POLITECNICO DI MILANO
Facoltà di Ingegneria Civile, Ambientale e Territoriale

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Master of Science in
Environmental and Land Use Engineering

CARBONACEOUS SPECIES IN PM10 AND PM2.5 IN LOMBARDY

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SPECIE CARBONIOSE NEL PM10 E PM2.5 IN LOMBARDIA

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Dang Nguyen Nhung

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SUMMARY

In Lombardy, the more industrialized region in Italy, the standard of air quality for particulate matter (PM) is frequently exceeded. PM10 (particles that are 10 μm or less in diameter) concentration is at present the legislative standard for particulate matter in Italy, as in the European Union. However, PM2.5 (particles that are 2.5 μm or less in diameter) data are introduced in most recent Air Quality Directive (Directive 2008/50/EC)– promulgated by the European Council – in prevision of an annual limit value entering into force in 2015.

In Italy, there is a lack of information on PM10 and PM2.5 which has been regularly monitored only in recent few years. In many other European countries, and in the United States, a great deal of PM10 monitoring takes place. On the contrary, very few measurements of PM2.5 have been carried out in Europe up to now and, according to the Directive 1999/30/CE, Member States of the European Community have to gather information on PM2.5 concentration at typical locations. Therefore, the assessment of PM2.5 and PM10 data in the most industrialized and populated area of Northern Italy may give a valuable contribution for legislative and environmental purposes.

In order to update and complete previous investigation, a measurement campaign of daily sampling of PM10 and PM2.5 has been carried out in several sites in Lombardy between 2005 and 2007, within the framework of the PARFIL project (PARticolato atmosferico Fine Lombardia). This project, funded by the Lombardy regional authorities, was intended to provide a detailed knowledge of the PM features in Lombardy by performing extended PM10 and PM2.5 sampling campaigns in different environments of the region (urban, traffic, rural and remote sites). The main aim was to complete the existing studies of some areas with more investigations, and to conduct some samplings in sites that were never investigated before. The PARFIL has been implemented by the Regional Authorities, coordinated by the Regional Environmental Agency (ARPA Lombardia) and developed by universities and research establishments present on the region.

This thesis uses one part of the PARFIL data set, focusing on the most relevant carbonaceous species in PM, organic carbon (OC) and elemental carbon (EC) to compare OC and EC levels between different sites, to assess the temporal and spatial variation of OC and EC levels, to assess the fraction by which OC and EC are present in coarse and fine PM, to analyse the OC/EC ratio and to split OC total into OC primary and OC secondary by using EC tracer method.

SOMMARIO

In Lombardia, la regione più industrializzata d'Italia, il limite di qualità dell'aria per il particolato atmosferico (PM) è frequentemente superato. La concentrazione del PM10 (particelle con un diametro uguale o inferiore a 10 μm) è attualmente lo standard di misura del particolato. Tuttavia, i dati relativi al PM2.5 (particelle con un diametro uguale o inferiore a 2.5 μm) sono stati introdotti nella recente Direttiva sulla Qualità dell'Aria (Direttiva 2008/50/EC)– promulgata dal Consiglio Europeo – in previsione di un valore limite annuale che entrerà in vigore nel 2015.

In generale in Italia c'è una limitata disponibilità di informazioni circa il PM10, ed il PM2.5 è stato monitorato solo negli ultimi anni. Tuttavia, in accordo alla Direttiva 1999/30/CE, gli Stati Membri dell'Unione Europea devono ottenere informazioni circa la concentrazione di PM2.5 a livello locale. Pertanto, l'acquisizione e la valutazione dei dati di PM2.5 e sul PM10 nelle zone più industrializzate e popolate del Nord Italia può dare un grande contributo sia a fini legislativi che ambientali.

Per aggiornare e completare le precedenti indagini, una campagna di misurazioni su campioni giornalieri di PM10 e PM2.5, facente parte del progetto PARFIL (PARticolato atmosferico Fine Lombardia), è stata effettuata in diverse zone in Lombardia dal 2005 al 2007. Questo progetto, finanziato dalle autorità regionali lombarde, ha lo scopo di fornire un conoscenza dettagliata sui valori del PM in Lombardia effettuando campionamenti sistematici a lungo termine di PM2.5 e PM10 in diverse aree della regione (urbane, trafficate, rurali e zone remote). Lo scopo principale è stato quello di completare gli studi esistenti in alcune aree con ulteriori indagini, e di condurre campionamenti in aree dove non erano mai state effettuate prima. PARFIL è stato implementato dalle Autorità Regionali, coordinato dall'Agenzia Regionale per l'Ambiente (ARPA Lombardia) e sviluppato dalle Università e dai centri di ricerca presenti nella regione.

Questa tesi usa una parte dei dati acquisiti con il progetto PARFIL, concentrandosi sulle più rilevanti specie carboniose nel PM, carbonio organico (OC) e carbonio elementare (EC), comparandone i livelli tra le differenti aree, analizzandone la variabilità spaziale e temporale, valutandone la ripartizione tra i differenti tagli granulometrici del PM (frazione grossolana e frazione fine), e studiando il rapporto OC/EC utile per suddividere l'OC totale tra OC di origine primaria, ovvero direttamente rilasciato in atmosfera dalle sorgenti di emissione, ed OC secondario, che ha origine da processi di trasformazione chimico/fisica in atmosfera.

1. INTRODUCTION

Particulate matters (PM) is the general term used for a type of air pollutant which is not a specific chemical entity but is a mixture of particles of different sizes, compositions and properties, coming from different sources. They are, on one hand, defined as particles such as dust, dirt, soot, or smoke, which are large or dark enough to be seen with the naked eye while others, are so small and can only be detected using an electron microscope. Particle diameters may range from approximately 0,005 μm to 100 μm, although the suspended portion generally consists of particles less than 40 μm. Particles are further classified as primary or secondary in nature. Primary particles are those emitted directly from sources into the atmosphere, whereas secondary particles are formed through physical or chemical transformations that take place in the atmosphere.

Since the particle diameters span over a wide range, different terms are used when dealing with particles in a given size range. In particular, the term PM10 refers to particles that are 10 μm or less in diameter. PM10 is generally subdivided in to a fine fraction, 2,5 μm or less in diameter (PM2.5) and a coarse fraction, more than 2,5 μm in diameter. Primary PM10 may result from natural or human activities. Natural sources include windblown dust, sea spray and wildfires. Anthropogenic sources include fuel combustion, industrial processes and transportation. High temperature combustion sources contribute to the fine fraction of PM10, whereas particles produced by grinding activities or wind erosion are predominantly found in the coarse fraction. Secondary particles are predominantly found in the fine fraction and can also be of either natural or anthropogenic origin. The behavior of particulate matter in the atmosphere and its potential to affect human health and atmospheric visibility are dependent on the source type and on formation processes that particles undergo at the source or in the atmosphere.

Coarse particles or “inhalable coarse particles” have an aerodynamic diameter larger than 2,5 micrometers and smaller than 10 micrometers. They are found near roadways and dusty industries such as mechanical disruption (e.g. crushing, grinding, and abrasion of surfaces), evaporation of sprays, and suspension of dust.

Fine particles (PM2.5) have diameter that are 2,5 micrometers and smaller. They are found in smoke and haze and can be directly emitted from sources such as forest fires, or they can form when gas emitted from power plants, industries and automobile react in the air.

The particles come in many sizes and shapes and can be made up of hundreds of different chemicals. A distinction is also made between primary and secondary particles. The distinction depends upon the formation of particles in air. Some particles, known as *primary particles* are emitted directly from a source, such as construction sites, unpaved roads, fields, smokestacks or fires. Others form in complicated reactions in the atmosphere of chemicals such as sulfur dioxides and nitrogen oxides that are emitted from power plants, industries and automobiles. These particles, known as *secondary particles*, make up most of the fine particle pollution in the country.

Particulate matters are formed in an atmosphere by a transformation of gaseous emissions. The chemical and physical compositions of PM depend on location, weather and time of year. 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.

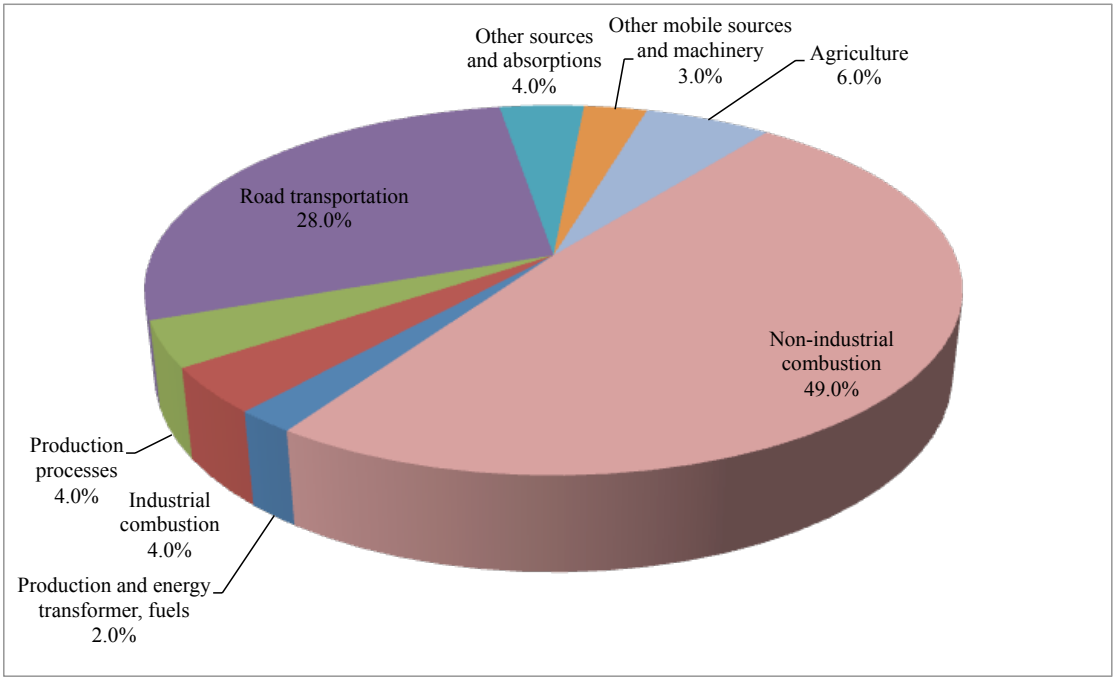


Figure 1-1: PM10 emission by sectors in Lombardy
Source: INEMAR (Atmospheric Emission Inventory) – version 2010

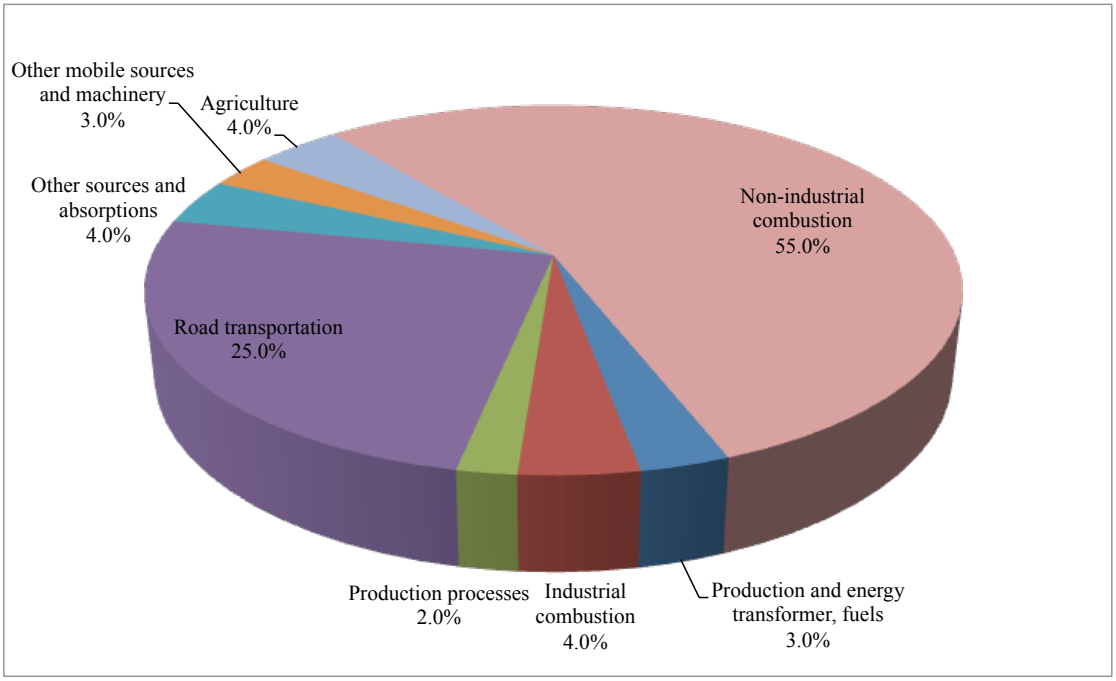


Figure 1-2: PM2.5 emission by sectors in Lombardy
Source: INEMAR (Atmospheric Emission Inventory) – version 2010

PM10 is composed of aluminosilicate and other oxides of crustal elements, and major sources including fugitive dust from roads, industry, agriculture, construction and demolition, and fly ash from fossil fuel combustion. The lifetime of PM10 is from minutes to hours, and its travel distance varies from <1km to 10 km.

The major sources of PM2.5 are fossil fuel combustion, vegetation burning, and the smelting and processing of metals. Their lifetime is from days to weeks and travel distance ranges from 100s to >1000s km.

Anthropogenic sources can be divided into stationary and mobile sources. Stationary sources include those such as (*US EPA*, 2004):

1. Fuel combustion for electrical utilities, residential space heating, and industrial processes;
2. Construction and demolition;
3. Metals, minerals, and petrochemicals;
4. Wood products processing;
5. Mills and elevators used in agriculture;
6. Erosion from tilled lands;
7. Waste disposal and recycling.

Mobile sources include direct emissions of primary particulate matter and secondary particulate matter precursors from highway vehicles and non-road sources as well as fugitive dust from paved and unpaved roads.

Prescribed Burning and wildfires: As a matter of fact, combustion is the main anthropogenic source of fine particles, with the vast majority of them included in the sub-micrometer range (*Cattaneo et al.*, 2009). Prescribed burning is used as a tool for hazard reduction, site preparation, wildlife habitat improvement, disease and insect control and ecosystem maintenance (*Smith and Stoneman*, 1992). The rates of particle emission vary depending on the type of fuel and on the phase of combustion (flaming, smoldering, or a combination of the two). According to *Lamn et al.*, 1992, 90% of particles from prescribed fires are less than 10μm in diameter and around 70% are less than 2.5μm in diameter. The fine fraction consists of approximately 40-70% organic carbon material, 2-15% graphitic carbon and the remainder inorganic ash material (*Ward and Hardy*, 1984).

Residential wood combustion: Most of particles emitted in wintertime in communities are caused by residential wood combustion using woodstoves. Particles emitted from wood-stoves are reported to be less than 0.4μm in diameter and almost entirely in the fine fraction (*Rau and Huntzicker*, 1984). Emissions of woodstove are predominantly consisting of organic carbon, elemental carbon and sulfate, with trace amounts of potassium, chloride and nitrate. More than 100 different organic compounds have been identified in woodsmoke.

Transportation sources: Transportation has been identified as a large source of particulate matter, generating emission through fuel combustion and engine wear. Motor vehicles also generate particulate matter through tire and brake wear and the resuspension of road dust. Both gasoline and diesel vehicles produce particle emissions that are most entirely smaller than 10μm in diameter and predominantly in the fine fraction. Measurements show that mass emission rates from diesel trucks are 6-100 times higher than those from gas automobiles (*Hildemann et al.*, 1991a; *NRCC*, 1982; *Williams et al*., 1989), while noncatalyst cars emit more submicrometer particles than catalyst cars (*Hildemann et al.*, 1991a).

Fossil fuel combustion: Boilers, heaters and furnaces associated with utilities, industry, and commercial/institutional and residential establishments are means of fuel combustion. Emission from fuel combustion depends on many factors, including the type of fuel burned, the source type and the type of emission controls employed. Coal is burning fossil fuel characterized by high ash content. The combustion of coal is a large contributor of particulate matter in utilities

and industrial sectors. Emission depends on type of coal burned and its ash content. For example, combustion of low-ash coal produces less particulate matter than that of high-ash coal. Major chemical components of particulate matter from coal combustion include oxides of silicon, aluminum and iron, with lesser amounts of sulfur, magnesium, potassium and calcium. The predominant types of fuel oil burned by combustion sources are distillate oils and residual oils. Distillate oils are more volatile and less viscous than residual oils. They contain little nitrogen or ash and less than 0,3 % sulfur by weight and are used mainly in domestic and small commercial applications. In contrast, residual oils contain significant quantities of ash, nitrogen and sulfur. They are used in utility, industry and large commercial applications.

Characteristics of particles emitted from distillate oil fired boilers are typically carbonaceous in nature and dependent on the completeness of combustion. For residual oil combustion, emission is typically high in carbon and sulfur levels and depends on oil sulfur content. Usually, the combustion of distillate oils produces less particulate matter than that of heavier residual oils. Reduced boiler loads may also contribute to decreased particle emissions.

Nonferrous metal industries: Nonferrous industries refereed to processes in which metals other than iron are smelted. This also includes the production of copper/ nickel, lead/zinc and aluminum. Emissions from copper smelters in particular have been found enriched in copper, arsenic, selenium, cadmium and indium. These characteristic chemical profiles have been used to identify the plumes and particulate matter from individual smelters (*Small et al.*, 1981). Aluminum smelters, a source of vaporized organic compounds and sulfur dioxide, are sources of various particle fluorides (cryolite, aluminum fluoride, calcium fluoride, chiolite), alumina and ferric oxide. They are also involved in secondary particle production.

Pulp and paper industry: Cellulose is extracted from wood by dissolving the lignin that binds the cellulose fibres together in wood pulping. Kraft, sulfite, neutral sulfite semi-chemical (NSSC) and soda (*US EPA*, 1992) are four major processes for chemical wood pulping. Kraft pulp mills generate particles that are primarily from the recovery furnace, the lime kiln and the smelt dissolving tank. They are mainly composed of sodium salts and some calcium salts from the lime kiln, and are caused by carryover of solids and sublimation and condensation of the inorganic chemicals.

Wood and wood-derived products industry: This industry includes sawmills and plywood and veneer manufacture. Plywood manufacturers are a source of both particulate matter and organic matter. This may also be a source of fugitive emissions as sawdust and other small wood particles, primarily from plywood cutting and sanding operations. (*Source: NAAQ Objectives For PM*, 1999)

Due to the health effects of particulate matter, various governments have created regulations both for the emissions allowed from certain types of pollution sources (motor vehicles, industrial emissions etc.) and for the ambient concentration of particulates. Many urban areas in the U.S and Europe still frequently violate the particulate standards, though urban air on these continents has become cleaner, on average, with respect to particulates over the last quarter of the 20th century. Much of the developing world, especially Asia, exceed standards by such a wide margin that even brief visits to these places may be unhealthy.

With regard to limit values, **European Union** (EU) already introduced the new Directive which was adopted on 21 May 2008 including new air quality objectives for PM2.5 with annual target value 25 μm m^{-3}. The target value entered into force from January 1, 2010 and limit value will

enter into force from January 1, 2015. This Directive still does not set the permitted exceedances each year for PM2.5. The limit value of PM10 is 50 μm m^{-3} for averaging period of 24-h (not to be exceeded more than 35 times a year) and 40 μm m^{-3} for annual averaging period (the permitted exceedances each year is not available).

European Union	**PM10**	**PM2.5 since 1/1/2015**
Yearly average	40 μg/m^3	25 μg/m^3
Daily average (24-hour)	50 μg/m^3	
Allowed number of exceedences per year	35	None

Some other regulations on limit values in different countries are given below.

Australia

Australia	**PM10**	**PM2.5**
Yearly average	None	8μg/m^3
Daily average (24-hour)	50 μg/m^3	25 μg/m^3
Allowed number of exceedences per year	None	None

Canada

Canada	**PM10**	**PM2.5 since 1/1/2015**
Yearly average	70 μg/m^3	30 μg/m^3
Daily average (24-hour)	120 μg/m^3	
Allowed number of exceedences per year		None

In Canada the standard for particulate matter is set nationally by the federal-provincial Canadian Council of Ministers of the Environment (CCME). Jurisdictions (provinces) may set more stringent standards. The CCME standard for PM2.5 is 30 μg/m^3 (daily average, i.e. 24-hour period, 3 year average, 98th percentile).

Hong Kong

Hong Kong has set limits for particulates in the air as below:

Hong Kong	**PM10**	**PM2.5**
Yearly average	50 μg/m^3	35 μg/m^3
Daily average (24-hour)	100 μg/m^3	75 μg/m^3
Allowed number of exceedences per year	9	9

Hong Kong has proposed new limits on particulates and is planning to enforce them around 2014. Proposed limit on PM10 is 50 $\mu g/m^3$ yearly average and 100 $\mu g/m^3$ daily average. Proposed limit on PM2.5 is 35 $\mu g/m^3$ yearly average and 75 $\mu g/m^3$ daily average. Both daily averages may be exceeded 9 times per year.

Japan

Japan has set limits for particulates in the air as below:

Japan	PM10	PM2.5 since 21/9/2009
Yearly average	None	15 $\mu g/m^3$
Daily average (24-hour)	100 $\mu g/m^3$	35 $\mu g/m^3$
Allowed number of exceedences per year	None	None

China

China has set limits for particulates in the air:

China	PM10 since 1/1/2016	PM2.5 since 21/9/2009
Yearly average	40 $\mu g/m^3$	15 $\mu g/m^3$
Daily average (24-hour)	50 $\mu g/m^3$	35 $\mu g/m^3$
Allowed number of exceedences per year	None	None

South Korea

South Korea has set limits for particulates in the air:

South Korea	PM10 since 4/12/2006	PM2.5 since 1/1/2015
Yearly average	50 $\mu g/m^3$	25 $\mu g/m^3$
Daily average (24-hour)	100 $\mu g/m^3$	50 $\mu g/m^3$
Allowed number of exceedences per year	None	None

United States

The Unites States Environmental Protection Agency (EPA) has set standards for PM10 and PM2.5 concentrations as below:

United States	PM10 daily limit since 1987 annual limit removed since 2006	PM2.5 daily limit since 2006 annual limit since 1997
Yearly average	None	15 μg/m^3
Daily average (24-hour)	150 μg/m^3	35 μg/m^3
Allowed number of exceedences per year	1	None

Concerning to limit value, the World Health Organization (WHO) recommended a guideline below:

WHO	PM10	PM2.5
Yearly average	20 μg/m^3	10 μg/m^3
Daily average (24-hour)	50 μg/m^3	25 μg/m^3

In addition to guideline values, the Air Quality Guidelines provide interim targets for concentrations of PM10 and PM2.5 aimed at promoting a gradual shift from high to lower concentrations.

If these interim targets were to be achieved, significant reductions in risks for acute and chronic health effects from air pollution can be expected. Progress towards the guideline values, however, should be the ultimate objective.

The effects of PM on health occur at levels of exposure currently being experienced by many people both in urban and rural areas and in developed and developing countries – although exposures in many fast-developing cities today are often far higher than in developed cities of comparable size.

"WHO Air Quality Guidelines" estimate that reducing annual average particulate matter (PM10) concentrations from levels of 70 μg/m^3, common in many developing cities, to the WHO guideline level of 20 μg/m^3, could reduce air pollution-related deaths by around 15%. However, even in the European Union, where PM concentrations in many cities do comply with Guideline levels, it is estimated that average life expectancy is 8.6 months lower than it would otherwise be, due to PM exposures from human sources.

In developing countries, indoor exposure to pollutants from the household combustion of solid fuels on open fires or traditional stoves increases the risk of acute lower respiratory infections and associated mortality among young children; indoor air pollution from solid fuel use is also a major risk factor for cardiovascular disease, chronic obstructive pulmonary disease and lung cancer among adults

2. OC AND EC IN PARTICULATE MATTERS

The chemical species found within the fine and coarse fractions vary significantly. The major components of the fine fractions include sulfate, nitrate, ammonium, and inorganic and organic carbon compounds. Carbonaceous PM (organic and elemental carbon species) typically is the first or second (after sulfate PM) largest contributor to PM mass concentration. Carbonaceous is also the aerosol component with the greatest difference in concentration between urban and remote monitoring location, giving it the distinction of being one of the most important locally-controllable PM components.

Carbonaceous aerosols, including organic (OC) and elemental (EC) carbon, are ubiquitous in the atmosphere and therefore contribute significantly to particulate matter, both the PM2.5 fraction and coarse (PM2.5-10) fraction, and they contribute to visibility degradation and climate forcing due to their ability to scatter and absorb solar radiation. Carbonaceous aerosols also adversely affect health. EC plays a significant role in climate forcing, and a recent review suggests that the climate warming effects of EC are greater than previously thought, although large uncertainties still exist. Characterizing and predicting the complex nature of OC and EC are challenging from both a measurement and modeling framework. However, this characterization is necessary given the importance of OC and EC to many atmospheric processes and climate impacts.

Inorganic or elemental carbon (EC) , also known as graphitic or black carbon, is a product of the incomplete combustion of carbon-based materials and fuels, and is solely primary in origin. The predominant sources of elemental carbon include fossil fuel combustion and biomass burning (*Penner et al*., 1993). Vehicle engine exhaust, also, is found to include elemental carbon which contributes to the formation of ultrafine particles (elemental carbon is a significant components of diesel exhaust).

Elemental carbon particles are typically less than 1 μm in diameter. Size distribution measurements of elemental carbon in ambient air and vehicular emissions have been found to exhibit a bimodal distribution with peaks in the range of 0,05-0,12 μm and 0,5-1,0 μm (*Venkataraman and Friedlander*, 1994). Because elemental carbon particles are both very small and very inert, they can remain in the atmosphere for extended periods before being removed by scavenging processes. This poses a potential health problem, as these particles can penetrate deeply into the lungs and act as adsorption sites for toxic pollutants. A characteristically large surface area together with its impurities makes elemental carbon the principal light-absorbing aerosol species, with the potential to affect both visibility and climate (*Charlock and Sellers*, 1980; *Charlson et al*., 1992). It is estimated that elemental carbonis responsible for more than 90% of light absorption and 25-45% of overall visibility reduction (*Hamilton and Mansfield*, 1991).

Ultrafine elemental carbon particles are formed primarily by the condensation of C_2 molecules generated during the combustion process; they can nucleate even at high temperatures because of their very low equilibrium vapor pressure (*Kittelson*, 1998); *Morawska et al*., 1998).

Organic carbon (OC) particles can be directly released to the atmosphere or produced via secondary gas-to-particle conversion processes. The dependence of an organic compound's gas-aerosol partitioning on temperature and aerosol composition has the effect of blurring the

distinction between primary and secondary aerosol formation. For example, gases may be emitted that will partition largely to particulate matter (or condense onto the surfaces of buildings and vegetation) once they have cooled to ambient temperature. A lower temperature emission of the same chemical may result in particulate formation at the point of emission (*PM2.5 Report Canada*, 2004). Organic carbon is predominantly found in the fine fractions. In several studies in United States, meat-cooking operations, paved road dust and fireplaces have been estimated to account for more than 50% of fine organic carbon particle emissions in an urbanized area, and the associated organic species have been found to number in the hundreds. Both biogenic and anthropogenic sources contribute to primary and secondary organic particulate matter.

The total particulate organic matter (POM) is composed by a primary fraction (POM_P) and a secondary fraction, well known as secondary organic aerosol (SOA). Since no direct chemical analysis method to discriminate the secondary components of the particulate organic matter is available, several indirect methods such as elemental carbon tracer methosc (*Chu and Macias*, 1981; *Wolff et al*., 1983; *Novakov*, 1982; *Gray et al*., 1986; *Huntzicker et al*., 1986; *Turpin*, 1991; *Turpin and Huntzicker*, 1995; *Strader et al*., 1999; *Cadaba et al*., 2004), receptor modeling (*Schauer et al*., 1996; *Schauer and Cass*, 2000; *Zheng et al*., 2002) and chemical transport modeling (*Pandis et al*., 1992; *Hildemann et al*., 1993; *Strader et al*., 1999; *Yu et al*., 2004) are employed to estimate the amount of primary and secondary components. Among theses methods, EC tracer methods used in this thesis relies on ambient measurements only.

3. MATERIALS AND METHODS

The Lombardy region is not an homogenous territory, both from a geographical and PM's emissions standpoint. Geographically, from North to South the region could be split up into three parts. In the northern part there are Alps and a typical alpine environment; moving southwards there are the Prealps, characterized by a lower height and a larger number of important towns; finally in the southern part, there is the Pianura Padana, a wide plane cut for its longitude by Po river which also states the border of the region. About PM emissions, the situation of the major contributors is also variable, some important urban areas are characterized by larger contribution due to vehicle traffic emissions, some others are known to have more contributes to PM belonging from industrial sources, depending on the human activities present on the specific territory. Each dataset present in the ARPA database is related to one site and each site has been retained representative of one specific area of the region.

Different types of analysis were conducted on the PM samples collected: carbonaceous elements (EC, OC), inoic species (nitrate, sulfate, chloride and ammonium) and trace elements (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb). Carbonaceous elements were detected by means of the Thermal Optical Transmittance method.

Data main charactersitics are resumed in the tables 3-1 – 3-11

Table 3-1: Abbadia Cerreto dataset

Sampling site	Abbadia Cerreto	
Type of environment		
Description		
	PM2.5	PM10
Sampling period	From 11/08/05 to 16/06/07	From 08/08/05 to 12/06/07
Number of PM measuremen		
Warm season		
Cold season		
	Carbonaceous species	
Number of sampling days	23	28
Warm season	8	10
Cold season	15	18

Table 3-2: Alpe San Colombano dataset

Sampling site	Alpe San Colombano	
Type of environment	Alpine	
Description	Samplers were installed in a field at 2250m on the sea level, far from any possible source of pollution. The samplers are located 400m from a refuge.	
	PM2.5	PM10
Sampling period	From 24/01/05 to 15/07/07	From 31/03/04 to 15/07/07
Number of PM measuremen	240	228
Warm season	147	92
Cold season	93	136
	Carbonaceous species	
Number of sampling days	93	97
Warm season	56	57
Cold season	37	40

Table 3-3: Bosco Fontana dataset

Sampling site	Bosco Fontana	
Type of environment	Rural	
Description	Samplers were installed next to the air quality monitoring station located inside a natural reserve 8km from Mantova.	
	PM2.5	PM10
Sampling period	From 13/04/04 to 24/07/07	From 13/01/04 to 29/07/07
Number of PM measuremen	174	211
Warm season	152	133
Cold season	22	78
	Carbonaceous species	
Number of sampling days	25	59
Warm season	1	7
Cold season	24	52

Table 3-4: Brescia dataset

Sampling site	Brescia	
Type of environment	Urban	
Description		
	PM2.5	PM10
Sampling period	From 31/10/05 to 28/12/06	From 04/11/05 to 29/07/07
Number of PM measuremen		
Warm season		
Cold season		
	Carbonaceous species	
Number of sampling days	27	69
Warm season	9	41
Cold season	18	28

Table 3-5: Cantù dataset

Sampling site	Cantù	
Type of environment	Urban	
Description	Samplers were installed inside the air quality monitoring station's fenced area, in a small park. Along one side of the park there is a street with scarce traffic. In the area there are some industrial and craft activities related to woodworking, especially for furniture production.	
	PM2.5	PM10
Sampling period	From 01/04/04 to 28/06/07	From 08/04/04 to 30/06/07
Number of PM measuremen	451	508
Warm season	220	263
Cold season	231	245
	Carbonaceous species	
Number of sampling days	87	108
Warm season	50	59
Cold season	37	49

Table 3-6: Como dataset

Sampling site	Como
Type of environment	Urban
Description	Samplers were placed next to the sidewalk on a road with a daily traffic of more than 24000 vehicles (more than 2000 vehicles per rush hour).
	PM10
Sampling period	From 27/09/04 to 17/06/07
Number of PM10 measurement	291
Warm season	153
Cold season	138
	Carbonaceous species
Number of sampling days	78
Warm season	42
Cold season	36

Table 3-7: Lodi dataset

Sampling site	Lodi	
Type of environment	Urban	
Description	Samplers were positioned close to a school inside average traffic condition environment.	
	PM2.5	PM10
Sampling period	From 07/03/05 to 17/06/07	From 17/01/05 to 16/06/07
Number of PM measuremen	249	329
Warm season	148	193
Cold season	101	136
	Carbonaceous species	
Number of sampling days	41	73
Warm season	20	44
Cold season	21	29

Table 3-8: Mantova dataset

Sampling site	Mantova	
Type of environment	Urban	
Description	Samplers were placed on the lawn of a traffic island at the jointure between a secondary road and the city ring road. The main industrial area is 1 km eastward.	
	PM2.5	PM10
Sampling period	From 10/05/04 to 26/07/07	From 13/04/04 to 26/07/07
Number of PM measuremen	124	174
Warm season	92	145
Cold season	32	29
	Carbonaceous species	
Number of sampling days	20	42
Warm season	14	35
Cold season	6	7

Table 3-9: Milano dataset

Sampling site	Milano	
Type of environment	Urban	
Description	Samplers were positioned inside the gardens of the Politecnico di Milano university. The site is surrounded by streets with low traffic volume which changes to a high volume only during rush hours. On one of the surrounding streets there is a tran's line.	
	PM2.5	PM10
Sampling period	From 17/01/05 to 01/07/07	From 25/02/05 to 30/06/07
Number of PM measuremen	331	463
Warm season	170	238
Cold season	161	225
	Carbonaceous species	
Number of sampling days	79	114
Warm season	38	46
Cold season	41	68

Table 3-10: Sondrio dataset

Sampling site	Sondrio
Type of environment	Traffic
Description	Samplers were positioned inside a parking lot situated aside of the town's main road.
	PM10
Sampling period	From 24/01/05 to 15/07/07
Number of PM measuremen	309
Warm season	173
Cold season	136
	Carbonaceous species
Number of sampling days	116
Warm season	66
Cold season	50

Table 3-11: Varese dataset

Sampling site	Varese	
Type of environment	Urban	
Description	Samplers were positioned on the terrace of the Varese Province Department building. Samplers were taken at a height of 4m and the terrace is in front of a street with low traffic volume.	
	PM2.5	PM10
Sampling period	From 10/05/04 to 02/07/07	From 10/05/04 to 11/03/07
Number of PM measuremen	361	377
Warm season	178	177
Cold season	183	200
	Carbonaceous species	
Number of sampling days	29	76
Warm season	0	29
Cold season	29	47

The statistics of annual average of PM10 and PM2.5 concentrations are shown in Table 3-12.

Table 3-12: Statistics of annual average of PM10 and PM2.5 concentrations (μgm^{-3})

Sites	PM10					PM2.5				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	50,47	31,13	143,0	12,00	45,42	28,95	17,51	76,43	8,92	26,28
A.S.Colombano	8,74	7,12	32,00	1,00	6,86	7,98	6,19	30,17	1,00	5,66
B.Fontana	40,78	28,96	154,2	10,40	29,24	19,95	12,57	55,70	4,30	18,65
Brescia	41,53	34,78	178,7	5,00	30,45	36,28	21,58	77,00	3,91	36,84
Cantù	49,03	38,27	226,7	6,58	37,51	25,46	15,84	64,77	3,08	22,88
Como	57,00	45,87	188,4	4,95	36,25					
Lodi	45,02	29,38	171,9	12,18	4,73	29,62	18,37	77,09	7,00	26,00
Mantova	60,51	30,44	130,5	12,95	53,42	27,46	18,07	67,00	7,05	22,54
Milano	69,67	41,31	191,4	4,07	58,94	41,49	25,21	125,4	7,32	37,67
Sondrio	38,93	29,96	151,0	6,87	27,07					
Varese	46,67	27,34	120,5	5,17	41,16	32,11	17,08	73,64	8,41	29,84

4. ANALYTICAL RESULTS

4.1 Assessment of OC and EC annual average concentrations at different sites

The presence of organic carbon (OC) and elemental carbon (EC) was considered for the chemical characterization of PM10 and PM2.5 samples. Summary statistics of organic carbon and elemental carbon daily average concentrations from 2005 to 2007 are given in Table 4-1 and 4-2.

Table 4-1: Statistic of annual average of OC and EC concentrations of PM10 (μgm^{-3})

Sites	OC					EC				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	7,81	3,66	16,02	2,54	7,12	1,53	0,93	4,64	0,47	1,25
A.S.Colombano	1,65	0,86	4,40	0,47	1,40	0,13	0,13	0,71	0,05	0,10
B.Fontana	6,64	2,80	15,99	3,42	5,68	0,96	0,46	2,17	0,33	0,87
Brescia	9,36	7,09	35,66	2,87	6,44	2,11	2,58	19,43	0,30	1,37
Cantù	11,03	7,53	46,85	4,24	8,30	2,37	1,57	8,40	0,34	2,00
Como	14,48	12,57	67,56	2,98	9,30	4,77	2,05	9,43	0,77	4,60
Lodi	8,85	5,67	37,04	3,70	6,82	2,08	1,35	6,39	0,74	1,63
Mantova	9,05	3,76	19,77	3,49	7,53	2,03	0,90	4,56	0,66	1,96
Milano	12,88	8,09	39,94	2,46	10,50	3,91	2,68	13,72	0,21	3,30
Sondrio	10,60	7,47	41,96	2,68	8,20	2,65	2,35	11,45	0,05	1,80
Varese	10,19	4,79	24,06	2,79	10,10	2,42	1,48	6,60	0,35	2,10

Table 4-2: Statistic of annual average of OC and EC concentrations of PM2.5 (μgm^{-3})

Sites	OC					EC				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	6,01	2,94	13,47	2,80	4,82	1,12	0,67	2,58	0,39	0,88
A.S.Colombano	1,77	0,94	4,57	0,49	1,47	0,13	0,10	0,42	0,05	0,08
B.Fontana	4,20	1,32	7,69	2,30	4,03	0,70	0,40	1,73	0,25	0,54
Brescia	9,19	4,79	22,81	4,25	7,72	1,97	1,78	10,07	0,28	1,47
Cantù	7,02	3,70	18,06	2,57	5,52	1,64	1,09	6,32	0,20	1,41
Como										
Lodi	6,34	4,07	20,76	2,12	4,73	1,67	1,40	6,67	0,20	1,40
Mantova	5,38	2,71	11,86	2,62	3,96	1,26	0,61	2,25	0,39	1,15
Milano	8,73	5,47	32,80	3,06	6,82	3,18	1,95	10,19	0,73	2,65
Sondrio										
Varese	9,15	3,00	19,07	4,56	8,83	2,13	0,75	3,93	0,75	2,05

OC mean concentration to PM10 ranges from 1,65 μgm^{-3} (A.S. Colombano, alpine environment) to 14,48 μgm^{-3} (Como, traffic environment). With the only exception of A.S. Colombano in which both OC, EC concentrations in PM10 and PM2.5 are much smaller, these levels in other sites (most of them are classified as urban areas) are respectively not much

different. It can be observed that OC mean contributions in PM2.5 are reduced by 20-40% with respect to PM10, with concentration levels ranging from 1,77 μgm^{-3} (A.S.Colombano) to 8,73 μgm^{-3} (Milano) on annual basis. (see Figure 4.1). EC mean contribution to PM10 varies from 0,13 μgm^{-3} (A.S.Colombano) to 4,77 μgm^{-3} (Como) while in PM2.5 ranges from 0,13 μgm^{-3} (A.S.Colombano) to 3,18 μgm^{-3} (Milano).
Considering PM10 and PM2.5 analysis, A.S.Colombano differs from the other sampling sites: the concentration is between 5 to 40 times lower.

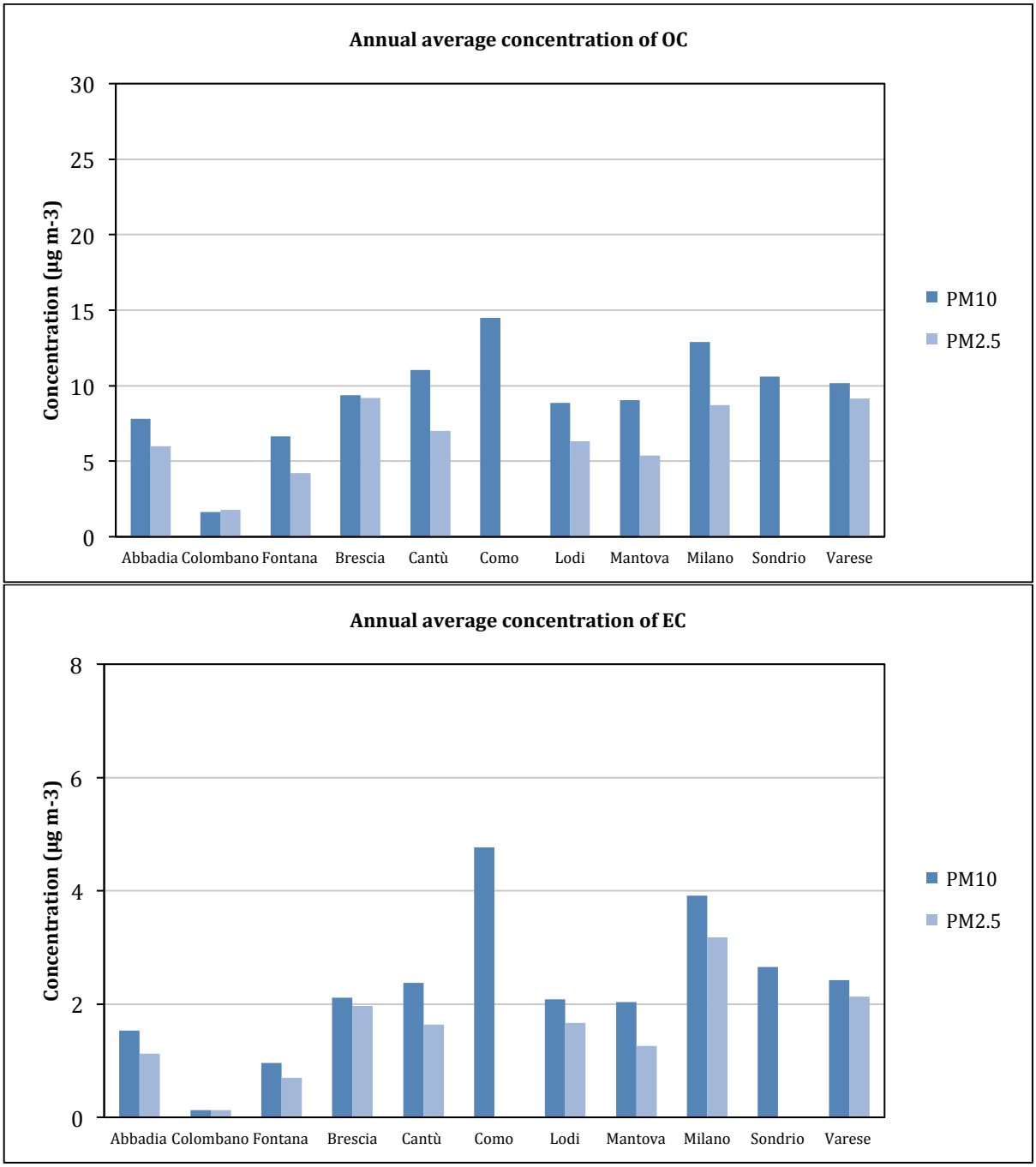


Figure 4-1: Annual average concentration of OC and EC

4.2 Assessment of temporal variability of OC and EC concentrations

The analysis of seasonal data points out relevant differences in concentration levels between warm and cold seasons (from April to September and from October to March).
The dataset of organic carbon and elemental carbon in warm and cold season is performed in Table 4-3 – 4-6.

Table 4-3: Summary of OC concentration in PM10 during warm and cold seasons (μgm^{-3})

Sites	Warm season					Cold season				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	5,38	1,09	7,38	4,16	5,22	9,17	3,90	16,01	2,54	9,43
A.S.Colombano	1,97	0,90	4,40	0,82	1,69	1,19	0,54	3,00	0,47	1,06
B.Fontana	5,91	1,70	10,65	3,42	5,46	12,07	3,55	15,98	6,70	9,82
Brescia	5,16	1,10	7,52	2,87	4,96	15,31	7,73	35,66	5,12	13,38
Cantù	7,31	2,62	13,06	4,24	7,09	15,51	9,12	46,85	4,46	11,73
Como	8,11	2,47	15,81	2,98	8,52	21,91	15,33	67,56	4,59	16,68
Lodi	6,65	1,73	11,20	3,70	6,25	12,30	7,72	37,04	3,75	11,22
Mantova	8,01	2,66	14,41	3,49	7,34	14,26	4,31	19,77	7,29	14,10
Milano	6,48	2,25	12,50	2,46	5,84	17,15	7,77	39,94	4,36	16,98
Sondrio	6,93	2,16	13,42	2,68	6,44	15,45	9,08	41,96	2,83	13,04
Varese	6,20	2,31	10,91	2,79	5,65	12,82	4,13	24,06	2,84	12,73

Table 4-4: Summary of EC concentration in PM10 during warm and cold seasons (μgm^{-3})

Sites	Warm season					Cold season				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	0,92	0,49	2,24	0,47	0,82	1,86	0,96	4,64	0,54	1,91
A.S.Colombano	0,15	0,15	0,71	0,05	0,11	0,10	0,08	0,38	0,05	0,05
B.Fontana	0,88	0,42	1,83	0,32	0,80	1,51	0,40	2,17	1,16	1,38
Brescia	1,08	0,56	2,61	0,30	0,96	3,57	3,50	0,50	19,43	2,71
Cantù	1,62	0,92	4,21	0,34	1,38	3,26	1,72	8,40	0,34	2,82
Como	3,70	1,45	6,99	0,77	4,02	6,01	1,95	9,43	1,91	6,16
Lodi	1,47	0,72	3,57	0,74	1,20	3,03	1,54	6,39	1,01	2,77
Mantova	1,87	0,76	3,59	0,66	1,86	2,84	1,15	4,56	1,46	2,20
Milano	2,21	1,14	6,14	0,21	2,04	5,05	2,82	13,72	1,44	4,44
Sondrio	1,50	0,67	3,68	0,05	1,49	4,14	2,88	11,45	0,05	3,75
Varese	1,47	0,75	3,58	0,36	1,29	3,05	1,51	6,60	0,61	2,75

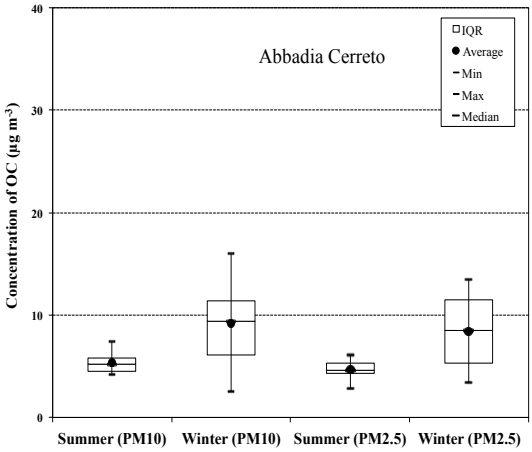
Table 4-5: Summary of OC concentration in PM2.5 during warm and cold seasons (μgm^{-3})

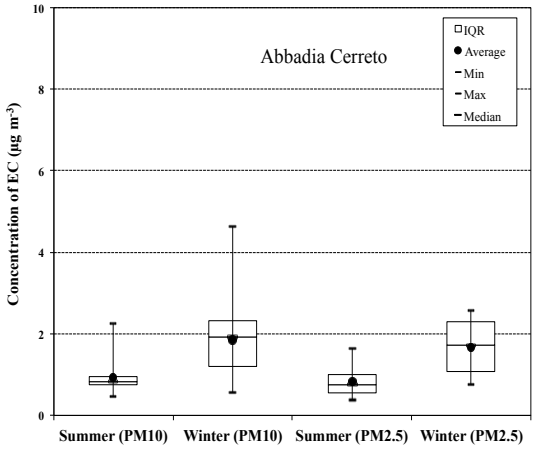
Sites	Warm season					Cold season				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	4,72	0,36	6,08	2,80	4,59	8,42	0,74	13,47	3,37	8,46
A.S.Colombano	2,14	0,95	4,57	0,83	1,89	1,19	0,55	2,80	0,49	1,04
B.Fontana	4,10	0,40	7,69	2,30	3,95					
Brescia	5,71	1,00	6,81	4,25	6,02	10,51	5,00	22,81	5,06	8,77
Cantù	4,89	1,50	8,94	2,57	4,62	9,91	3,84	18,06	4,51	9,37
Como										
Lodi	4,12	1,03	5,95	2,21	4,43	8,46	4,75	20,76	2,12	7,55
Mantova	3,86	0,60	5,19	2,62	3,83	8,92	2,34	11,86	5,97	8,85
Milano	4,98	1,54	9,91	3,06	4,65	11,90	5,61	32,80	3,75	11,48
Sondrio										
Varese						9,15	3,00	19,07	4,56	8,83

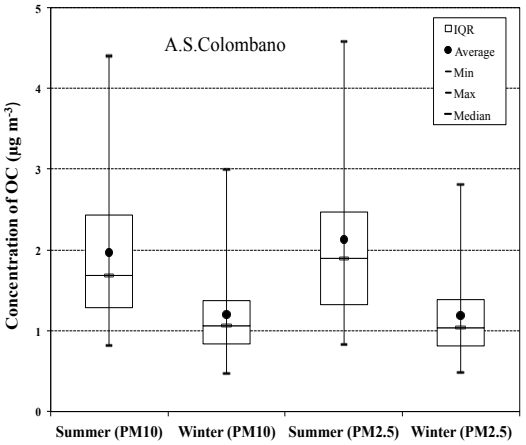
Table 4-6: Summary of EC concentration in PM2.5 during warm and cold seasons (μgm^{-3})

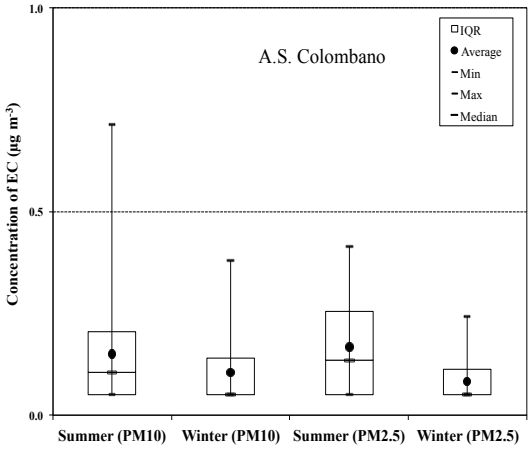
Sites	Warm season					Cold season				
	Mean	Std.dev	Max	Min	Median	Mean	Std.dev	Max	Min	Median
Abbadia C.	0,83	0,36	1,66	0,39	0,75	1,68	0,74	2,58	0,75	1,72
A.S.Colombano	0,17	0,12	0,42	0,05	0,13	0,08	0,06	0,24	0,05	0,05
B.Fontana	0,68	0,40	1,73	0,25	0,53					
Brescia	1,04	0,51	1,82	0,28	0,99	2,42	2,00	10,07	0,58	1,97
Cantù	1,24	0,62	2,65	0,20	1,17	2,18	1,34	6,32	0,31	2,03
Como										
Lodi	0,92	0,32	1,63	0,20	0,95	2,46	1,65	6,67	0,85	1,73
Mantova	1,02	0,51	1,94	0,39	0,88	1,82	0,44	2,25	1,17	1,90
Milano	2,09	0,95	4,16	0,73	1,83	4,13	2,12	10,19	1,28	4,13
Sondrio										
Varese						2,13	0,75	3,93	0,75	2,05

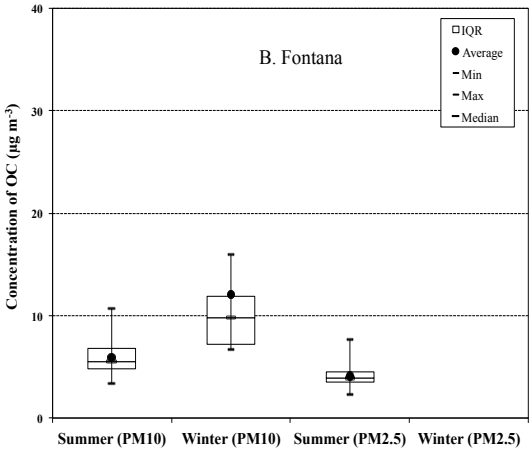
Seasonal variability of OC and EC concentration in different sites are compared in Figure 4-2.

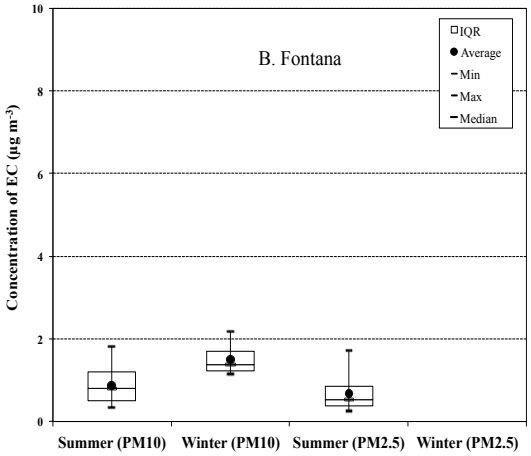

Abbadia Cerreto
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

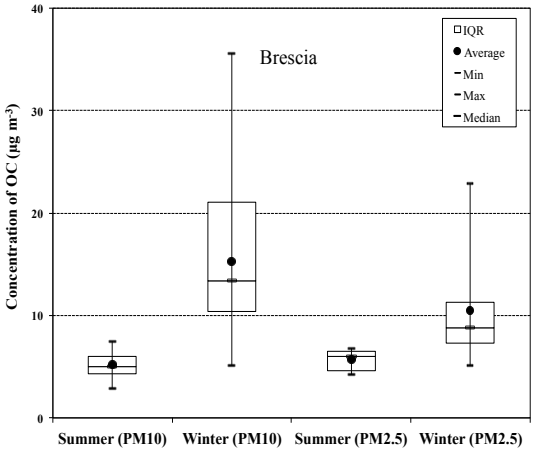

Abbadia Cerreto
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

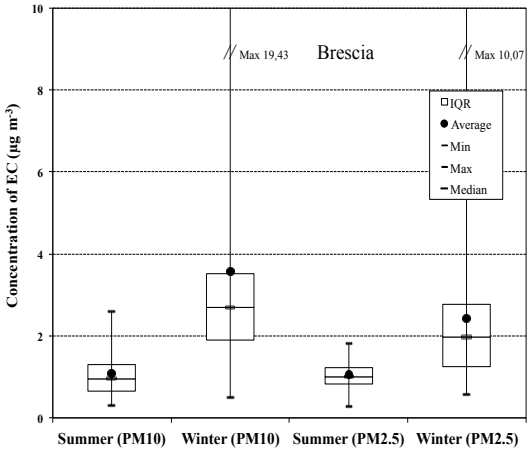

A.S.Colombano
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
1
2
3
4
5
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

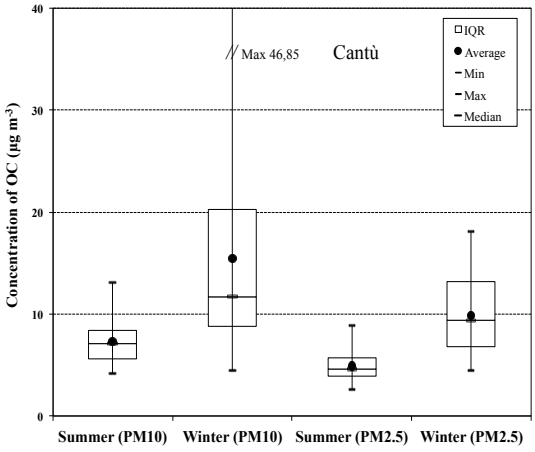

A.S. Colombano
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0.0
0.5
1.0
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

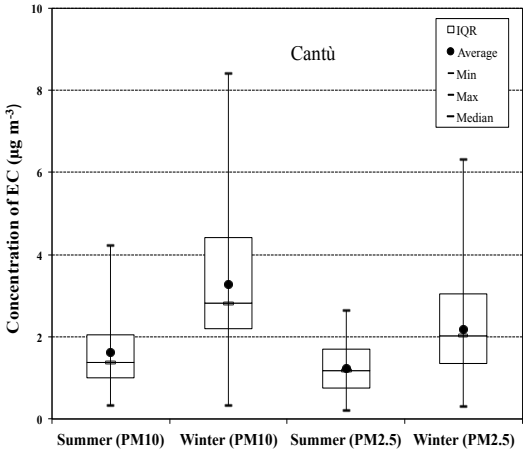

B. Fontana
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

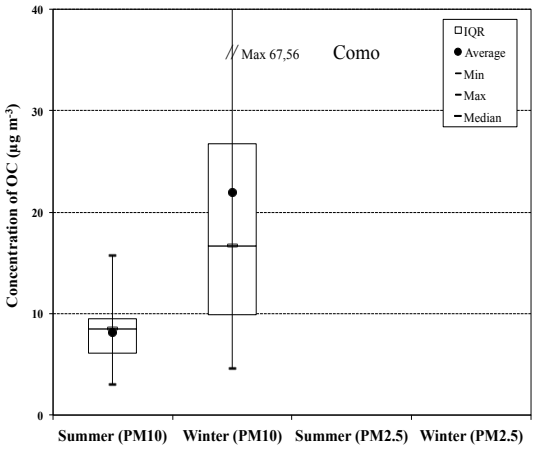

B. Fontana
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

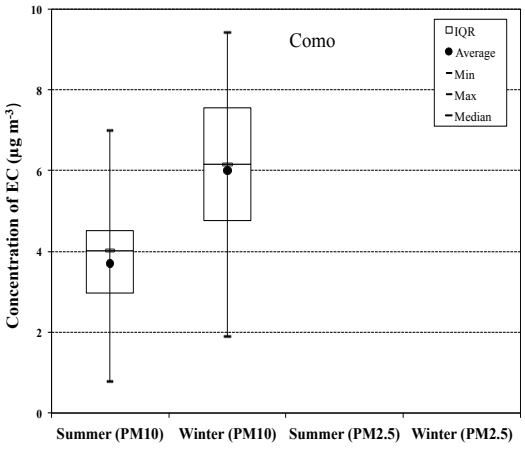

Brescia
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

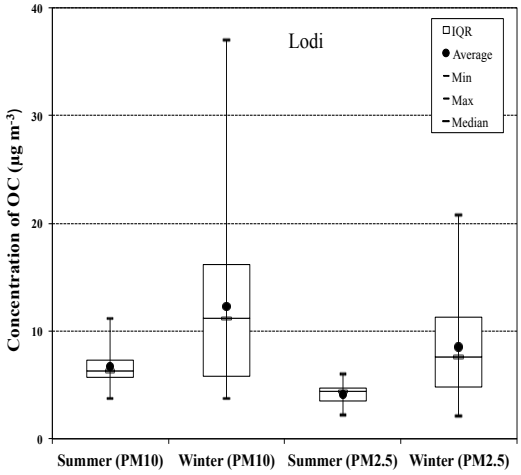

Max 19,43
Brescia
Max 10,07
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

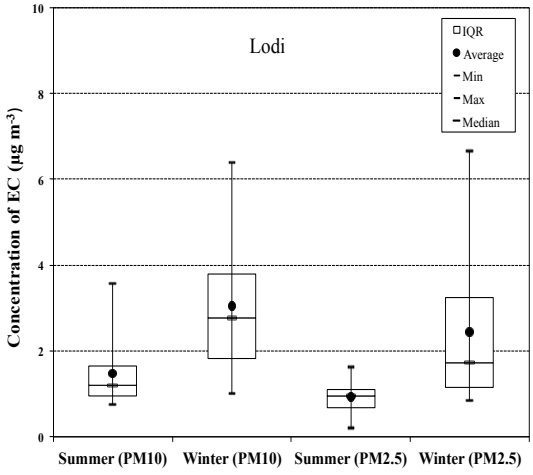

Max 46,85
Cantù
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

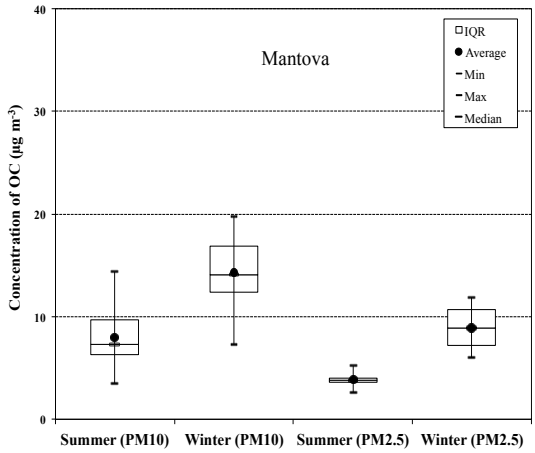

Cantù
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

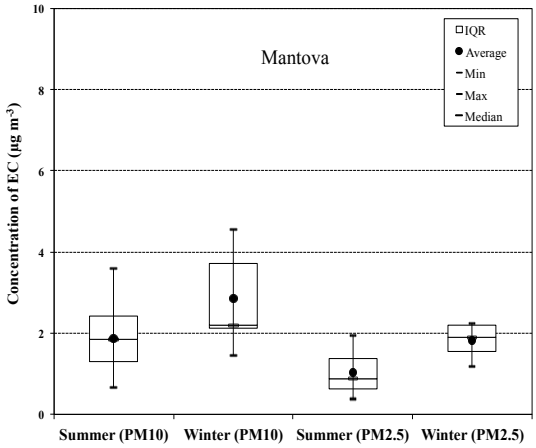

Max 67,56
Como
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

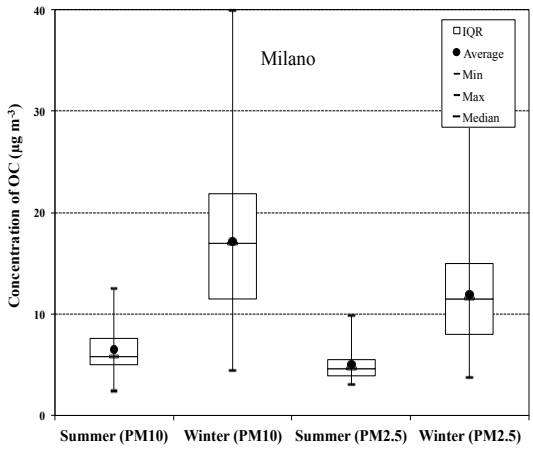

Como
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

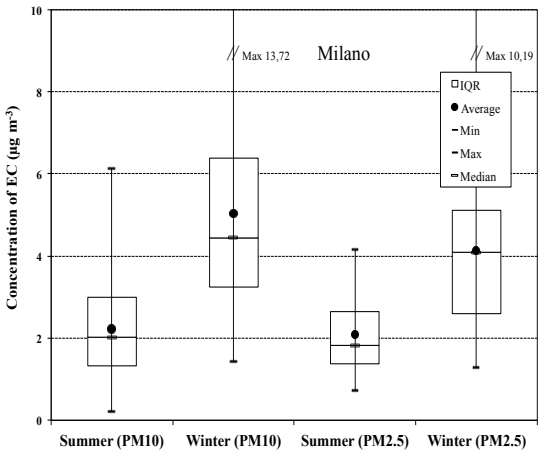

Lodi
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)


Lodi
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)


Mantova
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)


Mantova
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)


Milano
IQR
Average
Min
Max
Median
Concentration of OC (µg m-3)
0
10
20
30
40
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)


Max 13,72
Milano
Max 10,19
IQR
Average
Min
Max
Median
Concentration of EC (µg m-3)
0
2
4
6
8
10
Summer (PM10)
Winter (PM10)
Summer (PM2.5)
Winter (PM2.5)

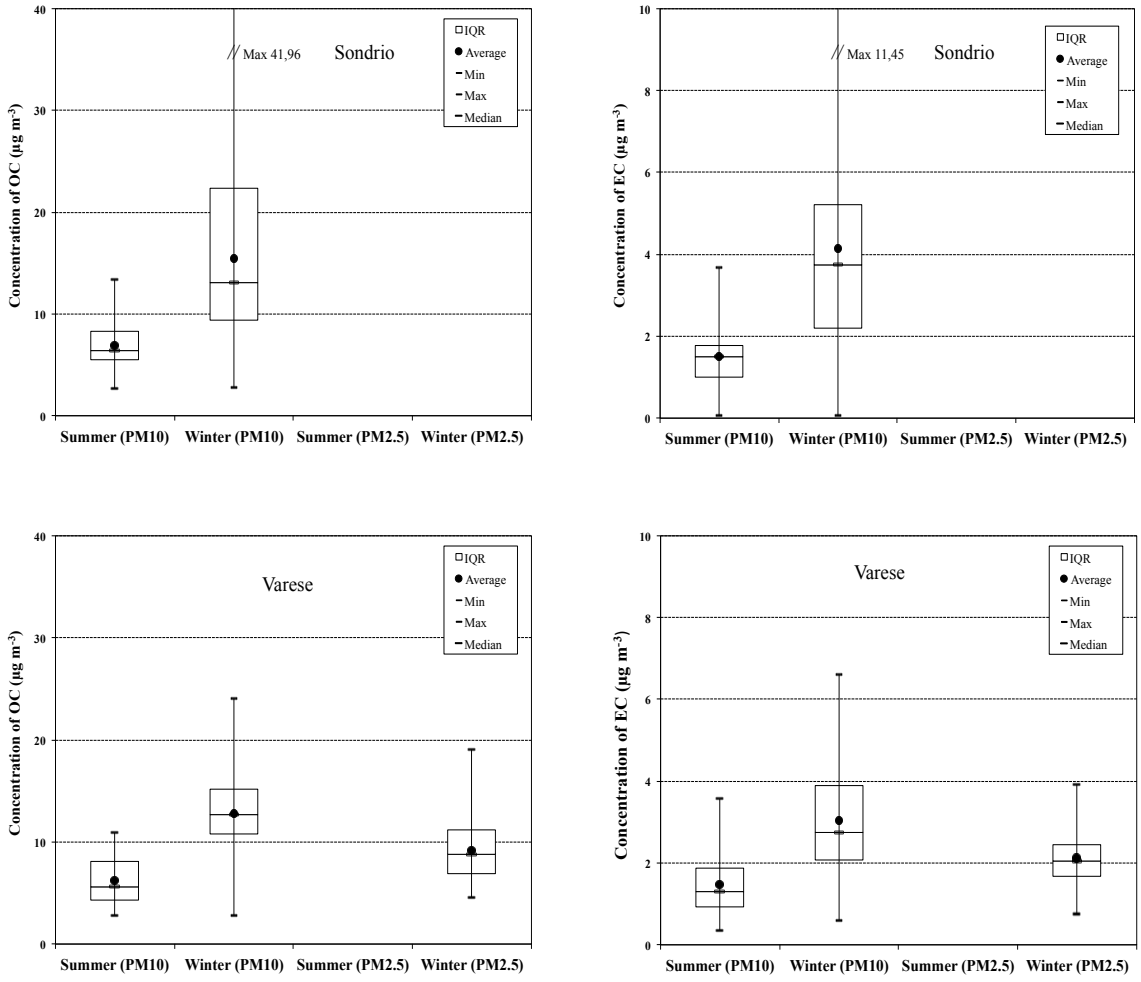


Figure 4-2: Seasonal variability of OC and EC in PM10 and PM2.5 during warm and cold seasons in diffirent sites

With the exception of A.S.Colombano in which both OC and EC mean concentration levels in PM2.5 and PM10 show a greater value during the warm season, at all the other sites the highest concentrations have been always observed only during the cold season. This increased levels are probably due to the increased cold season emissions (due to domestic heating) and to the different meterological and climate conditions in wintertime. During the cold season, thermal inversions and fog situations at ground level are very frequent and persistent and cause the accumulation of a considerable amount of air pollutants in the lower layers of the atmosphere. During warm season, instead, the pollutant dispersion is improved by the higher average wind velocity and the higher mixing layer (*Marcazzan et al*., 2001).

4.3 Assessment of spatial distribution of OC and EC concentrations

The distribution of data is shown in Tables 4-7 – 4-10.

Table 4-7: Main percentiles of annual average concentration of OC in PM10 (μgm^{-3})

Sites	OC in PM10				
	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
Abbadia C.	4,13	4,82	7,12	10,53	12,66
A.S.Colombano	0,81	1,03	1,36	2,12	2,84
B.Fontana	4,38	4,96	5,69	7,34	10,21
Brescia	3,93	4,82	6,44	11,62	21,14
Cantù	5,30	6,47	8,35	11,97	21,04
Como	5,48	7,67	9,34	16,34	27,45
Lodi	4,80	5,67	6,82	9,72	16,02
Mantova	5,20	6,37	7,53	11,21	14,06
Milano	4,68	6,01	10,51	18,52	24,43
Sondrio	4,58	5,76	8,17	12,63	22,58
Varese	4,05	5,81	10,06	13,65	15,69

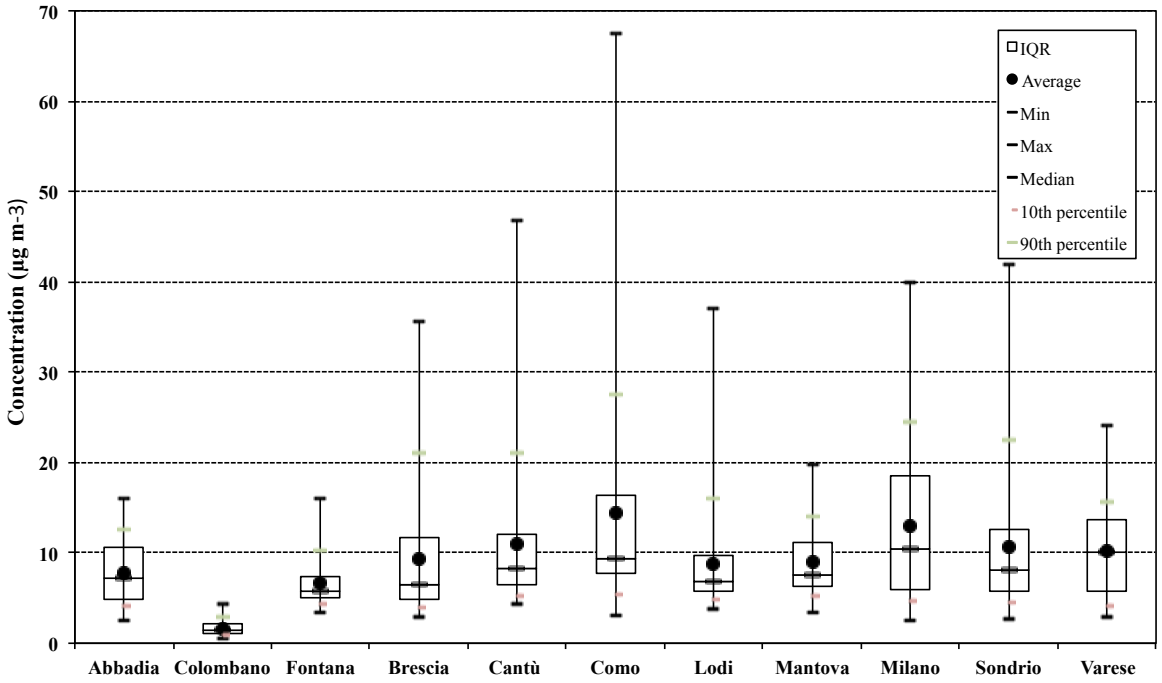


Figure 4-3: Main percentiles of annual average concentration of OC in PM10

It can be seen fom this figure that the sampling station in A.S. Colombano is completely different from the others due to its high-altitude location. Most of data of OC in PM10 in other sites vary between 5 μgm^{-3} to 15 μgm^{-3} except Como and Milano where there are some data higher than 15 μgm^{-3}.

Table 4-8: Main percentiles of annual average concentration of EC in PM10 (μgm^{-3})

Sites	EC in PM10				
	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
Abbadia C.	0,69	0,84	1,25	2,15	2,39
A.S.Colombano	0,05	0,05	0,05	0,18	0,28
B.Fontana	0,39	0,59	0,87	1,30	1,55
Brescia	0,58	0,88	1,37	2,49	3,62
Cantù	0,83	1,16	2,01	3,02	4,59
Como	2,09	3,38	4,56	6,17	7,62
Lodi	0,88	1,04	1,63	2,62	3,65
Mantova	0,85	1,46	1,96	2,46	3,08
Milano	1,34	2,04	3,31	4,95	7,28
Sondrio	0,74	1,22	1,76	3,22	5,52
Varese	0,85	1,26	2,14	3,04	4,50

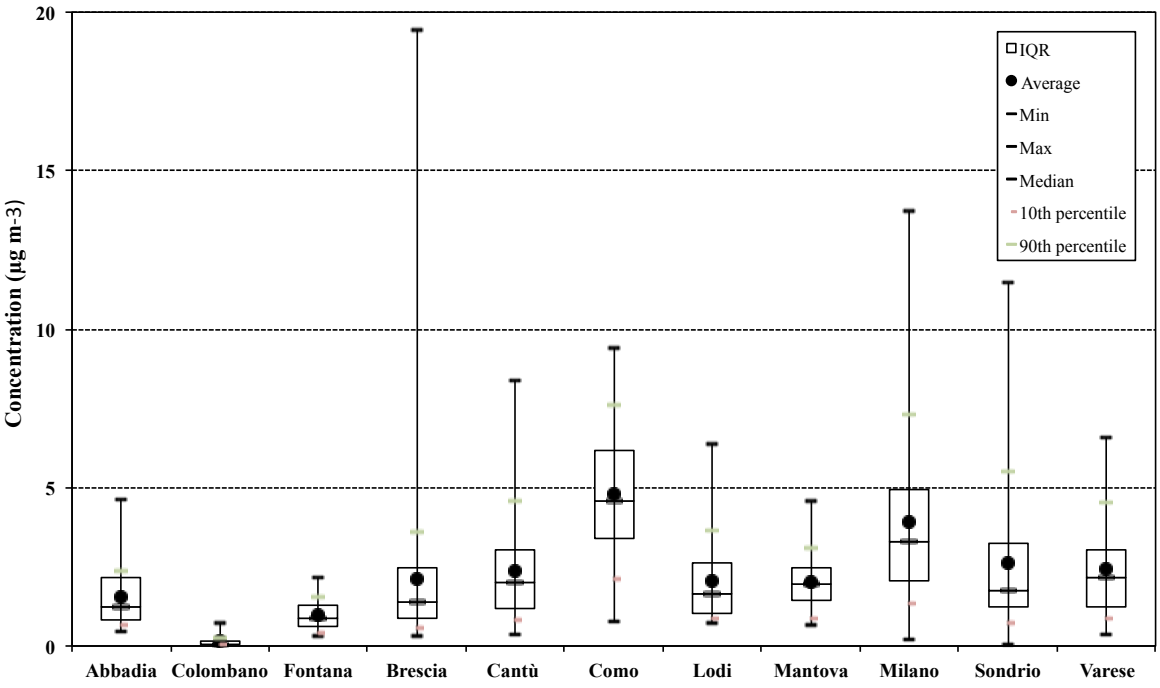


Figure 4-4: Main percentiles of annual average concentration of EC in PM10

Due to its special alpine terrain, the observations in A.S. Colombano are always much smaller than other locations'. Most of data from other sampling sites are under 5 μgm^{-3} except Como site which has many data higher than 5 μgm^{-3} because of its traffic environment.

Table 4-9: Main percentiles of annual average concentration of OC in PM2.5 (μgm^{-3})

Sites	OC in PM2.5				
	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
Abbadia C.	3,90	4,33	4,82	6,03	10,60
A.S.Colombano	0,81	1,07	1,47	2,21	3,24
B.Fontana	2,85	3,54	4,03	4,57	6,02
Brescia	5,02	6,34	7,72	10,08	16,03
Cantù	3,47	4,38	5,52	8,58	13,21
Como					
Lodi	2,98	4,08	4,73	7,55	11,74
Mantova	3,37	3,74	3,96	6,18	9,58
Milano	3,76	4,64	6,82	11,64	15,86
Sondrio					
Varese	6,20	6,91	8,84	11,21	12,26

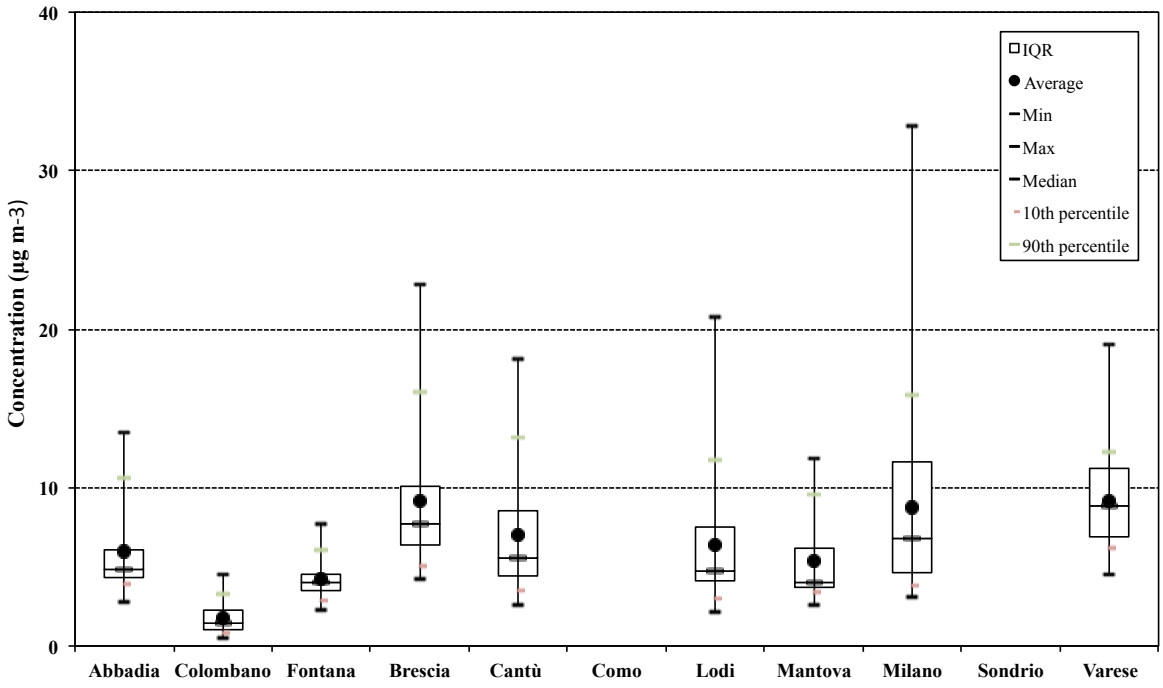


Figure 4-5: Main percentiles of annual average concentration of OC in PM2.5

As mentioned above, A.S. Colombano is always the site that has lowest concentration because it's an alpine site. The next ones are B. Fontana and Abbadia Cerreto because they are rural locations. The concentrations of other urban sites vary between 4 μgm^{-3} and 12 μgm^{-3}.

Table 4-10: Main percentiles of annual average concentration of EC in PM2.5 (μgm^{-3})

Sites	EC in PM2.5				
	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
Abbadia C.	0,51	0,67	0,88	1,35	2,20
A.S.Colombano	0,05	0,05	0,08	0,21	0,29
B.Fontana	0,33	0,39	0,54	1,02	1,21
Brescia	0,81	1,00	1,47	2,30	3,00
Cantù	0,49	0,80	1,41	2,20	3,04
Como					
Lodi	0,64	0,88	1,10	1,70	3,44
Mantova	0,49	0,84	1,15	1,71	2,14
Milano	1,28	1,72	2,65	4,16	5,54
Sondrio					
Varese	1,33	1,67	2,05	2,44	3,02

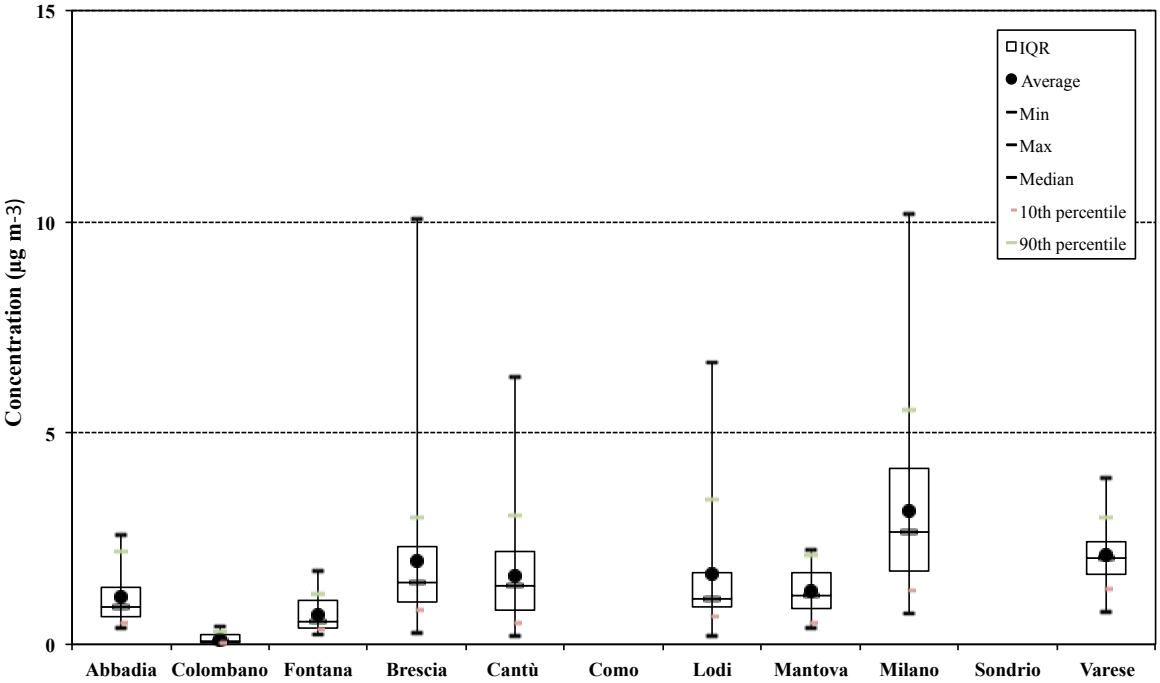


Figure 4-6: Main percentiles of annual average concentration of EC in PM2.5

With the same explanation above, Colombano is still completely different with the rest ones. The data of the others vary from around 1 μgm^{-3} to 3 μgm^{-3}.

4.4 Assessment of relative percentage of OC and EC in coarse and fine PM

The relative percentage values of OC and EC in coarse size range (PM2.5-10) are calculated by the following equations:

$$OC/PM_{2.5\text{-}10} = \frac{OC_{PM10} - OC_{PM2.5}}{OC_{PM10}} \cdot 100\% \quad (4.1)$$

$$EC/PM_{2.5\text{-}10} = \frac{EC_{PM10} - EC_{PM2.5}}{EC_{PM10}} \cdot 100\% \quad (4.2)$$

The relative partitioning of OC and EC in PM2.5 are calculated as below:

$$OC/PM_{2.5} = 100 - OC/PM_{2.5\text{-}10} \quad (4.3)$$

$$EC/PM_{2.5} = 100 - EC/PM_{2.5\text{-}10} \quad (4.4)$$

The result is shown in Table 4-11

Table 4-11: Partitioning of OC and EC: average annual percentage of total OC and EC mass in coarse and fine size range (%)

Sites	PM2.5-10		PM2.5	
	OC	EC	OC	EC
Abbadia C.	23,0	26,8	77,0	73,2
A.S.Colombano	19,1	27,4	80,9	72,6
B. Fontana	23,6	17,3	76,4	82,7
Brescia	18,1	24,7	81,9	75,3
Cantù	34,2	30,7	65,8	69,3
Como				
Lodi	25,1	21,4	74,9	78,6
Mantova	40,3	38,5	59,7	61,5
Milano	25,8	18,8	70,1	81,2
Sondrio				
Varese	45,0	32,6	55,0	67,4

This result is performed in Figure 4-7 and 4-8. It has been seen that with respect to concentration of OC and EC in PM10, a large partition of OC and EC goes to PM2.5, ranges from 55% to 81,9% with OC and 61,5% to 82,7% with EC. The rest percentages go to PM2.5-10.

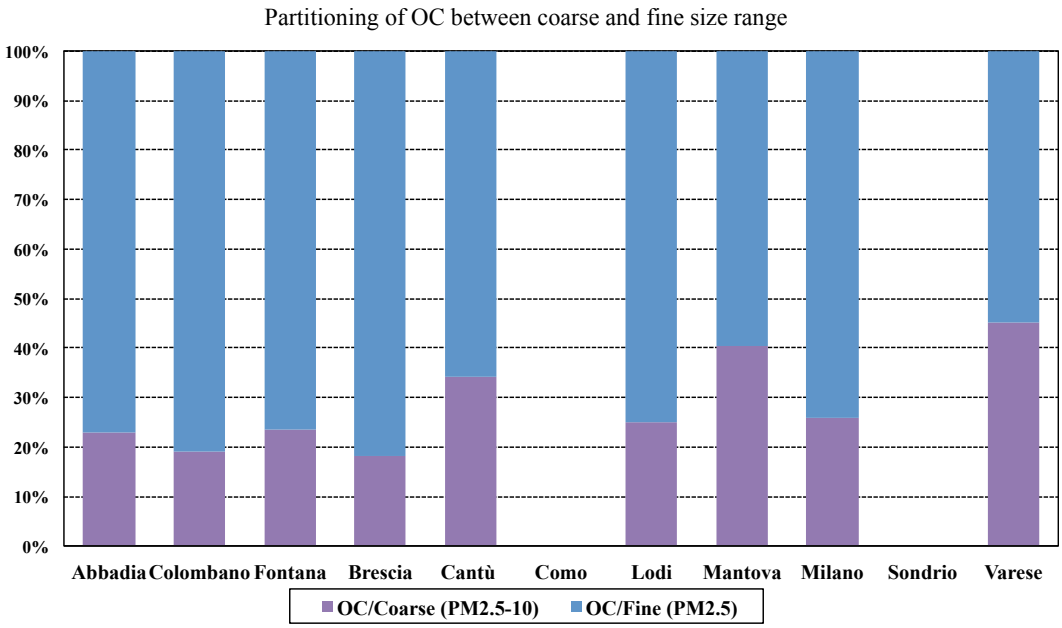


Figure 4-7: Partitioning of OC between coarse and fine size range

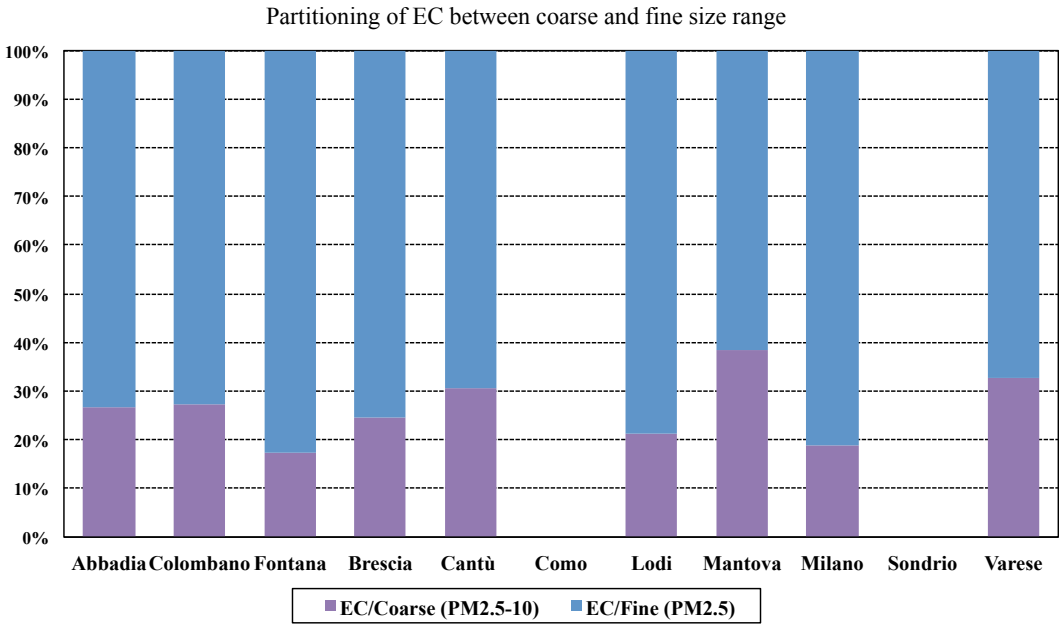


Figure 4-8: Partitioning of EC between coarse and fine size range

In temporal analyses, the partitioning to PM2.5 of organic carbon and elemental carbon is shown in Table 4-12.

Table 4-12: Seasonal partitioning of OC and EC: average percentage of total OC and EC mass in PM2.5 samples

Sites	OC		EC	
	Warm season	Cold season	Warm season	Cold season
Abbadia C.	87,8	91,8	90,2	90,3
A.S.Colombano	87,8	74,1	72,0	56,5
B. Fontana	75,3		82,2	
Brescia	98,1	76,0	79,0	69,1
Cantù	64,9	67,1	74,8	60,6
Como				
Lodi	71,3	78,9	55,1	66,0
Mantova	57,6	64,3	54,6	64,1
Milano	72,6	67,9	74,2	73,8
Sondrio				
Varese	27,8	64		67,4

Note: the percentage fractions of total OC and EC in coarse PM can be obtained by subtraction of reported figures from 100

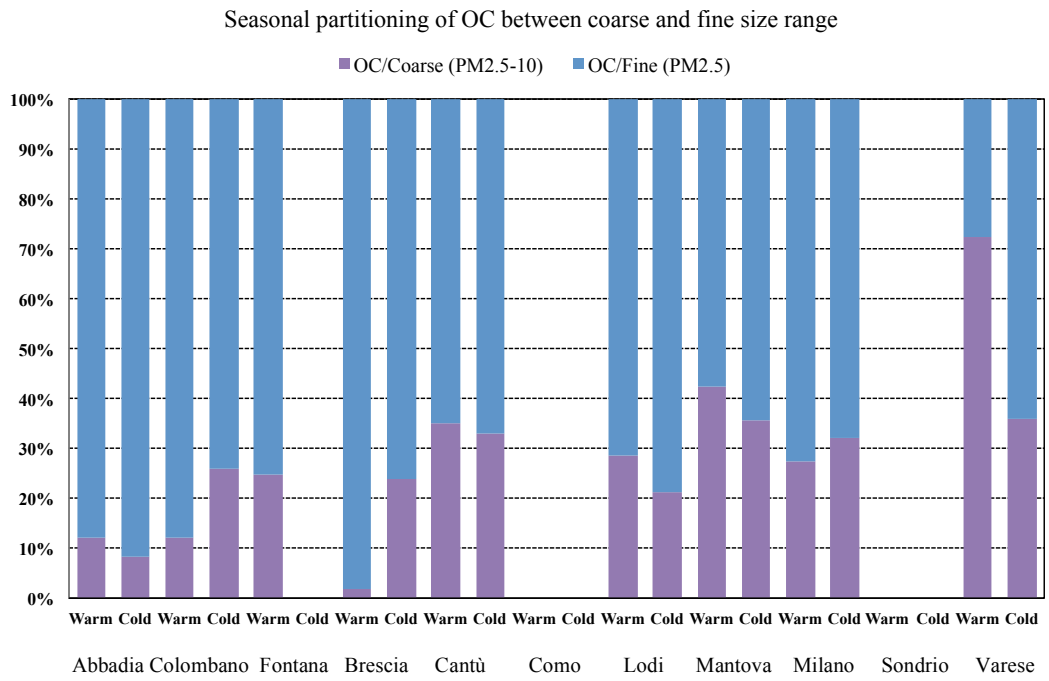


Figure 4-9: Seasonal partitioning of OC between coarse and fine size range

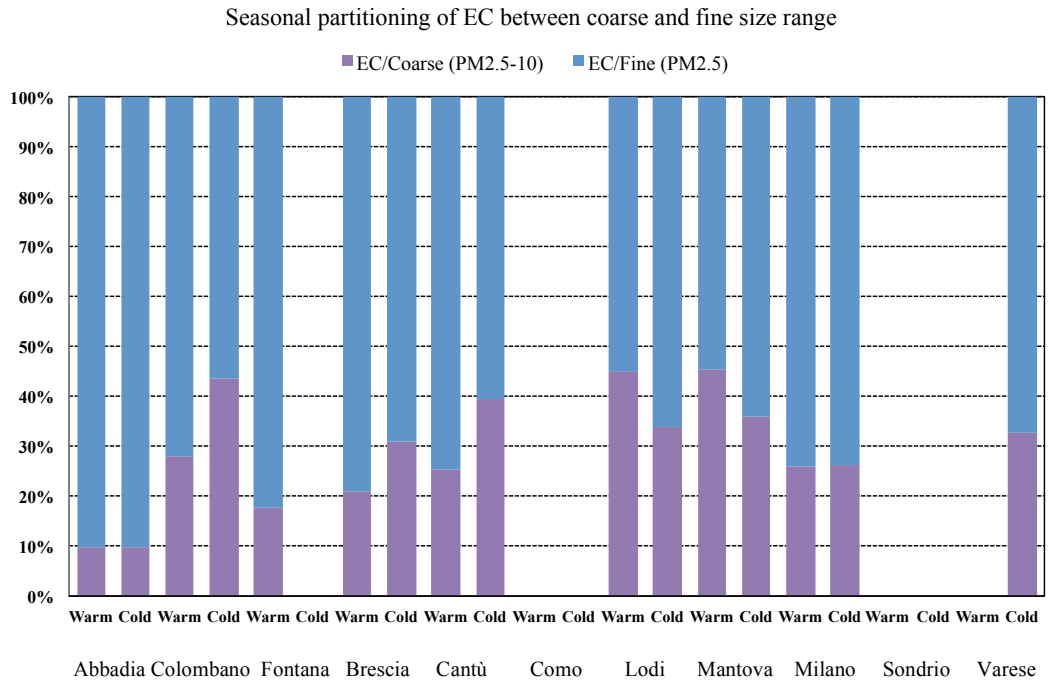


Figure 4-10: Seasonal partitioning of EC between coarse and fine size range

It can be seen from Figure 4-9 and 4-10 that some emission sources active in winter time appear to release to the atmosphere particles containing OC and EC with different sizes. In Figure 4-9, in some large cities such as Milano and Brescia, it seems that they are in the coarse size range, therefore we observe higher relative fractions of OC in coarse PM in winter than in summer; whereas in some smaller cities like Abbadia. C, Cantù, Lodi and Mantova, they are in the fine size range so that the relative fractions of OC in coarse PM are smaller in winter than in summer. In Figure 4-10, there is no differences between winter and summer time in Abbadia. C and Milano. In some sites like Lodi and Mantova, the fractions of EC in coarse size is higher in summer than in winter whereas it happens in contra in Colombano, Brescia and Cantù. Overall there is no evident pattern to conclude that the partitions of OC and EC in coarse and fine size range are affected by seasonality.
Seasonal average percentages of OC and EC in PM2.5 were tested for their statistical difference according to Welch's t test based on $\alpha = 0,05$ significant level and $|t_{ref}| = 1,96$. And the results are: OC differences were not significant at Cantù, Mantova and Milano and significant at Colombano, Brescia, Lodi and Varese. EC differences were not significant at most of sites except Lodi.

4.5 Analysis of OC/EC ratio

OC/EC ratios can be used to investigate the extent or secondary organic aerosol formation. Therefore it is important to have an accurate primary OC/EC ratio. The following techniques are applied in order to estimate the primary OC/EC ratio:

1. Ordinary least-square regression (OLR);
2. Deming regression (DR);
3. Ratio of average (ROA);
4. Median of ratios (MOR);
5. Geometric mean of ratios (GM);
6. Average of ratios (AOR);

Based on recent findings on performance of these statistical techniques (*Chu*, 2005), ROA technique is considered to be the best estimator of the expected primary OC/EC ratio, the only prequisite for its superb performance is negligibly small non-combustion organic carbon (e.g., organic carbon derivating from biogenic sources) concentration. MOR technique is considered to be the second best, while GM and DR perform similarly. ORL gives biased results as it considers the independent variable (elemental carbon in this case) free of errors which actually is not true. AOR technique is generally thought to be inaccurate because it is strongly influenced by random errors during measurement of low elemental carbon concentrations.

The high performance of ROA, MOR and GM techniques is due to their ability to deal with unrealistically large OC/EC ratios created by random errors at low elemental carbon concentrations. In particular, ROA performs well because the random measurement errors in each variable tend to cancel each other by nature while averaging and the bias introduced by measurement errors in the data base are reduced (*Chu and Meyer*, 1991) for ROA is actually a weight AOR, where the weight is directly proportional to the elemental carbon concentration. While MOR and GM do well as both are not sensitive to extreme values in a skewed distribution. According to Chu (*Chu*, 2005), MOR technique is almost as accurate as the ROA but not as precise (or stable) and AOR almost always overestimates the true OC/EC ratio.

In this study, ROA is chosen to be the method of OC/EC ratio calculation due to its advantage. The result is shown in Table 4-13.

Table 4-13: Statistics of OC/EC ratio in annual PM10 samples ($\mu g \mu g^{-1}$)

Sites	OC/EC in PM10				
	Mean	Min	Max	Std.dev	Ratio of average
Abbadia. C	5,70	3,28	11,59	1,96	5,12
A.S. Colombano	18,0	4,68	59,95	10,12	12,5
B. Fontana	7,90	3,18	17,07	3,20	6,95
Brescia	5,83	1,12	18,83	3,20	4,44
Cantù	5,37	1,92	16,83	2,46	4,67
Como	3,08	0,98	11,17	1,96	3,03
Lodi	4,80	2,27	9,47	1,93	4,27
Mantova	4,76	1,88	7,67	1,27	4,46
Milano	3,63	1,32	11,64	1,52	3,29
Sondrio	6,80	2,32	57,82	9,18	4,02
Varese	4,92	1,66	10,08	2,04	4,20

Table 4-14: Statistics of OC/EC ratio in annual PM2.5 samples (µgµg $^{-1}$)

Sites	OC/EC in PM2.5				
	Mean	Min	Max	Std.dev	Ratio of average
Abbadia. C	6,03	2,55	11,92	2,21	5,34
A.S. Colombano	16,76	4,62	36,59	7,80	13,3
B. Fontana	7,27	3,13	12,96	3,05	6,02
Brescia	5,63	3,08	14,97	2,43	4,66
Cantù	5,42	1,79	16,15	3,30	4,30
Como					
Lodi	4,38	1,97	11,62	2,05	3,80
Mantova	4,77	2,13	9,44	1,97	4,27
Milano	2,90	1,07	6,46	1,04	2,78
Sondrio					
Varese	4,62	1,97	8,34	1,62	4,30

It can be found in this study that the OC/EC ratios are almost larger than those registered for other urban sites around the world $[OC/EC]_{urban}$ = 1,3-3,9 (shown in Annex Table A-1). The high ratios in this study can be attributed more to low elemental carbon levels than to elevated OC concentrations. The rural site B. Fontana with the ratios 6,95 in PM10 and 6,02 in PM2.5 is comparable to those noted for rural sites $[OC/EC]_{rural}$ = 4,6-8,1 (see Annex Table A-1) . The highest ratio OC/EC was found in samples from remote site A. S. Colombano with 12,5 in PM10 and 13,3 in PM2.5. This very high ratios is caused due to very low elemental carbon observed in this site because of its remote location, totally far from primary sources.

Table 4-15: Statistics of OC/EC ratio in seasonal PM10 samples (µgµg $^{-1}$)

Sites	Warm season					Cold season				
	Mean	Min	Max	Std.dev	ROA	Mean	Min	Max	Std.dev	ROA
Abbadia C.	6,67	3,30	11,59	2,50	5,82	5,15	3,28	8,74	1,39	4,93
A.S.Colombano	19,97	5,09	59,95	11,31	13,1	15,15	4,68	31,48	7,34	11,42
B.Fontana	7,89	3,18	17,07	3,37	6,70	7,90	3,18	17,07	3,20	8,00
Brescia	5,76	2,41	13,19	2,46	4,80	5,93	1,12	18,83	4,07	4,29
Cantù	5,50	1,92	16,83	2,62	4,51	5,21	2,20	13,14	2,28	4,76
Como	2,48	1,18	7,06	1,09	2,19	3,77	0,98	11,17	2,47	3,65
Lodi	5,24	2,27	9,47	2,04	4,54	4,09	2,36	8,66	1,52	4,06
Mantova	4,66	1,88	7,67	1,30	4,29	5,25	3,27	6,43	1,04	5,02
Milano	3,48	1,44	11,64	1,65	2,93	3,74	1,32	9,06	1,44	3,40
Sondrio	6,08	2,58	53,67	6,78	4,63	7,75	2,32	57,82	11,62	3,74
Varese	4,81	2,28	9,87	1,86	4,22	5,00	1,66	10,08	2,17	4,20

Table 4-16: Statistics of OC/EC ratio in seasonal PM2.5 samples (μgμg $^{-1}$)

Sites	Warm season					Cold season				
	Mean	Min	Max	Std.dev	ROA	Mean	Min	Max	Std.dev	ROA
Abbadia C.	6,56	2,55	11,92	2,52	5,71	5,03	3,34	6,73	0,99	5,00
A.S.Colombano	16,81	4,62	36,59	8,63	12,73	16,69	5,12	35,28	7,04	14,33
B.Fontana	7,33	3,13	12,96	3,10	6,03					
Brescia	6,12	3,12	14,97	3,26	5,47	5,42	3,08	9,72	2,02	4,35
Cantù	4,66	1,79	12,68	1,98	3,95	6,44	2,81	16,15	4,33	4,55
Como										
Lodi	5,12	2,00	11,62	2,33	4,50	3,59	1,97	6,90	1,36	3,44
Mantova	4,71	2,13	9,44	2,35	3,79	4,92	4,11	5,52	0,62	4,90
Milano	2,72	1,07	5,31	1,04	2,38	3,06	1,42	6,46	1,04	2,88
Sondrio										
Varese						4,62	1,97	8,34	1,62	4,30

The data observed in warm season at most of sites are greater than other urban sites around the world ($[OC/EC]_{warm}$ = 1,3-3,9) except Cantù, Mantova and Milano. The cold season values are substantially larger with respect to those found in literature ($[OC/EC]_{cold}$ = 2,4-3,5) except Lodi and Milano. (see Annex Table A-1)

4.6 EC tracer method

The organic carbon measured includes two types of organic aerosols, primary organic aerosol (POA) and secondary organic aerosol (SOA). POA is the portion of organic carbon that is directly emitted from a source as particulate matter and remains unchanges in the atmosphere. SOA is particulate matter that was emitted from a source as gaseous material and changes into particulate matter in the atmosphere due to reactions with other compounds in the air. There is no direct way of knowing how much of the organic carbon measured is primary and how much is secondary, but an indirect method to estimate the POA and SOA in a sample has been developed (*Turpin and Huntzicker*, 1995). The EC tracer method estimates POA and SOA by considering the fact that POA and EC generally come from the same sources and an OC/EC ratio can be determined when the ambient temperature is low and SOA in unlikely to be produced, ussally in winter months (*Cabada et al*., 2004). The EC tracer method uses the following equations to determine SOA and POA:

$$[\mathrm{OC}]_{\mathrm{PRIMARY}} = [\mathrm{OC}]_{\mathrm{NC}} + \left[[\mathrm{EC}] \cdot \left(\frac{\mathrm{OC}}{\mathrm{EC}}\right)_{\mathrm{PRIMARY}}\right] \quad (4.5)$$

$$[\mathrm{OC}]_{\mathrm{SECONDARY}} = [\mathrm{OC}] - [\mathrm{OC}]_{\mathrm{PRIMARY}} \quad (4.6)$$

Where $[OC]_{NC}$ represents the non-combustion particulate organic matter (e.g., organic carbon derivating from biogenic source), and $(OC/EC)_{PRIMARY}$ is the ratio for the local primary source effecting the measured concentrations (*Turpin and Hunzicker*, 1995; *Cabada and Pandis*, 2002). The primary OC/EC ratio is not consistent from source to source but varies between sources (*Gray et al*., 1986). It has to be estimated at the time and/or location when the primary organic carbon emissions are dominant. [EC] is the measured EC concentration, $[OC]_{SECONDARY}$ is the secondary organic aerosol contribution to the total OC and [OC] is the measured OC concentration. All of these parameters are time dependent because of the temporal variations in anthropogenic emissions and in meteorology. The application of this method requires measurements of [OC], [EC] and the determination of the $[OC/EC]_{PRIMARY}$ ratio and the non-combustion primary OC contribution for the area and period of interest (*Turpin and huntzicker,* 1995). According to the study (*Chu*, 2005), mentioned in section 4.5, it is found that in case the non-combustion organic carbon is quite small, the best and the most robust estimator is the ratio of the organic carbon and elemental carbon average (ROA), and for this reason, it will be used in this study.

In warm season, three hypotheses can be made for area:

- Traffic is the source largely prevailing for primary carbon emissions;
- Particulate organic carbon emissions from non-combustion sources is negligibly small in urban area of Milan as there is not much green area;
- The $(OC/EC)_{PRIMARY}$ ratio observed in the tunnel site in Milan can be considered a tracer of the traffic sources;

In the summer, the reference value was made according to the literature of *Giugliano et al*., 2005, and $(OC/EC)_{primary}$ = **1,34**, determined by experimental analysis of carbon on filters

sampled into a tunnel in the city of Milan, where the variability of PM concentration levels, as well as that of the chemical composition, is mainly regulated by the variability of the traffic sources. In such operating conditions, the contribution of secondary organic carbon was found to be negligible and therefore the ratio OC/EC is representative of one primary component from traffic.

In winter, it is felt more reliable to use a value determined by a different mode of operation to estimate how much emissions of particulate carbon from traffic of primary source (EC and OC), in addition to the sources of emissions from domestic heating and biomass burning. Starting then from a data set with high temporal resolution which has been identified, through a study of meteorological parameters and atmospheric stability, pollution episodes dominated mainly by primary contributions due to the various sources and it is determined the average ratio of OC/EC representative of primary sources (*Piazzalunga*, 2007 Ph.D. Thesis); the value is equal to $(OC/EC)_{primary}$ = **1,58**.

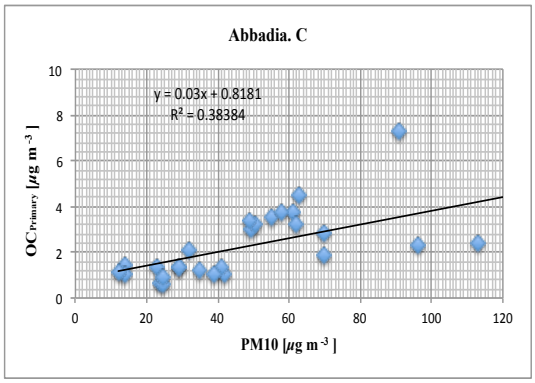
With these two ratios, equations (4.5) and (4.6) are applied to calculate $OC_{PRIMARY}$ and $OC_{SECONDARY}$ through data of 3 years. The result is shown in Table 4-17.

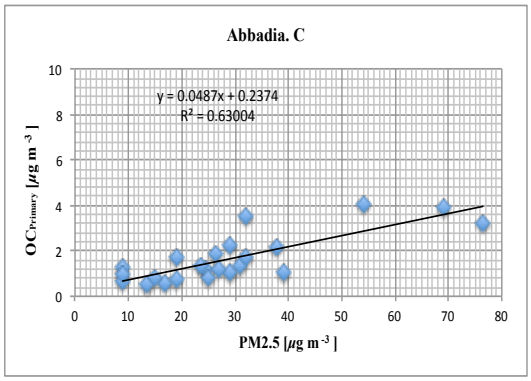
Table 4-17: The average of $OC_{PRIMARY}$ and $OC_{SECONDARY}$ in PM10 and PM2.5 (μgm^{-3})

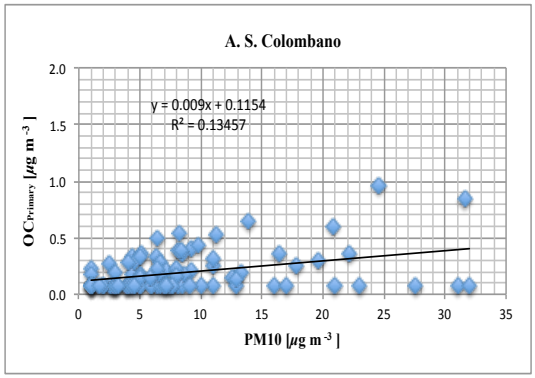
Sites	PM10		PM2.5	
	$OC_{PRIMARY}$	$OC_{SECONDARY}$	$OC_{PRIMARY}$	$OC_{SECONDARY}$
Abbadia C.	2,33	5,48	1,65	4,36
A.S.Colombano	0,19	1,47	0,19	1,58
B. Fontana	1,32	5,32	0,95	3,26
Brescia	3,18	6,18	2,63	6,56
Cantù	3,52	7,51	2,42	4,61
Como	6,69	7,79		
Lodi	3,06	5,79	2.52	2,87
Mantova	2,83	6,22	1,82	3,56
Milano	5,97	6,91	4,64	4,09
Sondrio	3,96	6,64		
Varese	3,69	6,50	3,37	4,27

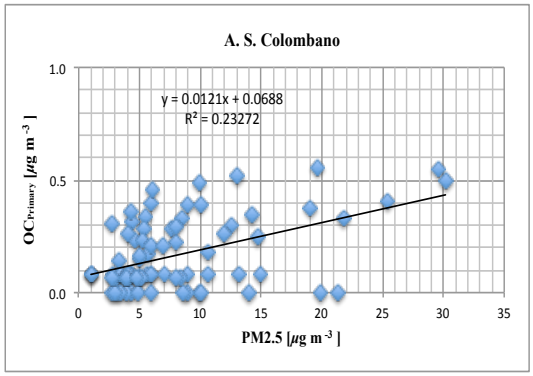
Considering the annual data set, scatterplots showing linear relationship between $OC_{PRIMARY}$ and PM10 and PM2.5 concentration are performed in Figure 4-11. It can be seen from this figure that there is a significant relationship between $OC_{PRIMARY}$ and PM10 and PM2.5: overall, $OC_{PRIMARY}$ is positively correlated with PM concentration, with increasing levels as PM concentration increases.

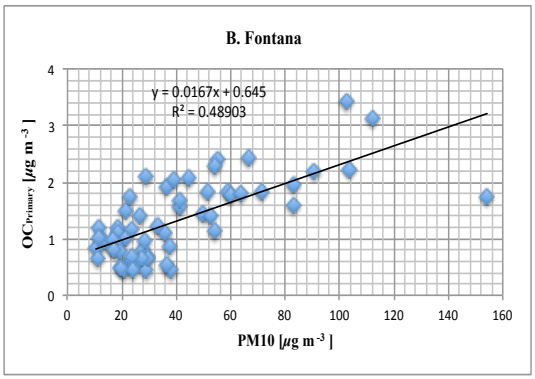
In some sites such as Abbadia. C, B. Fontana, Cantù, Como, Lodi, Mantova, Milano and Sondrio, rather good correlations ($0,6 < r < 0,8$) are observed, whereas at the other sites of A. S. Colombano, Brescia and Varese correlations are weaker ($r < 0,6$). For PM10 the slopes of the equations of linear regression data display values ranging between 0,035 and 0,084 at the urban stations and lower values at the rural stations 0,016 at Bosco Fontana, 0,03 at Abbadia Cerreto) and the lowest (0,009) at the remote site of A.S. Colombano where correlation is practically absent. For PM2.5 the regression slopes present more scattered values ranging between 0,003 and 0,079 and without a general pattern making distinction between urban and rural sites as for PM10.

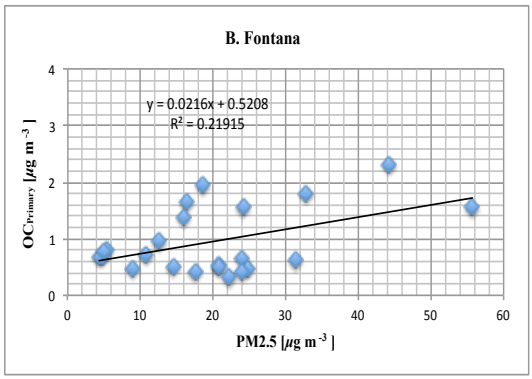

Abbadia. C
y = 0.03x + 0.8181
R² = 0.38384
OCPrimary [μg m-3]
PM10 [μg m-3]

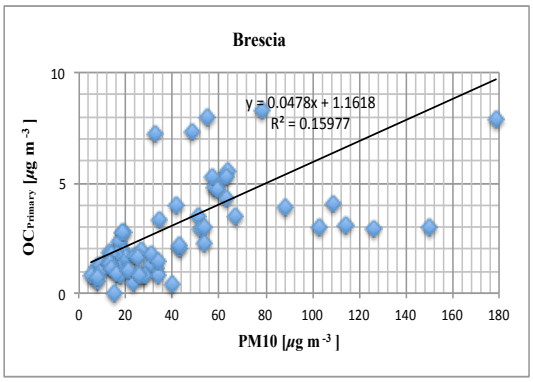

Abbadia. C
y = 0.0487x + 0.2374
R² = 0.63004
OCPrimary [μg m-3]
PM2.5 [μg m-3]

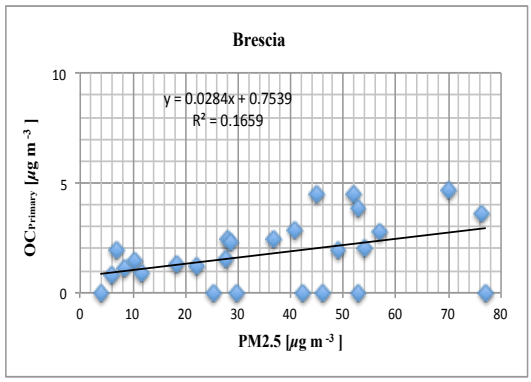

A. S. Colombano
y = 0.009x + 0.1154
R² = 0.13457
OCPrimary [μg m-3]
PM10 [μg m-3]

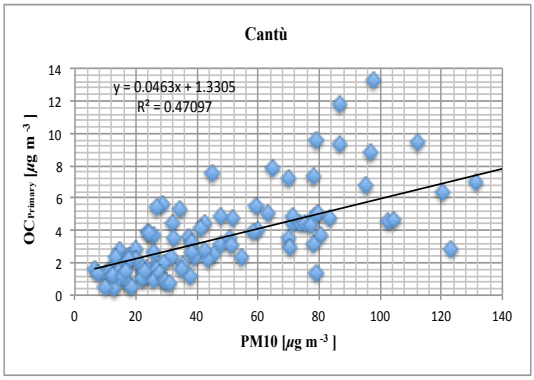

A. S. Colombano
y = 0.0121x + 0.0688
R² = 0.23272
OCPrimary [μg m-3]
PM2.5 [μg m-3]

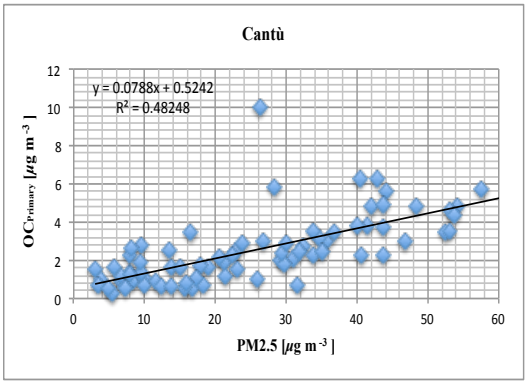

B. Fontana
y = 0.0167x + 0.645
R² = 0.48903
OCPrimary [μg m-3]
PM10 [μg m-3]

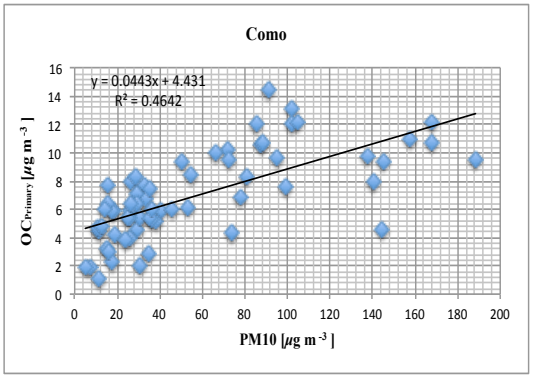

B. Fontana
y = 0.0216x + 0.5208
R² = 0.21915
OCPrimary [μg m-3]
PM2.5 [μg m-3]

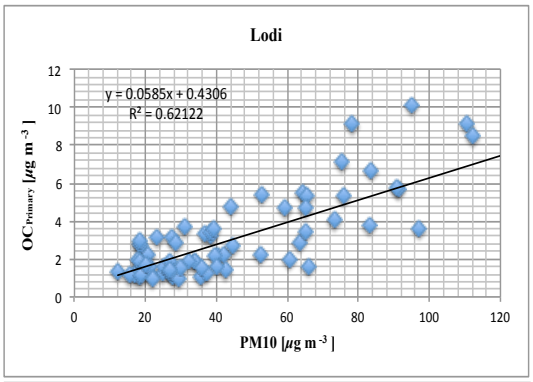

Brescia
y = 0.0478x + 1.1618
R² = 0.15977
OCPrimary [μg m-3]
PM10 [μg m-3]

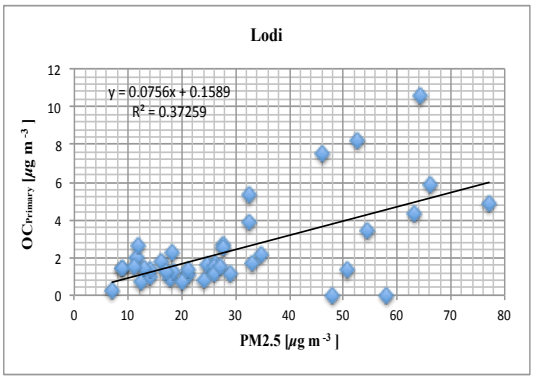

Brescia
y = 0.0284x + 0.7539
R² = 0.1659
OCPrimary [μg m-3]
PM2.5 [μg m-3]

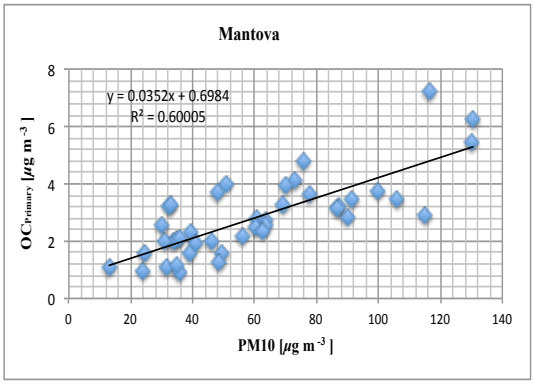

Cantù
y = 0.0463x + 1.3305
R² = 0.47097
OCPrimary [μg m-3]
PM10 [μg m-3]

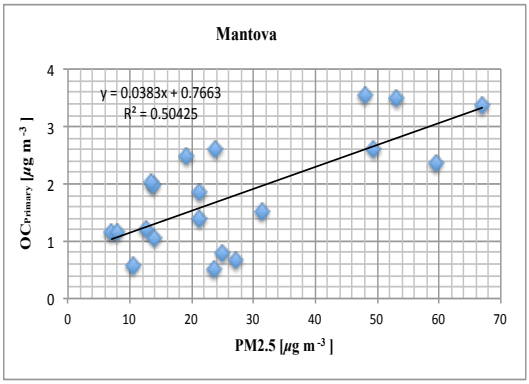

Cantù
y = 0.0788x + 0.5242
R² = 0.48248
OCPrimary [μg m-3]
PM2.5 [μg m-3]


Como
y = 0.0443x + 4.431
R² = 0.4642
OCPrimary [μg m-3]
PM10 [μg m-3]


Lodi
y = 0.0585x + 0.4306
R² = 0.62122
OCPrimary [μg m-3]
PM10 [μg m-3]


Lodi
y = 0.0756x + 0.1589
R² = 0.37259
OCPrimary [μg m-3]
PM2.5 [μg m-3]


Mantova
y = 0.0352x + 0.6984
R² = 0.60005
OCPrimary [μg m-3]
PM10 [μg m-3]


Mantova
y = 0.0383x + 0.7663
R² = 0.50425
OCPrimary [μg m-3]
PM2.5 [μg m-3]

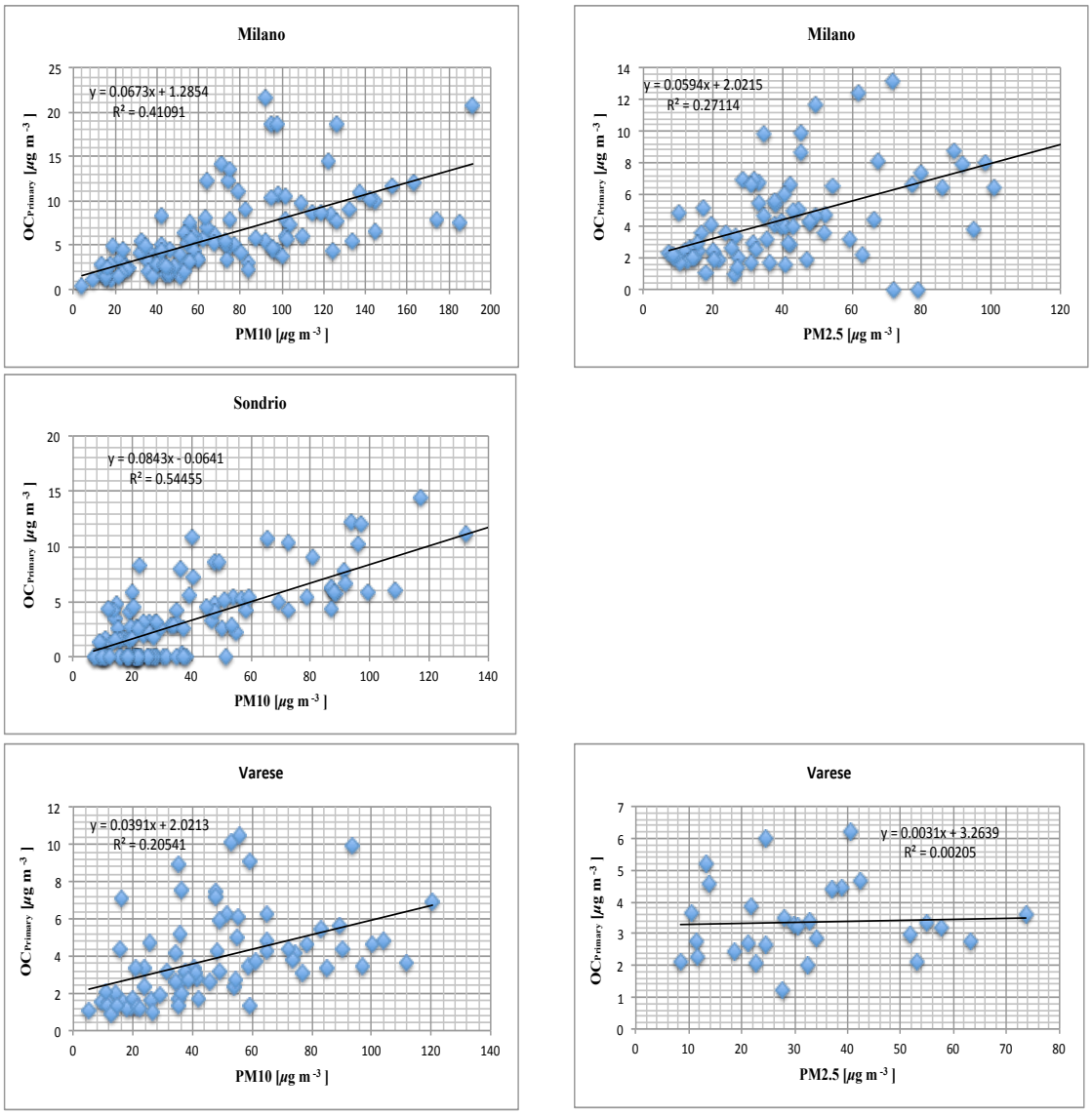


Figure 4-11: Scatterplots showing the linear relationships between $OC_{PRIMARY}$ concentration and PM10 and PM2.5 concentration.

From the result in Table 4-17, a calculation has been made to assess the partitioning of $OC_{PRIMARY}$ and $OC_{SECONDARY}$ between PM2.5 and PM coarse.

Table 4-18: Partitioning of $OC_{PRIMARY}$ and $OC_{SECONDARY}$ between fine and coarse PM

Sites	Fraction in PM2.5		Fraction in PM(2.5-10)	
	$OC_{PRIMARY}$	$OC_{SECONDARY}$	$OC_{PRIMARY}$	$OC_{SECONDARY}$
Abbadia C.	70.8%	79.6%	29.2%	20.4%
A.S.Colombano				
B. Fontana	72.0%	61.3%	28.0%	38.7%
Brescia	82.7%		17.3%	
Cantù	68.8%	61.4%	31.2%	38.6%
Como				
Lodi	82.4%	49.6%	17.6%	50.4%
Mantova	64.3%	57.2%	35.7%	42.8%
Milano	77.7%	59.2%	22.3%	40.8%
Sondrio				
Varese	91.3%	65.7%	8.7%	34.3%

It is seen from Table 4-18 that $OC_{PRIMARY}$ and $OC_{SECONDARY}$ present with a larger part in PM2.5 than in PM2.5-10 except in Lodi ($OC_{SECONDARY}$ is the same in PM2.5 and PM coarse). $OC_{PRIMARY}$ partition ranges from 64.3% to 91.3% in PM2.5 while $OC_{SECONDARY}$ partition varies between 49.6% and 79.6% in PM2.5.

CONCLUSIONS

Based on hundreds of PM10 and PM2.5 data from ARPA database collected from different sites representative for different environments in Lombardy from 2005 to 2007, it is found that OC concentration in PM10 ranges from 1,65 μgm^{-3} to 14,48 μgm^{-3} and in PM2.5 varies from 1,77 μgm^{-3} to 9,19 μgm^{-3}, while EC concentration in PM10 ranges between 0,13 μgm^{-3} and 4,77 μgm^{-3}, in PM2.5 varies between 0,13 μgm^{-3} and 3,18 μgm^{-3}.

With respect to PM10 and PM2.5, concentration levels at the site of A. S. Colombano strongly differs from those observed at all the other sites, with OC and EC concentrations from 5 up to 40 times lower. This results is due to the remote location of A. S. Colombano, far from the main sources.

A seasonal pattern for concentration levels can be observed at all sites, with differences between warm and cold season. The highest concentrations are always observed during the cold season. This can be explained both by the sources' activity, with the increase of emissions due to the contribution of domestic heating, and by meterological and climate conditions in winter time, with lower ventilation and stronger atmospheric stability.

In analysis of spatial distribution of OC and EC concentrations, except A.S.Colombano, other sites show similar distributions. Besides, Milano and Como have some data higher than other sites because of their traffic environment.

Size-resolved analysis of OC and EC partitioning show that they are mainly present in PM2.5: the fraction of total OC in PM2.5 ranges between 55% and 82,7% between sites, whereas for EC it varies between 61,5% and 82,7%. This means that most of OC and EC are released into the atmosphere in the fine particles size range. The analysis on seasonal bases does not show an evident pattern to conclude that the partition of OC and EC between the fine and coarse PM is influenced by seasonality.

The method Ratio of Average (ROA) was applied to calculate annual OC/EC ratios and seasonal OC/EC ratios. The results show that the annual OC/EC ratios for urban sites are larger than those reported for other urban sites around the world. This can be attributed more to low EC levels than to elevated OC levels. The highest OC/EC ratio found in A. S. Colombano can be explained by the very low EC observed in this site because of its remote location far from primary sources. The seasonal OC/EC ratios at all sites are higher than other reference sites in the world except Lodi and Milano.

The EC tracer method was used an an indirect method to estimate $OC_{PRIMARY}$ and $OC_{SECONDARY}$. Based on some reference documents, in summer a ratio $(OC/EC)_{primary} = 1,34$ and in winter a ratio $(OC/EC)_{primary} = 1,58$ are applied to split the total OC from analytical determination into $OC_{PRIMARY}$ and $OC_{SECONDARY}$ in PM10 and PM2.5. The results show that $OC_{PRIMARY}$ concentration ranges between 0,19 μgm^{-3} to 6,69 μgm^{-3} in PM10 and between 0,19 μgm^{-3} and 4,64 μgm^{-3} in PM2.5. Besides, $OC_{SECONDARY}$ concentrations fluctuate between 1,47 μgm^{-3} and 7,79 μgm^{-3} in PM10, and from 1,58 μgm^{-3} to 6,56 μgm^{-3}.

Some scatterplots are performed showing linear relationship between $OC_{PRIMARY}$ with PM10 and with PM2.5. $OC_{PRIMARY}$ is positively correlated with PM concentration. In some sites like Abadia, B. Fontana, Cantù, Como, Lodi, Mantova, Milano and Sondrio, rather good correlations are observed ($0,6<r<0,8$) whereas at other sites of A. S. Colombano, Brescia and Varese the correlations are weaker ($r<0,6$). For PM10 the slopes of the equations of linear regression data display values ranging between 0,035 and 0,084 at the urban stations

and lower values at the rural stations (0,016 at Bosco Fontana, 0,03 at Abbadia Cerreto) and the lowest (0,009) at the remote site of A.S. Colombano where the slope is nearly horizontal. For PM2.5 the regression slopes present more scattered values ranging between 0,003 and 0,079 and without a general pattern making distinction between urban and rural sites as for PM10.

Partitioning of $OC_{PRIMARY}$ and $OC_{SECONDARY}$ between fine and coarse PM is calculated. It can be seen from this analysis that $OC_{PRIMARY}$ and $OC_{SECONDARY}$ count a larger part in PM2.5 than in coarse PM except in Lodi ($OC_{SECONDARY}$ is the same in PM2.5 and PM coarse). In total $OC_{PRIMARY}$, its presence from 64,3% to 91,3% was found in PM2.5. Similarily, in total $OC_{SECONDARY}$, it counts for 49,6% up to 79,6% in PM2.5.

ANNEX

Table A-1: Literature values of observed organic and elemental carbon average concentrations, and the respective OC/EC ratios at various sites around the world (Adapted from *Dan et al*., 2004; *Lin and Tai*, 2001; *Yu et al*., 2004; *Na et al*., 2004)

Location	Period	Concentration [μg m^{-3}]	
		OC/EC	Reference
Beijing[u], China	6/2002-7/2002	2.2	1
	12/2002	3.5	1
Kaohsiung[u], Taiwan	11/1998-4/1999	2.6	2
Los Angeles[u] (CA), USA	6/1987-9/1987	3.5	3
	11/1987-12/1987	2.5	3
Long Beach[u] (CA), USA	6/1987-9/1987	3.4	3
	11/1987-12/1987	3.0	3
Anaheim[u], USA	6/1987-9/1987	3.9	3
	11/1987-12/1987	2.5	3
Seoul[u], Korea	6/1994	1.3	4
	27/11-9/12/1999	2.4	5
N. Birmingham[u] (AL), USA	15/6-31/8/1999	2.0	6
Centreville[r] (AL), USA	15/6-31/8/1999	5.4	6
Yorkville[r] (GA), USA	15/6-31/8/1999	4.6	6
Mira Loma[sr] (CA), USA	31/10/1997-2/11/1997	8.1	7
Riverside[r] (CA), USA	31/10/1997-2/11/1997	6.7	7

Note:
- 1 *Dan et al*., 2004.
- 2 *Lin and Tai*, 2001.
- 3 *Chow et al*., 1994.
- 4 *Kim et al*., 1999.
- 5 *Park et al*., 2002.
- 6 *Yu et al*., 2004.
- 7 *Allen at al*., 2000.
- [u]: urban; [r]: rural; [sr]: semirural.

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