3.1 Map of India showing study area: Andhra Pradesh

### 3.1.2 Andhra Pradesh

Geographically Andhra Pradesh is situated in the southern part of the country between  $12^{\circ}41'$  and  $22^{\circ}N$  latitude and  $77^{\circ}$  and  $84^{\circ}40'E$  longitude with coastline. According to census of India 2001, the population of the state is 76 million of which rural and urban population is 72% and 28% respectively. 21 districts out of 23 districts except Hyderabad were surveyed, because of non-availability of rural areas. We could collect samples from two villages (sites) of each district except Adilabad, Srikakulam, and Vizianagaram. As per our survey, approximately 90% village households in this state are engaged in cultivation practices. Study by Saud et al (2010) showed that about 70% village households use Chulha for cooking, whereas, only 30% use LPG. It suggested that use of biomass fuels depends primarily on the economic condition of the people. In area of Andhra Pradesh, the major crop

is rice. More than 77% of its crop is rice. Rice, sugarcane, cotton, Chili pepper, mango, and tobacco are the local crops. Recently, crops used for vegetable oil production such as sunflower and peanuts etc. are also produced as seasonal crops. The main crop residue is rice straw. Agricultural residues e.g. sunflower, peanuts, coconut, and cashew plants are used as fuel in this state. Rice straw is mostly used either for thatching or fodder for animals. Similarly, wheat straw is also used as food for domestic animals <sup>{120}</sup>.As per their estimation; total agricultural residue generation is 29.55 Mt yr<sup>-1</sup>. Average livestock density in Andhra Pradesh is very less (0.1 heads per household) as compared to other states in the country. Availability of manure is also very less in this state as compared to other states.

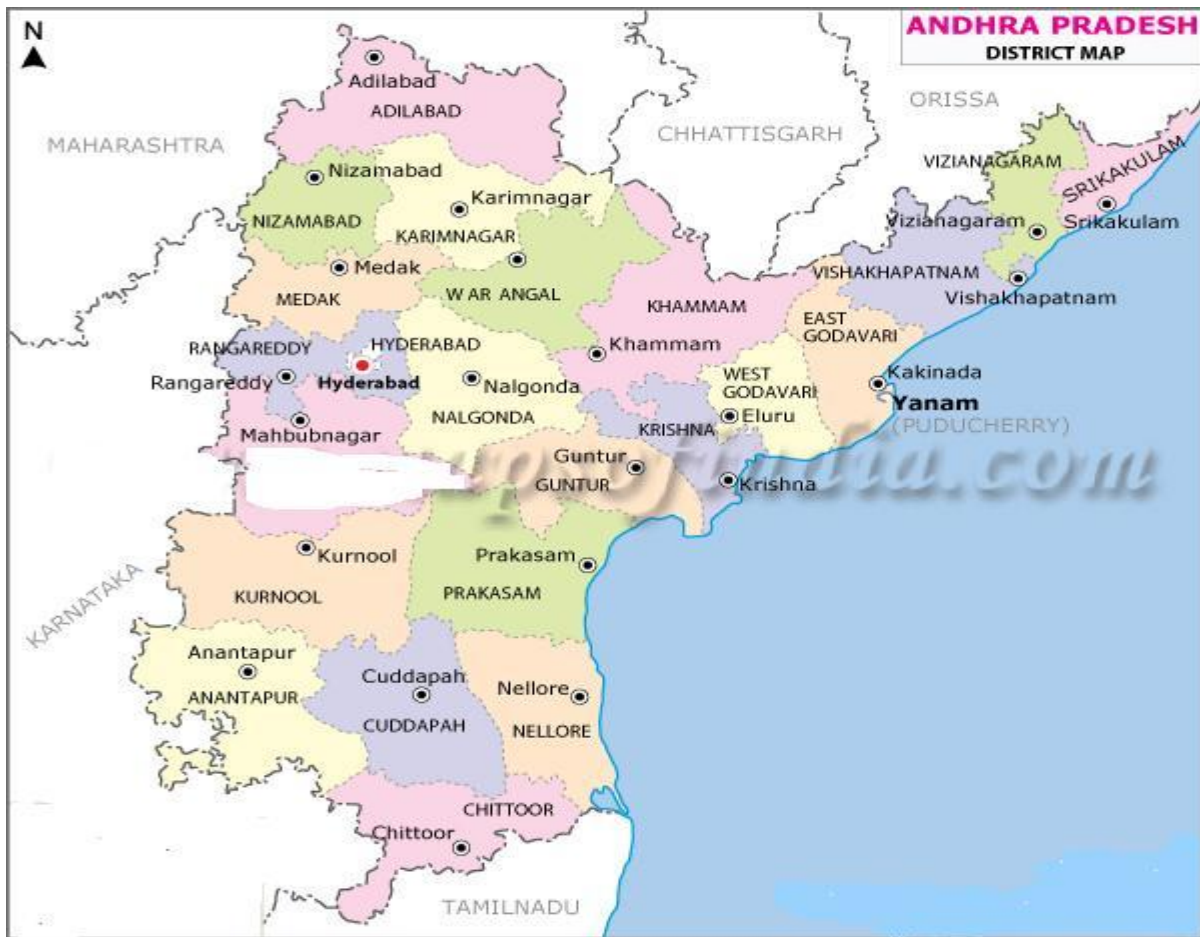


Fig. 3.2 Location of biomass fuel sample collection from Andhra Pradesh

## 3.2 Experimental Sampling

### 3.2.1. Biomass burning aerosol sampling

Biomass burning aerosol sampling : The experimental set up, called as Dilution Sampler, was designed and fabricated by G. Uma Maheshwara Rao, 1999, which is modified by is used to carry out the burning of typical biomass fuels sample (100g). The dilution sampler was designed to meet the considerations needed for accurate aerosol size-distribution measurements based on those identified for organic aerosols. These include sufficient dilution, cooling, and residence time to achieve the quenching typical of indoor environments and use of stainless steel (SS-304) with Teflon gaskets to avoid organic species contamination. Since biofuel combustion is natural-convection driven, it was important that emissions entrainment into the hood, by the fan, should not exert a draught that could alter combustion conditions and consequently the emissions. The sampler consists of a rectangular hood (0.8mX1.3 m), large enough to cover the largest stove and entrain the emissions without spillage. This is connected to a duct (dia.= 0.163 m) with an induced draught fan at its end, exhausting the an isokinetic sampling probe, placed 8 diameters downstream of the duct inlet and 1.5 diameters upstream of a bend for fully developed flow. A dilution plenum provides additional residence time for complete quenching and has four ports for connection to particle samplers.

The entrainment of lab air into the duct along with the combustion emissions gave average dilution ratios of 40-60 (calculated from measured combustion and duct temperatures) and allowed cooling of the combustion gases to 2-3°C above ambient in the dilution plenum. The extraction flow rate in the duct was adjusted by the fan rpm to provide this dilution, subject to a maximum of velocity of 1.5 ms<sup>-1</sup>. The midpoint velocity was measured by a platinum hot-wire sensor, calibrated for total flow rate using a standard orifice calibrator. A duct diameter of 0.163 m was provided resulting in an average volume flow rate of 0.022 m<sup>3</sup> s<sup>-1</sup> and Reynolds number of 10 800 (at 50 °C). Plenum residence times, calculated for 99% condensation of semi-volatile organic species, assuming heterogeneous condensation on an assumed particle number distribution, from a coal boiler ranged 280-420 s at the dilution ratios of 40-60. The pollutant sampling rate (46.7 L min<sup>-1</sup>), determined by the particle collection instruments, and an average dilution ratio of 50 (residence time of 350 s) allowed sizing of the plenum (0.272 m<sup>3</sup>) and the nozzle diameter (25.7 mm) required for isokinetic sampling emissions to the outside. Air is drawn from the duct in a way that from the total

pollutant sampling rate ( $46.7 \text{ L min}^{-1}$ ),  $30 \text{ L min}^{-1}$  was allowed to pass through a Teflon filter paper mounted over a quartz filter paper, where as rest of  $16 \text{ L min}^{-1}$  was passed through a quartz filter paper. Burning setup also consists of Velocity Monitor so as to record the pressure flow and combustion temperature. Also it comprises of Stack Monitor so as to record Upper Stack Temperature and Lower Stack Temperature during biomass burning. These parameters will further help to generate emission factor inventory for different biomass samples.

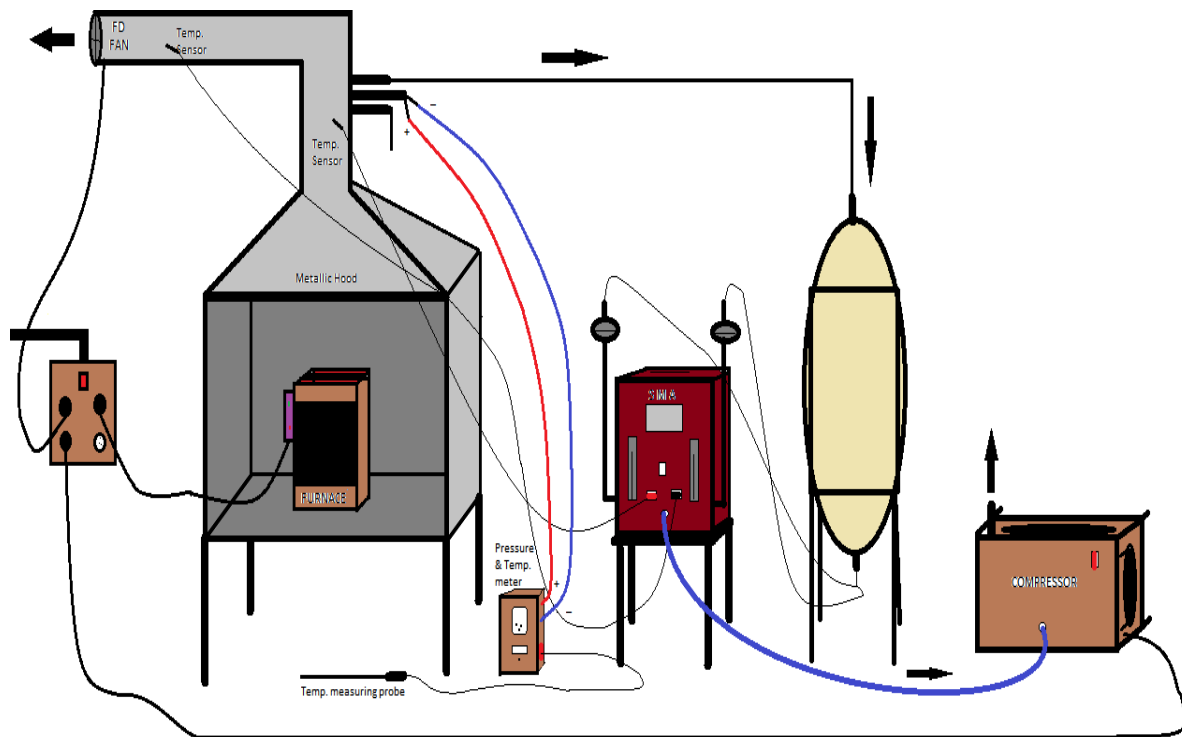


Fig.3.4 Diagrammatic of dilution sampler and burning setup.

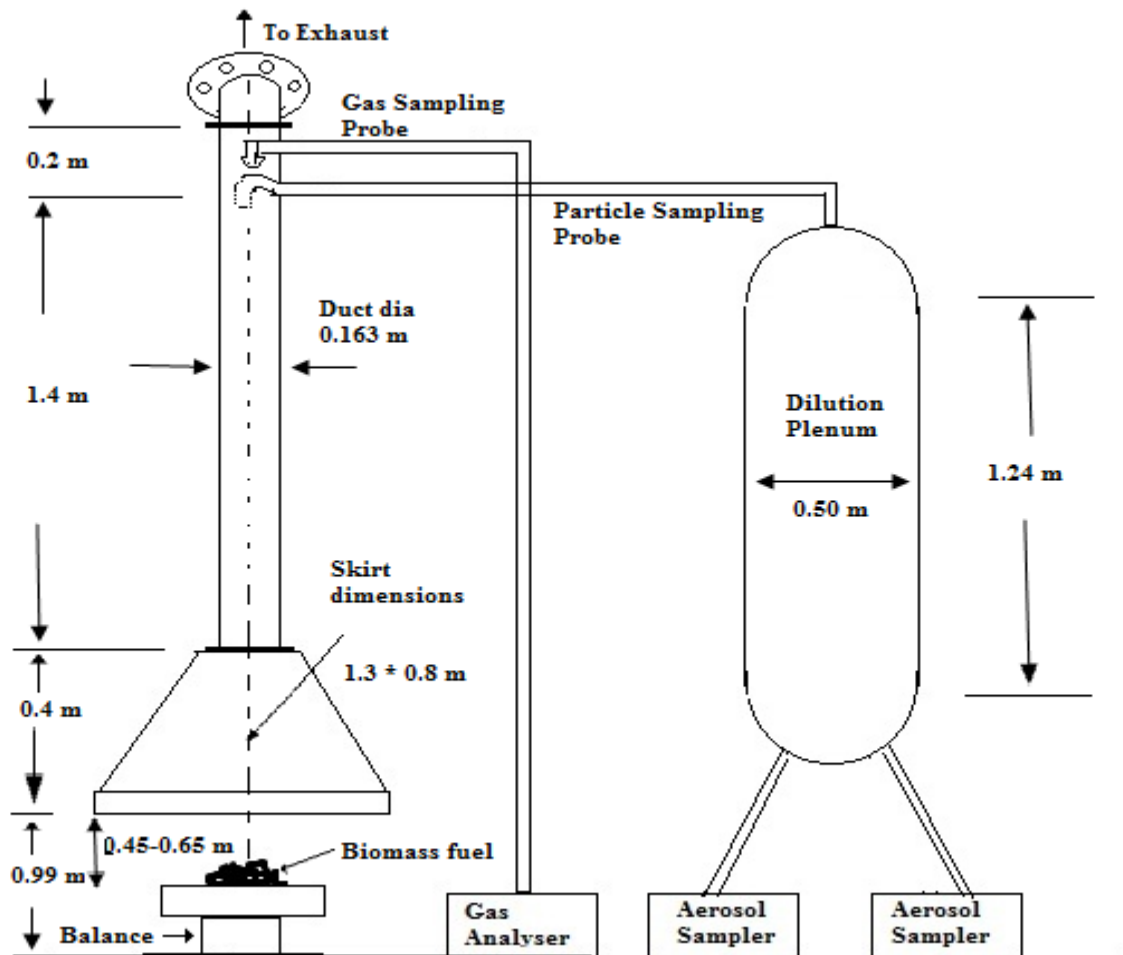


Fig. 3.5 Schematics of dilution sampler and burning setup (Source: C. Venkataraman, 2001)

### 3.2.3 Sample Preparation and Storage for Biomass Burning Aerosols

Biomass burning sampling two types of filter papers are used namely, Teflon (Whatman PFTE 46.2mm, predessicated for 24 hrs.) and Quartz (Whatman grade QMA, Size 4.5cm, preheated at 500°C and predessicated for 24 hrs) at different flow rates. After collection of aerosol sample, filters were withdrawn and kept in dessicators, since air borne particulates and filters used in the impactor have hygroscopic characteristics.

Aerosol samples collected on the filter paper by the setup were stored in polyethene bags and kept in a desiccators till analysis. For the extraction, a 6.124 cm<sup>2</sup> size portion was cut from a QM/A filter and extracted with de-ionized water (20ml) by using ultrasonic system (Oscar Ultrasonic Cleaner) for 90 mins, finally the volume was made 25 ml by adding de-ionized water. The samples were then filtered into pre-cleansed polypropylene bottles. A total of 52 samples were collected from simulated from biomass burning.

### 3.3 Aerosol Analysis

Table 2.2 Instruments used for analysis of aerosols

S. No.	Equipment Type	Model Type	Remark
1.	Desiccators	Secador Desiccators	To remove moisture from filter papers
2.	Ion Chromatograph	DIONEX ICS-3000	To determine concentration of ionic species in aerosols
3.	EC/OC Analyser	DRI/Thermal Optical Carbon Analyser (MODEL 2001 A)	To determine EC/OC in aerosols
4.	Deionised water system	Millipore Elix	Deionised water system
5.	Microbalance	Sartorius Microbalance	To determine the weights of total PM on filter paper
6.	Ultra-Sonicator	Oscar Ultrasonic Cleaner	To extract the ions from the aqueous solution
7.	Syringe Filter	Sterlitech Stainless Steel Syringe Filter	To filter the sonicated extract

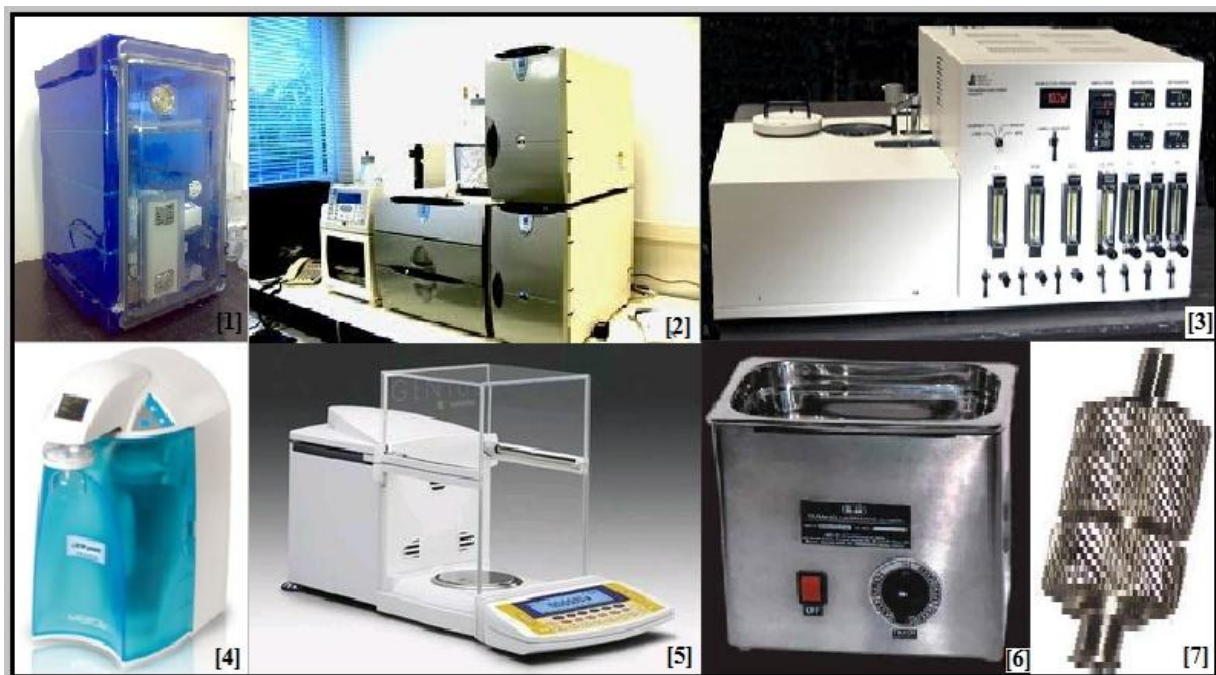


Fig 3.5 Instruments used for analysis of aerosols

### 3.3.1 Aerosol mass concentration

Aerosol mass in each filter was measured using a gravimetric method by the mass difference before and after sampling. Filters were conditioned in a desiccator for 24 hours before and after sampling.

### 3.3.2. Characterization of water soluble ions

The Ions (cations and anions) present in water soluble samples were determined using Ion Chromatograph (DIONEX, ICS-3000). The ion chromatograph is based on the separation of a mixture of compounds into its individual components i.e. ions based on their relative interactions with an inert matrix. A mobile phase, usually a liquid is used to transport the analytes through the stationary phase. Samples were analysed for major anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) and cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $NH_4^+$ ). The anions were separated on Ionpac AS11-HC (4X250 mm) analytical column and AG11-HC (4X50 mm) guard column, in conjunction with an Anion Self-Regenerating Suppressor ASRS-300 (4mm), using 20 mM methanesulphonic acid as an eluent. The self-regenerating suppressors are used for the post-

column eluent suppression. Eluent used for the separation of anions and cations were 20 mM (50%w/w) and 5Mm MSA at the flow rate of 1.5 and 1ml/min respectively. The conductivity detector was CD-20 used for the detection of eluted analyst. The IC system was fitted with a 25 µm nylon membrane filters (Millipore) and degassed by ultra-sonication. The glassware used in the extraction and analysis were washed several times with de-ionised water to remove any adhered impurities. Chromatographic data were collected at 5 Hz and chromatograms were processed using the Chromeleon software. The chromatogram of cations is shown below as an example.

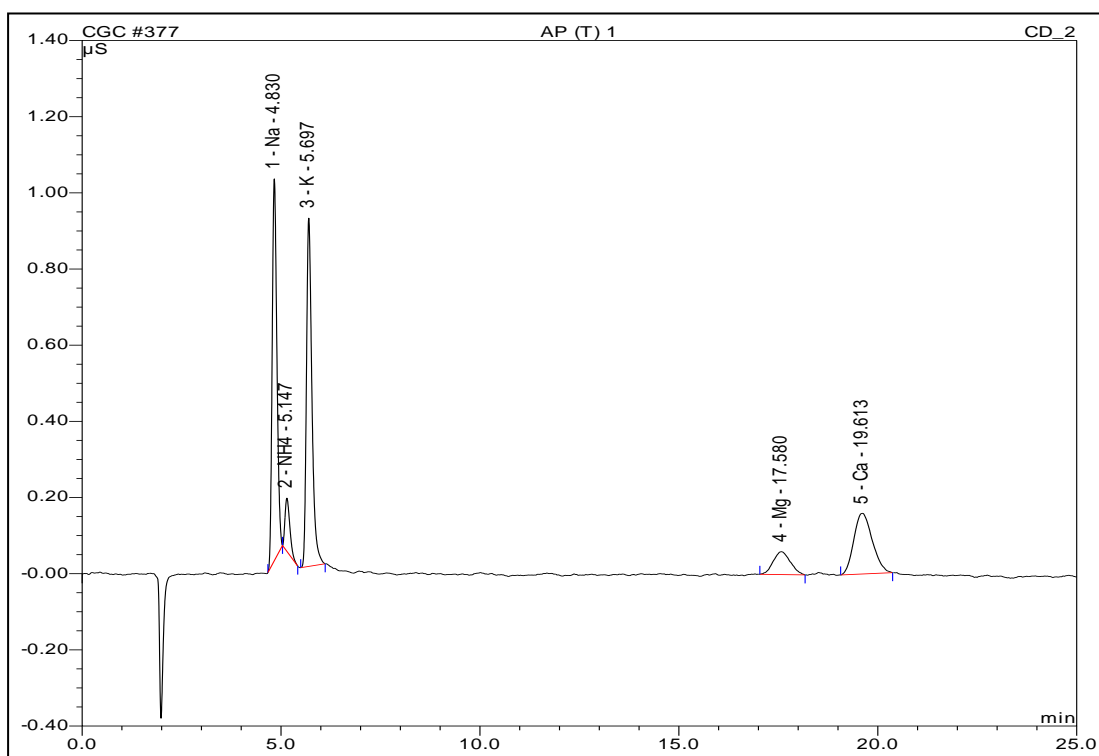


Fig. 3.6 Chromatogram of cations emitted from biomass burning

### 3.3.2.1. Calibration

Calibrations of the Ion-Chromatograph (Anions and Cations) were carried out with standard solutions covering the desired concentration range of the analyte in the sample. Working standards were prepared from stock standard solutions procured from DIONEX, USA for calibration and these solutions were diluted upto working range.

### 3.3.3. Characterization of carbonaceous aerosol

The carbonaceous species, i.e, TC, EC and OC present in aerosol sample were determined by using DRI Model 2001 Thermal/Optical Carbon Analyser following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol and assuming carbonate carbon in the samples to be negligible. The operation of this Analyser is based on the preferential oxidation of organic and elemental carbon (OC and EC) compounds at different temperatures. Its function relies on the fact that organic compounds can be volatilized from the sample deposit in a non-oxidizing helium (He) atmosphere, while EC must be combusted with an oxidizer.

The analyzer operates by:

- 1) Liberating carbon compounds under different temperature and oxidation environments from a small sample punch taken from a quartz filter,
- 2) Converting these compounds to carbon dioxide (CO<sub>2</sub>) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO<sub>2</sub>),
- 3) Reducing CO<sub>2</sub> to methane (CH<sub>4</sub>) by passing the flow through a methanator (hydrogen-enriched nickel catalyst) and,
- 4) Quantifying CH<sub>4</sub> equivalents with a flame ionization detector (FID). The thermal/optical reflectance method of carbon analysis developed by <sup>{121}</sup>, is studied at temperatures 120,250,450 and 550<sup>0</sup>C in a pure helium atmosphere, then to combustion at temperatures of 550, 700 and 800<sup>0</sup>C in a 2% oxygen and 98% helium atmosphere. In this method a 0.5cm<sup>2</sup> punch from a 8”X10” QM/A filter paper used for the analysis. The organic carbon was volatilized from the filter paper by heating in an atmosphere of pure helium at temperatures of 300, 400 and 600<sup>0</sup>C. Elemental carbon was determined by heating the sample in atmosphere 2% O<sub>2</sub>, and 98% He. The CO<sub>2</sub>, evolved at temperatures of 400, 550 and 700<sup>0</sup>C was measured in the same manner as for organic carbon. To correct for pyrolytic conversion of organic analysis, the filter reflectance was continuously monitored with a He-Ne laser (633nm). The correction was taken to be the amount of elemental carbon oxidation necessary to return the filter reflectance to its initial value (i.e., before pyrolytic conversion of organic to elemental carbon occurred). The thermogram of OC and EC is shown below for example.

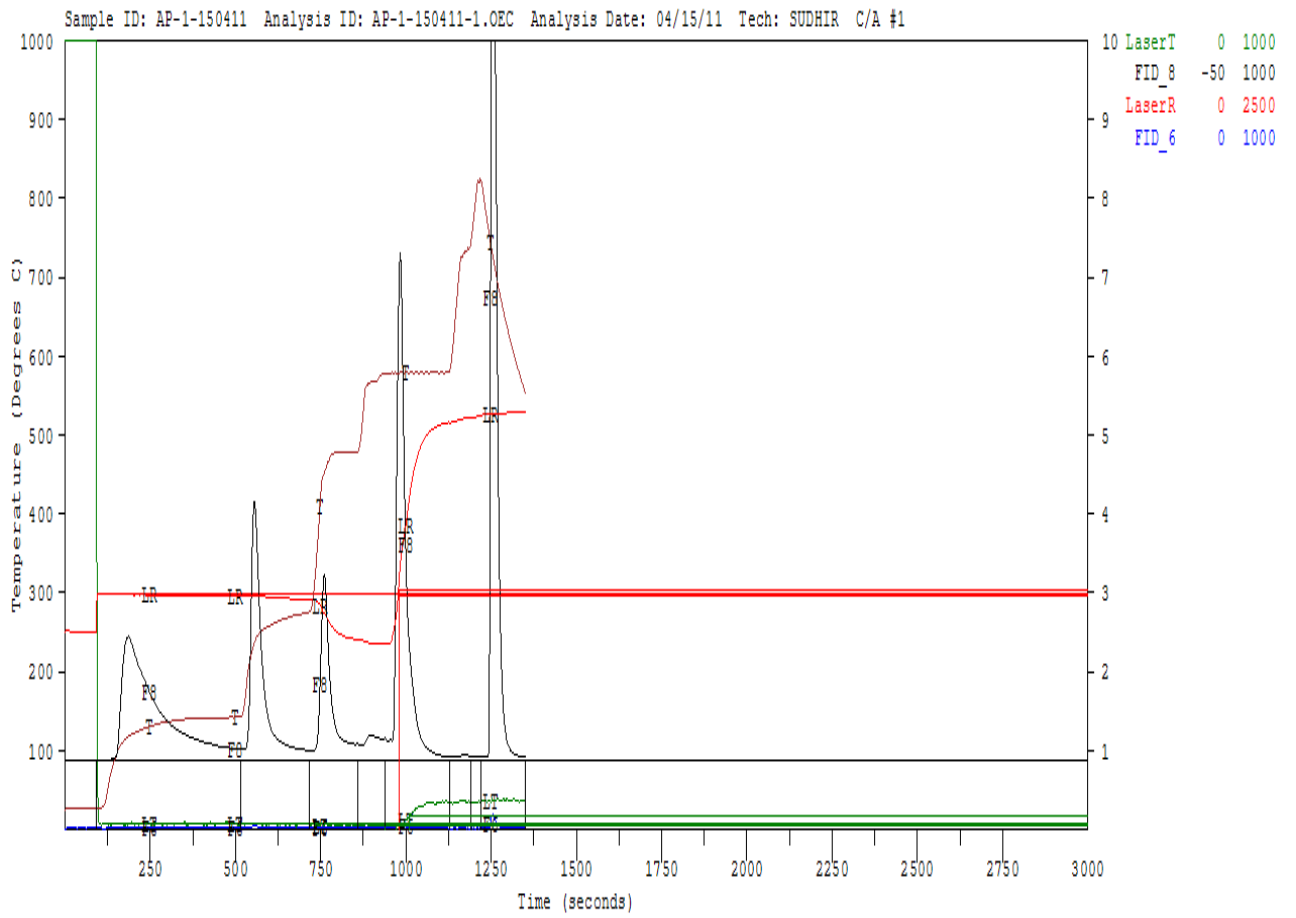


Fig. 3.8 The thermogram of OC and EC from burning of Kampa katti sample

#### 4.1. Biofuel distribution

Based on earlier survey over there, It is noticed seen that approximately 20% village households use dung cake as their main energy source for cooking. During this survey, it is also observed that there is a tradition of using ‘Kampa katti (keekar). Dung sticks/balls are produced manually mainly during dry season so that these sticks/balls dry properly in the open. Fuelwood e.g., kampa katti (50%), vepa (neem) (15%), coconut (7%) are used as fuel in this state According to TEDDY, 2007 report, fuelwood consumption is 45% in this state as compared to other states in the India. The total forest area over this region is 20.52%. Hence very large amount of forest wood is used here as biomass fuel.

Table: 3.1 Different Biomass fuel samples collected from Andhra Pradesh

S.No	Biomass sample	12.	Sugar cane
1.	Kampa katti	13.	Cow pada
2.	Neredu	14.	Rice husk
3.	Vepa	15.	Cashew sticks
4.	Coconut	16.	Ari katti
5.	Cotton	17.	Mirchi
6.	Coffee	18.	Chenangi katti
7.	Subav	19.	Vulindo katti
8.	Thuma katti	20.	Nallarangi katti
9.	Sarkori katti	21.	Munaga katti
10.	Avusu katti	22.	Tanarind katti
11.	Dirsin katti	23.	Neelagiri

24.	Pomoi katti	31.	Kanuga
25.	Sankasula katti	32.	Dry custard plant
26.	Sitaphalam katti	33.	Bandar wood
27.	Isukareni	34.	Konda katti
28.	Eucalyptus	35.	Coconut leaves
29.	Mango	36.	Forest wood
30.	Sena katti	37.	Sun flower

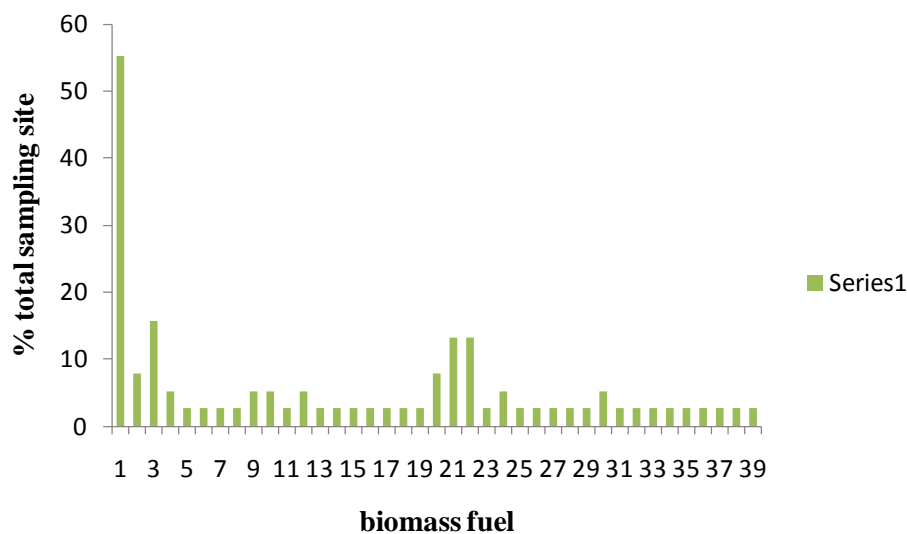


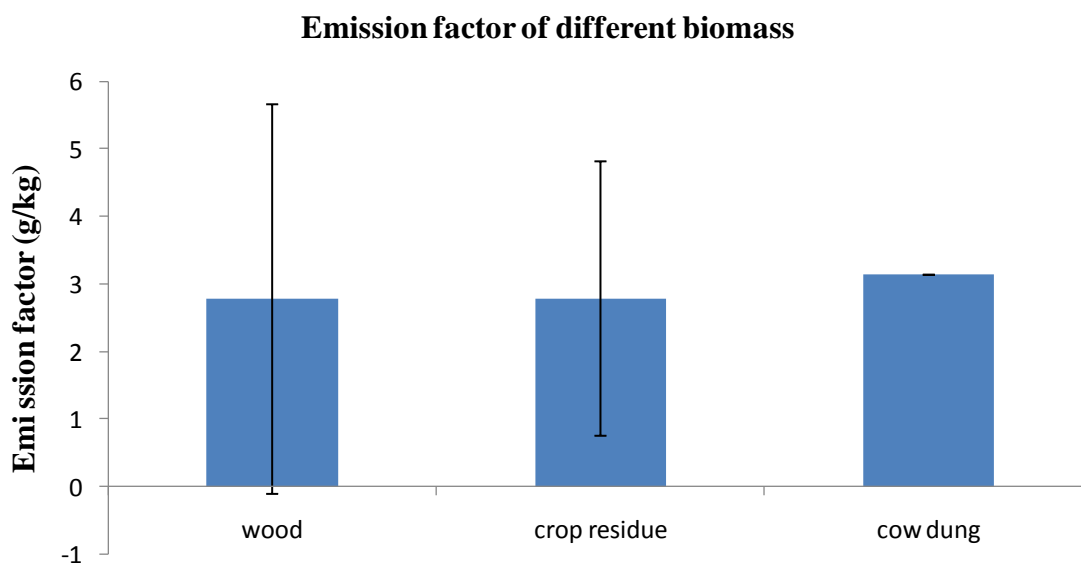
fig 4.1 Distribution of Biomass fuel uses over Andhra Pradesh

The people of this state depend only on fuelwood as primary energy for cooking. Hence consumption of fuelwood is more in this region as compared to other regions of the south india. Households mostly use fuelwood e.g., Kampa katti (55%), Neem (15%), Suabav (13%), Thuma katti (13%), coconut (8%), Bandar wood (5%) and konda katti (5%) as mixed fuel for cooking (Fig. 4.1). In the Andhra Pradesh, dung cake uses only (2%), which is very less than the fuel wood consumption. the crop residue uses Rice husk (2%), Coffee(2%), Sugar cane(2%), Dry custard plant(5%).

## 4.2 Aerosol emitted from different bio-fuels

### 4.2.1 Aerosol mass concentration

The bio-fuel samples (100 g) were collected from state of southern India (Andhra Pradesh). Figure 4.2 shows the emission factor of total suspended particulate matter from simulated burning of bio-fuel samples i.e. cow dung cake, crop residue, fuel wood collected from Andhra Pradesh. A total of 52 samples data were collected from biomass burning, the data of all these sample give in the appendix 1. For the graphical representation, we have divided in three categories-Dung cake, Crop residue, fuel wood, and take the average of the samples emission factor.



**Fig 4.2 Variation of Emission factor in various Biofuels used over Andhra Pradesh.**

The average emission factor of PM emitted from dung cake, crop residue, and wood was 3.14, 2.79, 2.78 g/kg respectively. As shown in fig. 4.2, the emission factor of dung cake was the highest than the crop residue and fuel wood in the samples which were collected from the

Andhra Pradesh. A PM emission from the dung cake burning was significantly higher than PM emissions from crop residue combustion. However, PM emissions from crop residue combustion are significantly higher than fuelwood combustion. The study's results suggest that emission factors of biomass are strongly dependent on the type of fuel burned. The differences of carbonaceous aerosol emissions can be partially explained by characteristics of the different biomass fuels. Fuelwood has higher lignin content and more compact fibers relative to crop waste. Some studies have shown that high lignin content can increase soot emissions. The volatile matter in woody fuel with compact fibers is released slowly and is burned more completely than crop wastes with loose fibers. This is especially true in the initial stage of the burning cycle and when fuel is added. As a result, woody fuel combustion generates less PM emissions.

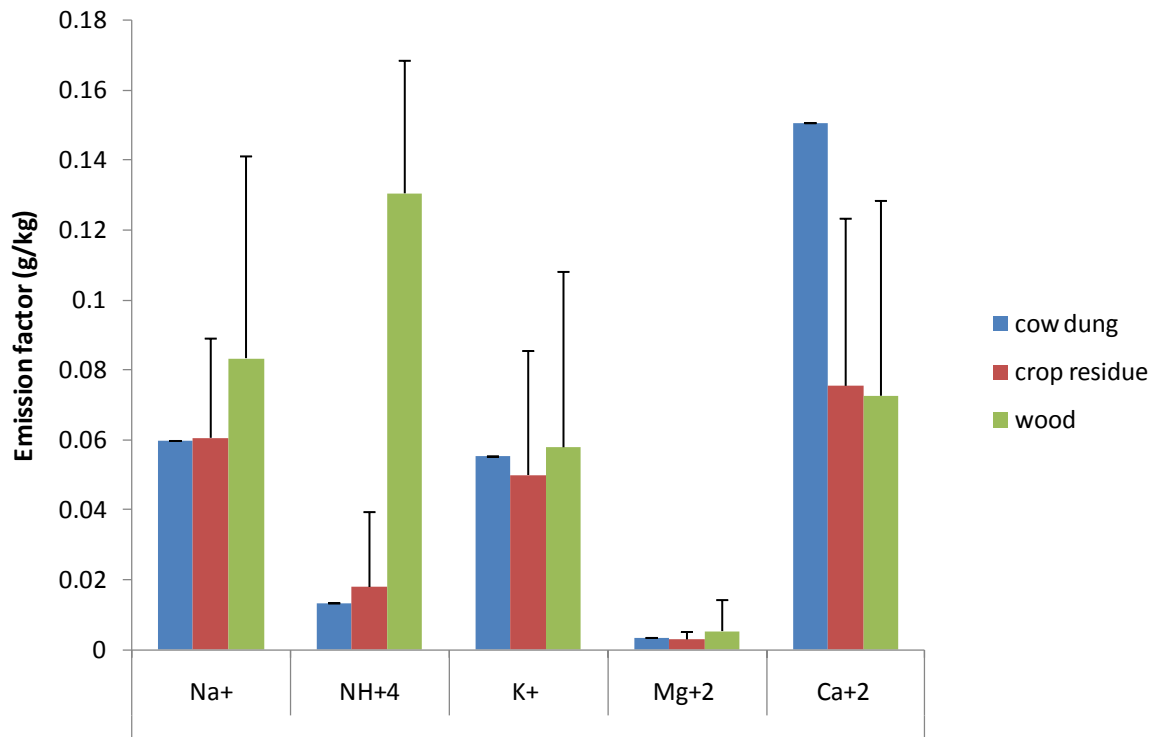
#### **4.2.2 Characteristics of water soluble ions emitted from different bio-fuels**

Water soluble ionic concentration of PM analyzed by using Ion Chromatographic technique to estimate the ionic species in aerosol emitted from burning of cow dung cake, crop residue, wood collected from Andhra Pradesh. Water soluble Cations i.e.  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$  and Anions i. e.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^-$ ,  $\text{NO}_3^-$  are generally presented in all the bio-fuel samples.

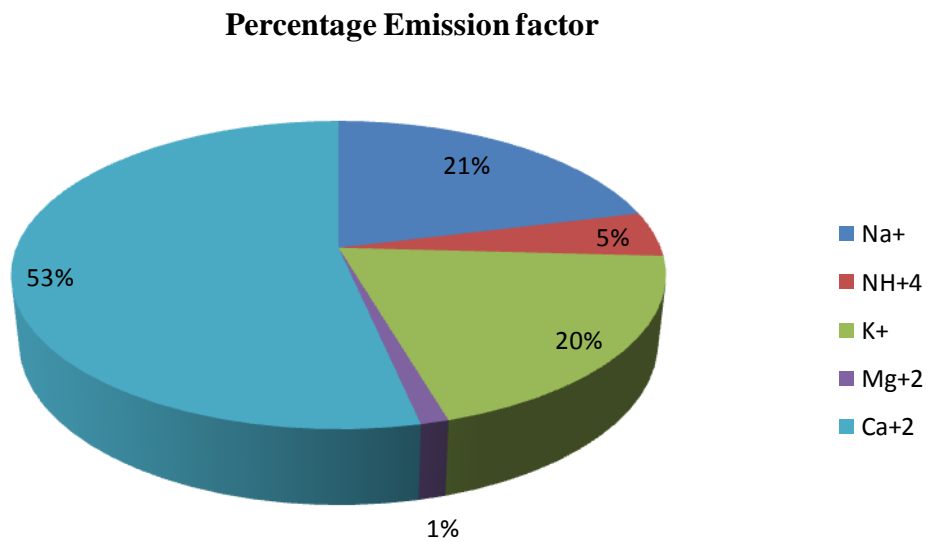
##### **4.2.2.1 Cations**

The concentration of water soluble cations i.e.  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$  present in simulated burning of cow dung cake, crop residue, wood collected from Andhra Pradesh. In the present study, the average concentration of  $\text{NH}_4^+$  was observed highest in all the bio-fuels sample collected from AP as compared to other ions, except in cow dung in which  $\text{Ca}^{+2}$  was observed highest the value. The  $\text{NH}_4^+$  values ranged from .013 to .13 g/kg with an average value 0.053 g/kg. The other cations i.e.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$  ranged from 0.06 to 0.09 g/kg. The average concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$  were 0.04, 0.03, 0.04, .003, 0.06 g/kg.

The emission factor of Magnesium ( $\text{Mg}^{+2}$ ) was observed lowest in all the Biofuels sample. As expected the concentration  $\text{K}^+$  ions were present in all the bio-fuels <sup>{118}</sup>.



**Fig.4.3 cations (g/kg) in various bio-fuels used over Andhra Pradesh**

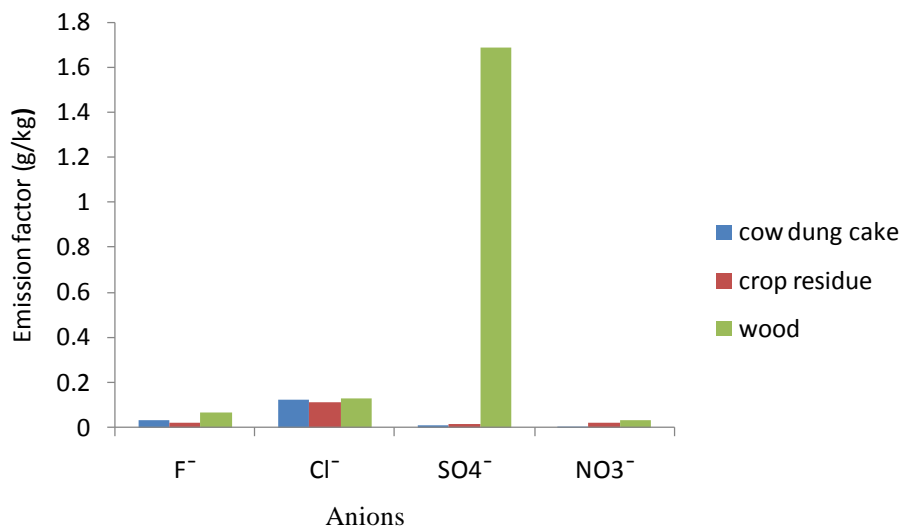


**Fig: 4.4 Percentage emissions of Cations from Biofuels used over Andhra Pradesh**

Fig 4.3 shows the percentage emissions of cations of typical biomass collected from Andhra Pradesh and these were in order of  $\text{Ca}^{+2} > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{+2}$ . In these typical samples, we observed that the emission of  $\text{Ca}^{+2}$  was higher and might be due to higher calcium concentration present in soil, water and plant. The emission factor of  $\text{Na}^+$  was highest in the biomass sample except  $\text{Ca}^{+2}$ . In the table 4.2, shows the Emission factor of different type of biomass sample which was collected from the Andhra Pradesh.

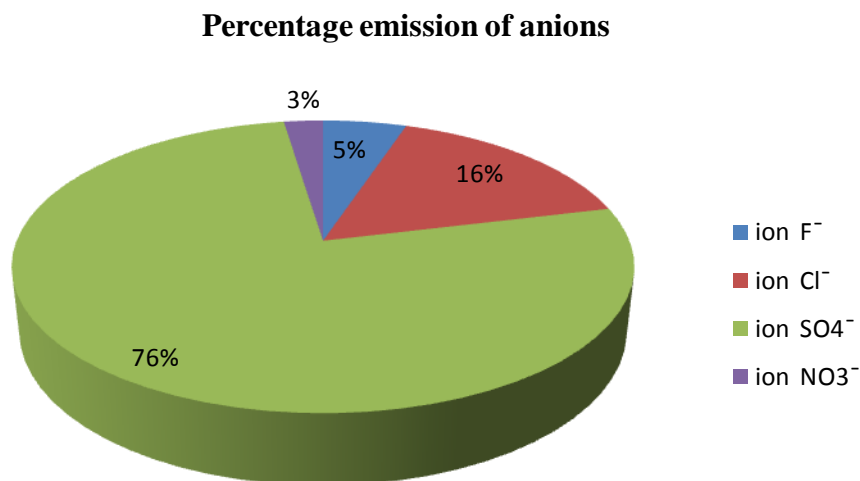
#### 4.2.2.2: Anions

Fig 4.4 shows the concentration of water soluble anions i.e.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^-$ ,  $\text{NO}_3^-$  in samples obtained from simulated burning of cow dung cake, crop residue, wood in Andhra Pradesh.



**Fig. 4.5 Anions emission factor in various Biofuels used over Andhra Pradesh**

In the present study, the average emission factor of  $\text{SO}_4^-$  was observed higher in all the Biofuels samples which was collected from the Andhra Pradesh, and ranged 0.01g/kg to 1.68 g/kg with an average 0.57 g/kg. The other anions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  ranged from 0.003g/kg to 0.12 g/kg.

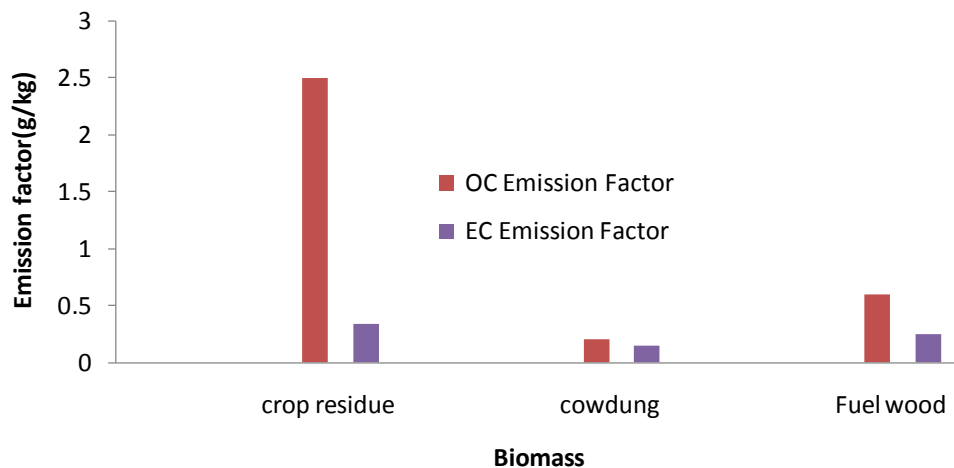


**Fig 4.6 Percentage of Emission of anions from Biomass fuels used over Andhra Pradesh**

Fig4.6 shows the percentage emission of anions of typical bio-fuels collected from Andhra Pradesh and these were in order of  $SO_4^- > Cl^- > F^- > NO_3^-$ . In these typical samples, we observed that the emission of  $SO_4^-$  was higher and might be due to higher sulphate concentration present in soil, water and plant. The second highest emission of  $Cl^-$  was observed. The other anions were present but the emission factor was very less compared to the  $SO_4^-$  and  $Cl^-$ .

#### **4.2.3 Characteristics of carbonaceous aerosols emitted from different bio-fuels**

A total 52 samples were burnt and the data of the samples given in Appendix 1. The concentration of organic carbon (OC) and elemental carbon (EC) of the collected aerosol samples of typical Biofuels of Andhra Pradesh were analyzed using OC/EC carbon analyzer (DRI-2001).



**Fig 4.7 Emissions of carbonaceous aerosols (g/kg) from bio-fuels used over Andhra Pradesh**

Average emission factor of OC emitted from dung cake, crop residue, fuel wood collected from Andhra Pradesh was 2.50, 0.205, 0.59 g/kg respectively. Similarly average emission factor of EC was estimated as 0.33, 0.15, 0.24 g/kg from dung cake, crop residue, fuel wood respectively. Higher emission factor of OC was released from crop residue as compared to fuel wood and dung cake. The lowest emission factor was released from the dung cake. Higher emission factor of EC was released from the crop residue as compared to the dung cake and fuel wood. Lowest emission factor was released from the dung cake.

### 4.3 Emission factor Budget estimations

After the chemical analysis of PM collected from simulated burning of biomass fuel samples of Andhra Pradesh, emission factors were calculated for particulate matter, cations, anions and carbonaceous aerosols (OC and EC). State-wise aerosol emission budget were estimated using the data of annual consumption of various biomass fuels of Andhra Pradesh under study from TEDDY, 2007.

In Andhra Pradesh, according to TEDDY, 2007 consumption rates for dung cake, crop residue and fuel wood are 9.5, 18.6 and 23.2 Mt/yr, respectively. Using this, emission factor budget inventory was developed for particulate matter emissions, cations, anions and carbonaceous aerosols (OC and EC) collected by burning of biomass fuels used over Andhra

Pradesh region. Table 4.4 shows the annual emissions (Gg/yr) of aerosols emitted from biomass burning. It was observed that fuel wood burning contributes higher emissions of PM (64.54 Gg/yr) and EC (5.08 Gg/yr) in crop residue compared to dung cake, whereas higher emission of OC was estimated from the burning of crop residue (46.54 Gg/yr). The emissions of almost all the cations and anions was observed to be highest from burning of fuel woods except  $Mg^{2+}$  whose lowest emission was observed from all the samples(dung cake, crop residue ,fuel wood) burning.

**Table 3.2 Budget estimates (Gg/yr) for emission factors of various chemical species present in the PM collected from burning various biomass fuels used over Andhra Pradesh**

<b>Biomass fuel type</b>	<b>Dung Cake</b>	<b>Crop Residue</b>	<b>Fuel wood</b>
PM	29.84	51.89 ± 37.78	64.54 ± .66.90
OC	1.95	46.54 ± 81.24	6.30 ± 21.41
EC	1.44	13.87 ± 10.16	5.71 ± 3.17
<b>Cations</b>			
Na <sup>+</sup>	0.56	1.12 ± 0.52	1.93 ± 1.33
NH <sub>4</sub> <sup>+</sup>	0.12	0.33 ± 0.39	3.02 ± 0.87
K <sup>+</sup>	0.52	0.92 ± 0.65	1.34 ± 1.16
Mg <sup>+</sup>	0.03	0.05 ± 0.03	0.12 ± 0.20
Ca <sup>+</sup>	1.43	1.40 ± 0.88	1.68 ± 1.29
<b>Anions</b>			
F <sup>-</sup>	0.28	0.38 ± 0.17	1.50 ± 4.37
Cl <sup>-</sup>	1.16	2.03 ± 1.19	2.98 ± 2.79
SO <sub>4</sub> <sup>2-</sup>	0.11	0.24 ± 0.12	0.81 ± 0.49
NO <sub>3</sub> <sup>-</sup>	0.02	0.37 ± 0.44	0.71 ± 1.11

Residentially biomass fuels are still widely used as energy sources for house heating and cooking in the world. Such usage is particularly important in developing countries including India. The present study demonstrates that intensive domestic biomass fuel (crop residue, dung cake, fuel wood) burning can significantly contribute to anthropogenic aerosols and consequently has a great impact on the chemical composition of atmospheric particles and local air quality. One of the major sources of atmospheric fine particle organic carbon is biomass burning. Smoke from wild and prescribed fires can have a significant impact on PM<sub>2.5</sub> concentrations, affecting air quality from local to regional and global scales. Smoke can be a significant contributor in causing visibility impairment and affecting the Earth's radiation balance. Additionally, in populated areas, residential wood combustion can be an important source of fine particles. Residential biomass-fuels are still widely used globally as energy sources for domestic heating and cooking. Such usage is particularly important in developing nations including India. The present study demonstrates that intensive domestic biomass-fuels (Dung cake, crop residues and fuel wood) burning can significantly contribute to anthropogenic aerosols and consequently has a great impact on the chemical composition of atmospheric particles and local air quality.

We have done study on chemical characterization of aerosol emitted from Biofuels burning since chemical composition of natural biomass depends on various factors namely:

- 1) Type of biomass, plant species or part of plants
- 2) Cow dung condition such as geographic location .climate, soil types, nutrients, edge of forest, and near sea or polluted area
- 3) Fertilizer and pesticide doses used which are highly important for some elements (Cl, K, N, P, Sand certain trace elements).
- 4) Plant distance from sources of pollution such as highways, cities, factories and ore mines.

5) Pick up of extraneous material like dust, dirt and entrained as during biomass harvesting transport and handling.

In this study, the biomass fuel samples were collected from various site of Andhra Pradesh, burnt in natural condition to study the chemical properties of aerosol emitted from biomass burning. The average emission factor of particulate emitted from dung cake, crop residue, fuel wood collected from South India 3.14, 2.79, 2.78 g/kg respectively. The emission factor of  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$  were estimated in ranged 0.003 to 0.15 g/kg. The average  $\text{Na}^+$  emission factor was highest from Andhra Pradesh among all the cations followed by  $\text{Ca}^{+2}$  and  $\text{K}^+$ . The average emission factor of anions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^-$ , and  $\text{NO}_3^-$  were ranged 0.003 to 1.68 g/kg. The average  $\text{SO}_4^-$  emission factor is highest from Andhra Pradesh among all India followed by  $\text{Cl}^-$ , and  $\text{F}^-$ . Carbonaceous aerosol consisting of organic carbon (OC) and elemental carbon is a by product of the incomplete combustion of both bio fuel/biomass and is therefore a ubiquitous component of anthropogenic aerosols. In the present study, the average OC concentration from dung cake, crop residue and fuel wood from Andhra Pradesh were 2.5, 0.2, 0.59 g/kg respectively and the average concentration of EC were 0.33, 0.15, 0.24 g/kg respectively. In the above data the highest organic carbon generates from the dung cake and in the elemental carbon also the dung cake generates the highest elemental carbon in the burning of the Andhra Pradesh biomass fuel.

This study shown that burning of dung cake ,crop residue and fuel wood in Andhra Pradesh can be a source of some part of the ionic species and some part of the carbonaceous species of ambient aerosols .The other sources can be fossil fuel burning and soil dust.

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## Appendix: 1

Emission factor of cations, anions, PM (particulate matter), OC (organic matter), EC (elemental carbon), TC(total carbon) (g/kg) emitted from bio-fuels burning used in Andhra Pradesh

Biomass	Cations				Anions					PM	OC	EC	TC
	F <sup>-</sup>	Cl <sup>-</sup>	S04 <sup>-</sup>	NO3 <sup>-</sup>	Na <sup>+</sup>	NH4 <sup>+</sup>	K <sup>+</sup>	Mg <sup>+</sup>	Ca <sup>+</sup>				
Chennangi katti	0.0175	0.04223	0.01183	0.0048	0.0212	0.0056	0.0348	0.0031	0.0036	4.3445	0.9176	0.3353	1.3246
Nalrangay katti	0.0108	0.06259	0.01380	0.0054	0.0435	0.0055	0.0293	0.0049	0.0126	1.1528	0.5157	0.1884	0.7444
Vulindo katti	0.0347	0.08738	0.01792	0.0102	0.0822	0.0090	0.0312	0.0065	0.0224	4.1688	0.4938	0.3991	1.0446
Thumpa katti	0.0087	0.17595	0.05392	0.0100	0.1333	0.0037	0.0126	0.0303	0.0737	0.8219	0.5247	0.1091	0.6701
Sitapahal	0.0194	0.20589	0.02062	Nil	0.0685	0.0309	0.1259	0.0067	0.0155	4.3574	0.1234	0.1105	0.3344
Kampa	0.0367	0.49444	0.03375	0.0088	0.0901	0.1152	0.1411	0.0090	0.0222	3.6416	0.6919	0.2716	1.0442
Eucalyptis	0.0254	0.28310	0.02486	0.0069	0.0647	0.0913	0.1152	0.0082	0.0379	4.4030	1.0783	0.4454	1.6537
Thuma	0.0117	0.05911	0.01239	Nil	0.0550	0.0556	0.1170	0.0100	0.028	7.3832	0.9105	0.4535	1.4749
Ushri	0.0228	0.10575	0.02212	0.0035	0.0560	0.0073	0.0243	0.0099	0.0147	2.75	0.5602	0.1884	0.7811
Coffee	0.0358	0.06886	0.02238	0.0081	0.0713	0.0072	0.0559	0.0025	0.0925	1.6738	0.7888	0.1247	0.9588
Ari katteki	0.0187	0.2082	0.01829	0.0051	0.0483	0.0124	0.0202	0.0017	0.0714	11.0861	0.5336	0.4045	1.0525

Kolaah katteki	0.0529	0.0852	0.01587	0.0082	0.0215	0.0167	0.0011	0.0443	Nil	8.5823	5.5932	0.2760	5.9996
Neredu(jamun)	0.0259	0.0908	0.02419	0.0059	0.0696	0.0060	0.0112	0.0042	0.1168	12.932	1.9674	0.3078	2.3529
Pradantu katti	0.0255	0.1482	0.01433	0.0050	0.1211	0.0041	0.0351	0.0029	0.1174	1.4957	1.8952	0.0773	2.0103
Cow dung	0.0296	0.1222	0.01179	0.0030	0.0596	0.0132	0.0551	0.0033	0.1506	3.1416	0.2053	0.1520	0.3974
Sugar cane	0.0195	0.1087	0.01385	0.0046	0.1079	0.0035	0.0233	0.0033	0.1207	6.1310	0.2478	0.0271	0.2868
Coconut	0.0295	0.1489	0.01381	0.0126	0.0543	0.0095	0.0437	0.0012	0.0709	0.1615	11.282	1.4459	13.137
Akashmari	0.0091	0.0345	0.01845	0.0662	0.0835	0.0068	0.0652	0.0022	0.0775	2.5638	0.3032	0.072	0.4315
Kampa	0.0215	0.0952	0.01420	Nil	0.0293	0.0049	0.0253	0.0014	0.0477	1.7060	0.2424	0.2076	0.4959
Bandar lathi	0.0140	0.0803	0.01574	Nil	0.0827	0.0057	0.0332	0.0019	0.0618	1.2195	0.1510	0.258	0.4925
Kampa	0.0073	0.0370	0.00809	Nil	0.0262	0.0065	0.0247	0.0007	0.0263	1.4276	0.0867	0.3274	0.5439
Kampa katti	0.0099	0.0994	0.01284	Nil	0.0586	0.0119	0.0477	0.0017	0.0623	1.2273	0.1483	0.1104	0.2895
Kampa katti	0.0069	0.0629	0.01977	Nil	0.0287	0.0246	0.0399	0.0020	0.0989	1.1554	0.3926	0.3347	0.8734
Sena katti	0.0069	0.0500	0.01328	Nil	0.0504	0.0048	0.0222	0.0014	0.0509	0.65480	0.0110	0.1094	0.1914
Kampa	1.1216	0.0441	0.0092	Nil	0.0428	0.0042	0.0177	0.0009	0.0344	1.1514	0.1046	0.3185	0.5314
Mango	0.0093	0.0453	0.0056	Nil	0.0353	0.0025	0.0173	0.0006	0.0274	2.4992	0.1130	0.1232	0.2635
Neem	0.0048	0.0471	0.0068	Nil	0.0830	0.0069	0.0706	0.0011	0.0594	0.8350	0.3426	0.3504	0.8212

Kampa	0.0094	0.0477	0.0051	Nil	0.0388	0.0026	0.0188	0.0006	0.0299	3.8974	0.9820	0.298	1.3413
Kampa	0.0563	0.3125	0.0207	Nil	0.2749	0.0060	0.1290	0.0027	0.1771	2.5293	0.3638	0.2333	0.6780
Coconut	0.0211	0.1544	0.0063	Nil	0.0311	0.0616	0.0246	Nil	Nil	1.8557	0.2488	0.0760	0.3652
kampa katti	0.0067	0.2030	0.0238	Nil	0.0952	0.0584	0.1058	0.0019	0.1042	1.7010	0.4552	0.3263	0.9387
Isukareni	0.0111	0.1682	0.0226	0.0063	0.1200	0.0106	0.0912	0.0039	0.099	2.4237	0.4298	0.1513	0.650
Pomoil katti	0.5661	0.4842	0.0241	Nil	0.2404	0.0947	0.1943	0.0028	0.1785	2.9102	0.2439	0.1989	0.4987
Kampa	0.0281	0.2101	0.0168	Nil	0.1151	0.0388	0.1298	0.0020	0.1338	0.9613	0.1768	0.3261	0.6261
Sobuku katti	0.0055	0.0504	0.0062	Nil	0.0982	0.0242	0.0708	0.0013	0.0949	2.8561	0.2274	0.2692	0.6071
Swavab	0.0055	0.0732	0.0085	Nil	0.0820	0.0135	0.0429	Nil	Nil	1.7863	0.0533	0.2407	0.4033
Rice husk	0.0111	0.0414	0.0055	Nil	0.0680	0.0085	0.0320	0.0029	0.1289	1.4854	0.0099	0.046	0.0786
Coconut	0.0089	0.0359	0.0081	0.0555	0.0221	0.0039	0.0440	0.0006	0.0242	0.6975	0.0477	0.0585	0.1374
Sarkori dirsin	0.0014	0.0063	0.0021	Nil	0.0161	0.0015	0.0071	0.0003	0.0144	0.7257	0.0568	0.0680	0.1571
Vepa(Neem)	0.0114	0.0446	0.0142	0.0777	0.1084	0.0081	0.0226	0.0034	0.1181	1.9962	0.1188	0.1361	0.3387
Sinkeshula	0.0120	0.0708	0.0070	0.0920	0.0966	0.0038	0.0258	0.0007	Nil	4.1193	2.2118	0.6956	3.1201
Sunkasula	0.014	0.3050	0.0193	Nil	0.1290	0.1680	0.1657	Nil	Nil	3.3002	0.725	0.2270	1.0177
Arbi katti	0.0208	0.1166	0.0242	0.1743	0.1746	0.0381	0.0348	0.0033	0.0036	1.9437	0.7475	0.3052	1.1273