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DOCTORAL THESIS

IDENTIFICATION AND QUANTIFICATION OF MOLECULAR MARKERS TO INDIVIDUATE THE CONTRIBUTION OF SOURCES IN PARTICULATE MATTER EMISSIONS

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“ Life is what happens to you
while you’re busy making other plans”

(Cit. John Lennon)

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Abstract

Nowadays, the atmospheric pollution entails a huge problem of public health and environmental conservation, increasing the necessity of creating new policies to regulate the emissions and to reduce the impact of this in the global climate. These characteristics make the aerosols the central topic of research in the current years. The composition of the particulate matter present in the atmosphere is so varied, being difficult to determine all the species present, and so, relate the pollution with precise sources.

Aerosol particles are involved in several atmospheric processes, such as cloud formation, precipitation and in the change of the optical properties, enhancing the absorbing and scattering by the particles. They have an effect in the distribution and abundance of the trace gases due to the participation in heterogeneous chemical reactions

In this work, we have direct the aim of the project to the development of extraction methods in order to improve the recovery of the different components and use new analytical techniques to obtain a more detailed characterization of molecular markers, molecules that can be linked to one emission source which help to identify them. The developed analytical techniques have been further applied to three different cases of study:

- A full characterization of the components in an urban background site, with a special interest on the organic fraction and the characterization of single molecules that act as markers of specific sources of emission.
- Analysis of the water soluble organic fraction in a rural site in the frame of the quantification of the contribution to the atmospheric pollution of biological aerosol.
- Analysis of water soluble organic compounds in a marine environment to identify the effect of harbour activities in the air quality of the cities.

1. General Introduction

It is well known that our planet is not a static system, but is continuously changing by natural sources, such as volcanos, forest fires, earthquakes and other natural disasters; and the effect of the civilization.

During the history, the relationship of the humans with the surrounding environment is changed based on their needs. Together with discovery of first tools and fire, the human being began to impose itself over the environment and started to modify it.

1.1.- Pollution:

The pollution is intended to be ‘the introduction of the contaminants into the natural environment that causes adverse changes in the ecological equilibrium, damaging the organisms that live in’. This means that the first pollution cases were when the humans began to use the fire, spreading smoke, dust and ash, produced by the combustion of wood, in the atmosphere, water and soil.

1.1.1.- Historic cases

The most influential period to this changing process was the Industrial Revolution, due to the implementation of the industrial activities using machines to develop the production processes, using fossil fuels.

It was took in the period from about 1760 to 1820-1840, going from the hand production methods to machines, new chemical manufacturing and iron production processes. It also included the change from wood to coal as fuel.

It marked the major point of turning in the history. In particular, average income and population began to exhibit unprecedented sustained growth.

Linked to the evolution of the industry, the presence of the burning coal and the residues became a huge problem of pollution. It is from the Industrial Revolution that began the environmental contamination as it is known today.

The Industrial Revolution brought an infusion and a large quantity of untreated chemical wastes into local streams that served as water supply.

In 1858, London recorded one of the earliest extreme cases of water quality problems with the great Stink of the Thames, which led to construction the London sewerage system. Pollution issues escalated as population growth increased, exceeding the ability of neighbourhood to handle their waste problems.

In 1870, the German Government brought scientists and engineers to solve the problem of waste-waters in the city of Berlin. This prevention action was recognized as '*the most complete application of science, order and public life'* by a British expert in 1906.

Water and soil pollution were the first two types to be studied because of the evident changes, such as dead of the animals living in the lakes or rivers, mutation in the plants in polluted zones or disappear of them.

1.2.- Types of pollution:

1.2.1.- Soil pollution:

It is caused by xenobiotic chemicals that are released by spill or underground leakage. It is typically caused by the industrial activity, agricultural chemicals or improper disposal of waste.

Figure 1.1.- Soil polluted

The most common compounds involved are petroleum hydrocarbons, pesticides, solvents, lead and other heavy metals. These last types of compounds are commonly due to the mining activities to extract the metals, to be used in the industrial processes of manufacturing products.

The concern over soil contamination stems primarily from health risks, from direct contact with contaminated soil, and from secondary contamination of water supplies within the underlying soils.

The causes of soil pollution are:

- Accidental spills
- Acid rain (by air pollution)
- Intense farming
- Mining and other industries
- Deforestation
- Landfill
- Land erosion
- Agricultural practices and pesticides
- Disposal of coal ash
- Industrial accidents
- Drainage of contaminated water into the soil

1.2.2.- Water pollution:

It is the contamination of water bodies, such as lakes, rivers, oceans. This form of pollution occurs when contaminants are directly or indirectly discharged into the water without an adequate treatment to remove harmful products. Water pollution affect to entire biosphere, plants and organism living in it.

Is mainly the pollution by the discharge of wastewater from commercial and industrial waste, discharges domestic sewage, and chemical contaminants from treated sewage, such as chlorine; release of waste and contaminants into surface, waste disposal and leaching into groundwater; eutrophication and littering.

Figure 1.2.- Water pollution

An important case of water pollution occurred in America, when was dumped in the Hudson River a huge quantity of polychlorinated biphenyl (PCB) by the General Electric company that resulted in a ban of fish consumption by the Environmental Protection Agency, in 1974.

1.3.- Air pollution:

Between the diverse forms of pollution, atmospheric contamination represents one of the risk factors to the human health and is mostly monitored in terms of surveillance of epidemiology and toxicology to better understand the behaviour.

The pollution of the air is always linked to the civilizations and it started in the prehistoric times when man began to use fire. Obviously, there was not any knowledge about the effect of the human in the environment due to the absence of visible signs, such as the dead of the animals for the water pollution.

During the history, there were several examples of high number of sick cases, but rarely were related with pollution events.

In 1272, King Edward I of England banned the use of coal, coming from the sea cliffs, after its smoke where too much in the atmosphere of the city, becoming a problem; but being so common fuel; the coal was still diffusively used.

After the World War II, the awareness of pollution was present, when an important case of contamination took place in 1952 in London, The Great Smog, which killed 4,000 people by the increasing of the volume of smoke from 0.2 mg/m^3 to 1.8 mg/m^3.

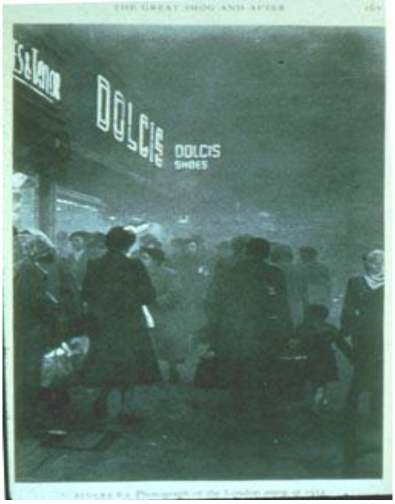


Figure 1.3.- The Great London Smog (1952)

Following this horrible event, was prompted to the first major modern environmental law, The Clean Air Act of 1956.

During the ‘70’s and ‘80’s was widely accepted the correlation between the atmospheric pollution and the effects on human health due to the knowledge about the previous events of pollution.

In the ‘90’s, the correlation was further confirmed by the new evidences of health effects even when the concentration of pollutants was low, with evidence at long time away after the exposure.

These particular cases have increased the interest about how is made our atmosphere and the identification of pollutants and the particulate matter containing them.

2. State of the art

2.1.- The atmosphere:

The atmosphere is the gas protection of our planet. Hold by the gravity, this air mass reaches the maximum density at sea level of 1 kg/m^3. The value of the density decrease with a factor of 10 each 15-16 km and the pressure follow the same behaviour due to the hydrostatic equation of the atmosphere $dp/dz=-g\rho$

At 80 km up of the Earth's surface, the gas composition of the air is almost homogeneous referred to its gas compounds, so being called *Homosphere*, in contrast to the overlying *Heterosphere*, characterized by the different spherical layers.

The gas composition of the atmosphere can be sub-divided in two classes based on their residence time in it: permanent gases and the variable gases.

- *Permanent gases*:

This class groups the gases that constitute almost 100% of the atmosphere and have the highest times of residence. In this group are contained:

Nitrogen → N_2: 78.084% vol.
Oxygen → O_2: 20.946% vol.
Argon → Ar: 0.934% vol.
Carbon dioxide → CO_2: 0.030% vol.
Hydrogen → H_2: $5\cdot10^{-5}$% vol.
Neon → Ne: $1.8\cdot10^{-3}$% vol.
Helium → He: $5.2\cdot10^{-4}$% vol.
Krypton → Kr: $1.14\cdot10^{-4}$% vol.
Xenon → Xe: $8.7\cdot10^{-6}$% vol.

- *Variable gases*:

They are characterized by a short time residence in the atmosphere and lower concentrations in volume respect from the permanent gases.

Water → H_2O: 0.1 - 2.8% vol.

Methane → CH_4: $1.5 \cdot 10^{-4}$% vol.

Carbon monoxide → CO: $6 \cdot 10^{-6}$-$1 \cdot 10^{-4}$% vol.

Sulphur dioxide → SO_2: $1.0 \cdot 10^{-4}$% vol.

Nitrous oxide → N_2O: $5 \cdot 10^{-5}$% vol.

Ozone → O_3: 10^{-6} - 10^{-5}% vol.

Nitric dioxide → NO_2: $5 \cdot 10^{-8}$ – $2 \cdot 10^{-6}$% vol.

Radon → Rn: $6 \cdot 10^{-18}$% vol.

Nitric oxide → NO: traces

The upper limit of all the layers is about on 10,000 km, being contained the almost entire of the atmosphere in the first 29 km.

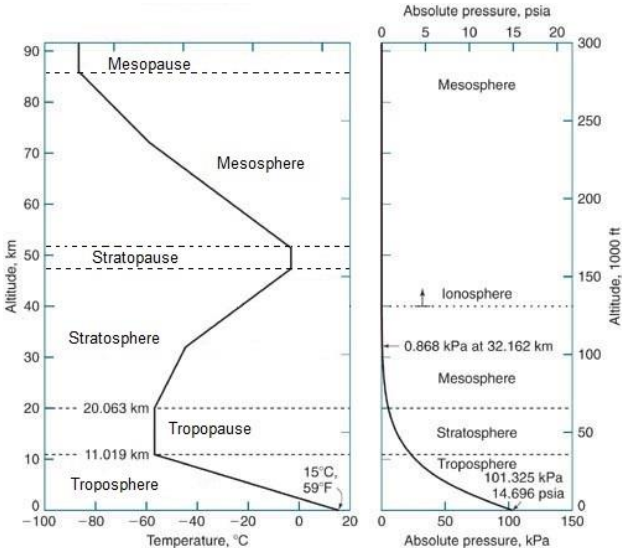


Figure 2.1.- Graphic atmospheric pressure and temperature vs altitude

The troposphere contains about 2/3 of the total mass of the atmosphere and its heating is due to the radiation emitted by the Earth's surface.

Its temperature decrease when the height increases up to the tropopause, at 10 km, where the temperature remains constant.

The stratosphere begin in the tropopause and ends at the next layer with a constant temperature, named stratopause. The average temperature is quite less in the lower part of the stratosphere, increasing rapidly in the upper layer.

From 15 to 45 km is present the ozonosphere, where the ozone layer is formed. Here the O_3 absorb the majority of the UV rays coming from the sun, producing a heating. The reaction of absorption is exothermal, explaining the higher temperature of the upper layers of the stratosphere.

The gas composition is the same to the troposphere, but in the stratosphere there is no aqueous vapour making the mixture dryer and cleaner, due to the absence of dust.

Planet boundary layer:

It is the lowest part of the atmosphere and is defined as '*the layer which suffers more directly the influence of the Earth's surface and responds to the forcing with a time scale of an hour or less*' (B. Stull, R. et al.).

This forcing includes heat transfer from the surface to the air, evaporation of liquid components, frictional pull-off, changes in flow induced by the terrain and emission of pollutants.

The thickness of this portion of atmosphere is a function of the roughness of the ground. It could be from 100 m to more than 1 km, when the atmosphere is free of the influence of the surface.

The structure of the planet boundary layer (PBL) is still a challenge of study to understand the behaviour of the meteorology and the turbulent flow inside of it.

There are four layers in which the PBL is sub-divided, being classified depending on their height.

Interfacial layer: Is comprised between 0 and 1 cm. Is the layer in which occurs the molecular transport of the components to the next one and there is not turbulence.

Surface layer: Its height is in the range of 0 - 100 m. Is the nearest sub-layer to the ground, having a strong gradient of transport and, in consequence, a great turbulence.

Mixed layer: Is characterized by a significant turbulence and well mixed stratum. It is between the 100m and 1 km.

Entrainment layer: Is the highest sub-layer of the PBL. In it, is produced the thermal inversion due to the intermittent turbulence.

The change in the temperature is the most studied characteristic inside of the PBL and is dependant of the cycle of the day.

During the day, there are two different moments in which the evolution of temperatures changes: in the daytime build-up, is formed the PBL with normal thickness and in the night there is a thermal inversion in the first 100-200 metres.

- *Before the dawn*: The PBL is static everywhere and in this situation there are only present a little bit of vertical vortices which are formed in the nearest part to the surface and less extensive in height.

- *After the dawn*: The energetic apportion from the outside of the PBL begins and the convective situation initiate to establish with a vertical extension.

In these two moments begin the convective expansion in the PBL producing large turbulence near the surface and growing up leading to a mixing of temperature and humidity.

- *During the night*: The thermal inversion is led by the radiative transfer and turbulence due to the absence of the convective flows creation, allowing the decay of turbulence. The layer that remains is called Residual Layer, with the properties of the previously mixed layer. The turbulence of this remaining zone is almost the same and the thermal inversion is neutral.

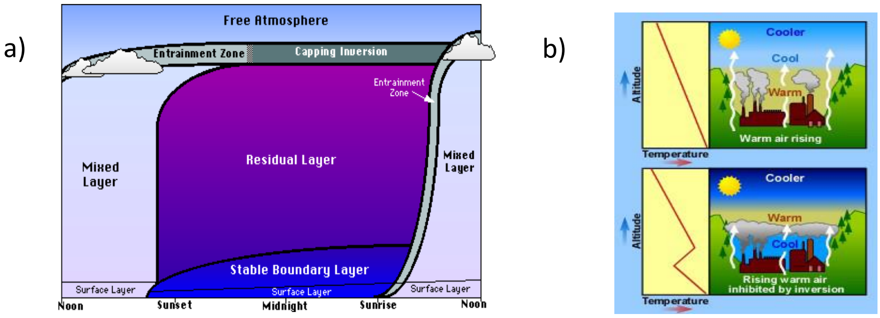


Figure 2.2.- (a) The structure of PBL during the cycle of the day (Adapted from Stull, 1988); (b) Inversion of temperatures in the PBL

- *The convective situation of the PBL:*

The characteristics that make unique the planet boundary layer are related to the convective situation inside of it. This happens by the effect of a heat source that act warming the gases contained in it and stabilizing two the turbulence modes in the surface-air interface. These are from different origin, mechanical and convective.

The mechanical source creates in the PBL vortices of different size caused by the interaction of a viscose fluid and a rough surface.

In the other hand, the convective source gives birth to the vortices of a higher dimension than those produced by mechanical sources, by the effect of thermal action and the force of Archimedes, in which the different density of the air contained in the vortices and the surrounding air, creates this *thermals*.

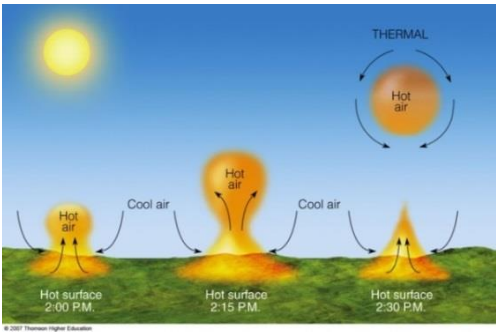


Figure 2.3.- Convective thermals

The importance of know how are produced this thermals resides in how they transport the compounds present in the PBL along all of the layers, especially the pollutants contained in it.

2.2.- Atmospheric pollution

The air pollution has different impacts in the atmosphere's conformation and in its protection function, damaging the ozone layer which constitutes the natural barrier of the Earth to the UV rays. The atmospheric equilibrium carries to a tightness of the balance of the positive or negative radiative forcing that changes the temperature.

For long time, it has been thought that pollution have an increasing effect on the average temperature due to the hole in the atmospheric ozone layer. When the interest in this subject has increased, the scientific community has addressed the investigation through this field.

2.2.1.- Greenhouse gases

To study the effect of the pollutants in the atmosphere, has to be understood the interaction of the solar radiation with our atmosphere.

There is a probability that gases present in the atmosphere absorb part of the solar radiation, depending on the wavelength of the incident light. The spectrum of the solar light is highly absorbed by larger optical thickness.

The molecules responsible of the absorption are the minority constituents in the atmosphere, these are *water vapour*, *carbon dioxide*, *ozone* and *oxygen*.

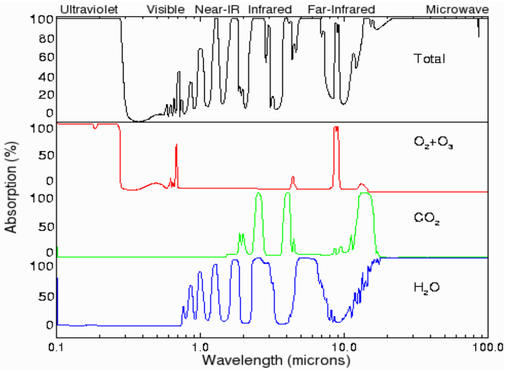


Figure 2.4.- Absorbance of solar radiation

This graphic shows the percentage of the solar radiation that is absorbed before arrive to the ground.

Because of the gases and particles present in the atmosphere, the radiation is absorbed and reflected in different range of wavelengths. There are some windows in the electromagnetic spectra that are not affected by the absorption, passing completely unaltered.

The two main ‘windows’ are situated in the range of so called ‘long’ wavelength and ‘short’ wavelength:

-*Long range:* Is located in the IR region, between the 8 and 13 µm. Its name is the atmospheric window and is not completely open because of the certain absorption bands of the atmospheric gases.

-*Short range:* Is also called the solar window, because the wavelength in which is included between the near infrared region and the entire visible band (0.3- 0.7 µm).

The greenhouse effect is a natural phenomenon which is produced by the difference between the easy entrance of the solar radiation to the Earth’s surface and the difficulty to the reflected IR radiation to exit from the atmosphere. These difficulties come from the different absorption of the outgoing infrared radiation by clouds and some atmospheric gases that reflect this radiation again to the surface, heating the atmosphere.

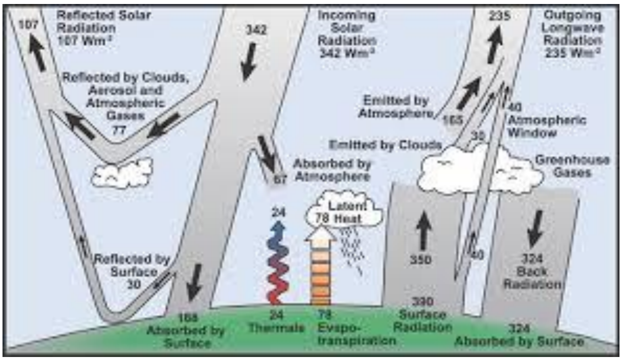


Figure 2.5.- Earth absorption and reflection of radiation (Source IPCC)

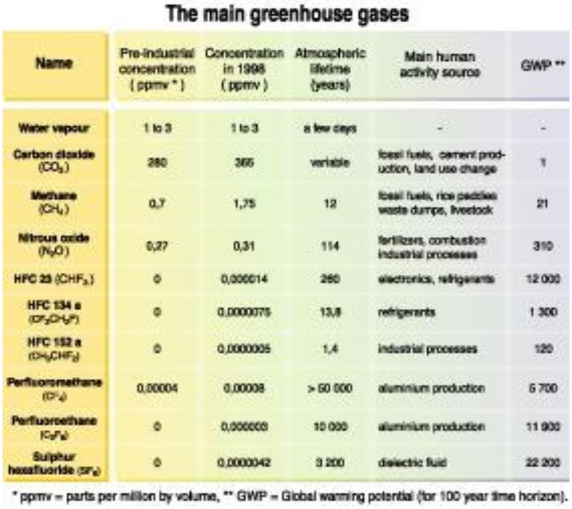
It is needed to specify that the ambient problem denominate *greenhouse effect* is more concretely an increasing of it. The changing in this effect can be due to the natural or anthropogenic causes.

During the history, several scientists had identified the first clue to define the increasing of the greenhouse effect:

- In 1896, Arrhenius hypothesized that the use of the carbon as a fossil fuel could increase the CO_2 quantity leading to a global heating.

- Callendar, in 1938, showed an increasing of a 10% in the quantity of CO_2 since 1890, but was not considered because it was thought that the ocean was capable to absorb the excess. This fact was refused, in 1956 when was proved that the oceans, because of their chemical composition, had a restricted capacity to absorb the exceedance in CO_2. As a result, in 1957, the scientific community began to make temperature measurements to control the variation in global temperature.

The causes of the increasing greenhouse effect, is mostly due to the increasing in the quantity of greenhouse gases emitted by anthropogenic sources.



The main greenhouse gases

Name	Pre-industrial concentration (ppmv *)	Concentration in 1998 (ppmv)	Atmospheric lifetime (years)	Main human activity source	GWP **
Water vapour	1 to 3	1 to 3	a few days	-	-
Carbon dioxide (CO_2)	280	365	variable	fossil fuels, cement production, land use change	1
Methane (CH_4)	0,7	1,75	12	fossil fuels, rice paddies waste dumps, livestock	21
Nitrous oxide (N_2O)	0,27	0,31	114	fertilizers, combustion industrial processes	310
HFC 23 (CHF_3)	0	0,000014	260	electronics, refrigerants	12 000
HFC 134 a (CF_3CH_2F)	0	0,0000075	13,8	refrigerants	1 300
HFC 152 a (CH_3CHF_2)	0	0,0000005	1,4	industrial processes	120
Perfluoromethane (CF_4)	0,00004	0,00008	> 50 000	aluminium production	5 700
Perfluoroethane (C_2F_6)	0	0,000003	10 000	aluminium production	11 900
Sulphur hexafluoride (SF_6)	0	0,0000042	3 200	dielectric fluid	22 200

* ppmv = parts per million by volume, ** GWP = Global warming potential (for 100 year time horizon).

Figure 2.6.- Main greenhouse gases (Source: UNEP/GRID-2005)

- *The CO_2, principle greenhouse gas (GHG):*

The increasing in the quantity of CO_2 in the atmosphere is mostly due to the use of fossil fuels and deforestation, accounting for at least a 75% of the all GHG emissions.

In the last 40-50 years, the increment in the concentration shows a trend of about 1.4 ppm/year, going from 315 ppm in the '60s to about 390 ppm now.

The CO_2 has a time residence in atmosphere of 100-200 years so is still a problem even though the emissions from fossil fuels are limited.

Apart from the GHG emitted by natural and anthropogenic sources, the absorption and reflection of the solar radiation is also made by the aerosol suspended in the air, with other effects in the environment.

2.2.2.- Particulate matter

The term atmospheric particulate matter (PM) is referred to liquid and solid particles suspended in air, commonly named as atmospheric aerosol. Atmospheric aerosol has an effect on the quality of the air and, as a consequence, on human health and ecosystem environments, playing an important role in Earth's climate system.

The particulate matter is denominated one of the six 'criteria pollutants' by the Environmental Protection Agency (EPA) of United States.

The other five are ozone, sulphur dioxide, nitrogen dioxide, carbon monoxide and lead. The EPA is the responsible to set national ambient air quality standards (NAAQS) to ensure a good public health.

In addition, the air quality is one of the World Health Organization's components signed as potentially carcinogenic, because of the amount of components present in the PM.

2.2.2.1. - Definition

The particulate matter is defined in terms of the source of emission and atmospheric conditions, which can vary greatly in size, shape and chemical composition of the PM.

The basic aerosol properties are:

- Chemical composition: elements, ions
- Speciation: chemical forms, oxidation
- Atmospheric residence time
- Water solubility
- Size
- Concentrations
- Morphology: shape of individual particles
- Hygroscopicity and deliquescence
- Optical properties: UV/Vis absorbance, reflectance.

The shape and size are often the key properties to describe the atmospheric aerosol.

The shape of the particles determines the source of origin and the processes in which the particle was involved.

- *Shape by fragmentation*: Are irregular and angular and rarely round.

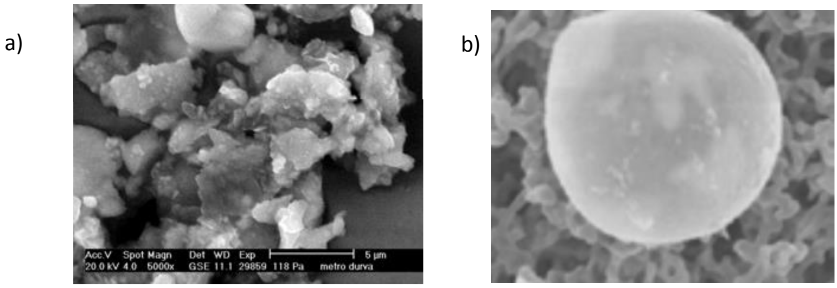


Figure 2.7.- (a) Particles from urban station; (b) Particle of Saharian dust.

- *Shape by combustion*: Are usually round particles or coccus, spherical or irregular.

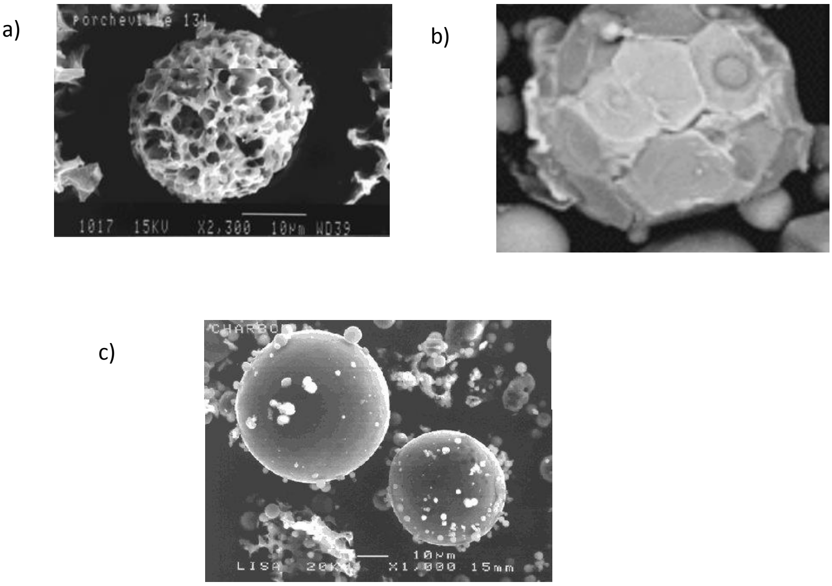


Figure 2.8.- (a) Carbonaceous fly ash (porous); (b) Iron oxide (in fly ash particle);

(c) Siliceous fly ash

- *Shape of ultrafine particles*: Are clusters, bunches or fractal structures of spheres

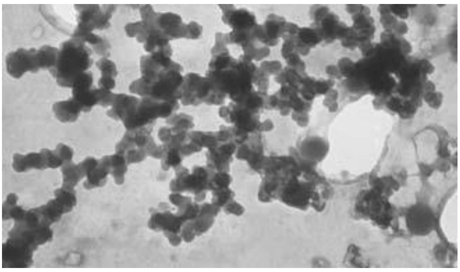


Figure 2.9.- Diesel soot (20-30 nm)

The classification of particulate matter is commonly made according to its size. Since the PM has usually an irregular shape is necessary to establish a particle size definition and use a standardized measure, referred to its aerodynamic radio measured in microns (µm).

The aerodynamic radio is a function of several characteristics that the particle under study must share with a sphere or a circle, such as diameter, volume, mass, volume/surface ratio, optical characteristics and aerodynamic equivalent diameter.

The most used characteristic to define PM is the aerodynamic radio, which is defined following the definitions of gravitational settings.

For a spherical particle, the gravity force and diffusive force are explained as:

$$F_d = 3\pi\eta v d \;\rightarrow\; \quad Increase\ with\ v$$

$$F_p = \left(\rho_p - \rho_{const}\right)\frac{d^3}{6}\,\pi g \quad when \quad \rho_p \gg \rho_{const}$$

When the two equations are equal so F_d=F_p

$$\upsilon_{TS} = \frac{\rho_p d^2 g}{18\eta} = const$$

where the v_{TS} is the terminal settling velocity; ρ_p and ρ_{cont}, the density of the particle and the air; and η, the coefficient of dynamic viscosity. Likewise, to an irregular particle is needed a correction for the shape, χ, because of the different resistance force related to a spherical particle.

$$\chi \equiv \frac{F_d}{F_{d_e}} = \frac{F_d}{3\pi\eta\upsilon d_e} \quad so \quad F_{d_e} = 3\pi\eta\upsilon d_e\chi$$

At the condition in which F_d=F_p, the definition of the terminal settling velocity for irregular particles is explained:

$\upsilon_{TS} = \frac{\rho_p d_e^2 g}{18\eta\chi}$ compared to the v_{TS} for a spherical particle: $\upsilon_{TS} = \frac{\rho_p d^2 g}{18\eta}$

To maintain the mathematical formulism, is obtained the definition of aerodynamic diameter:

$$d_a = \sqrt{\frac{\rho_p}{\rho_0\chi}}\, d_e \ ; \quad \upsilon_{TS} = \frac{\rho_0 d_a^2 g}{18\eta}$$

Like this, the aerodynamic diameter for an irregular particle is equivalent to the diameter of a spherical particle with density 1g/cm3 (water droplet) that has the same velocity as the particle under consideration.

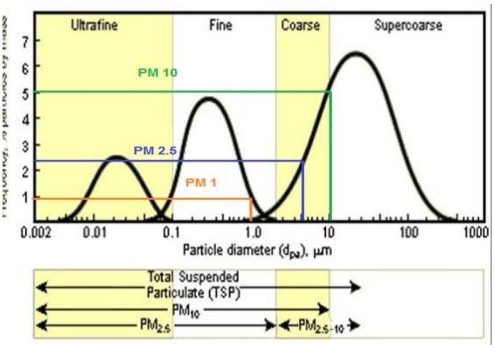
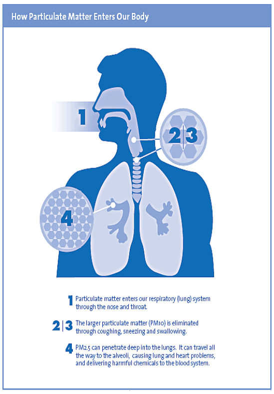


Figure 2.10.- Size distribution and modes

Based on its aerodynamic radio, the classification of PM is made, having different effects on health.

- <u>PM 10</u>: Is the fraction of molecules in which aerodynamic radio of particles is lower or equal to 10 µm. This group remains on the nose barriers.
- <u>PM 2.5</u>: It refers to the particles lower or equal to 2.5 µm and they pass the first barrier, being stopped in lungs.
- <u>PM 1</u>: Is the finest fraction of particles and collect those with aerodynamic radio of 1 µm or lower. These particles are the most dangerous due to their ability to pass into the blood.



How Particulate Matter Enters Our Body

1 Particulate matter enters our respiratory (lung) system through the nose and throat.

2|3 The larger particulate matter (PM_{10}) is eliminated through coughing, sneezing and swallowing.

4 $PM_{2.5}$ can penetrate deep into the lungs. It can travel all the way to the alveoli, causing lung and heart problems, and delivering harmful chemicals to the blood system.

Figure 2.11.- Respiratory barriers

The size distribution of atmospheric aerosol gives important information about the sources of emission and the formation processes.

The European Environment Agency in collaboration with the European Parliament have set threshold values of PM that have not be surpass in order to assess a better air quality. In the Italian case, the Ministry have been settled several regulations to control the maximum values. The Ministerial Decree 60 of 2nd April 2002, set alarm threshold values for some pollutants, among which are sulphur dioxide, NO_x and nitrogen oxide, particulate matter, lead, benzene and carbon monoxide.

The new directive *2008/CE/50*, expects a maximum daily value for the PM_{10} of 50 µg/m^3, that has not to be exceed more than 35 times in a year and a yearly maximum level of 40 µg/m^3 For the $PM_{2,5}$, is expected the maximum value of 25 µg/m^3 and is planned to be reduced within 2020.

2.2.2.2.- Formation processes:

The PM is composed by a several group of molecules. Each group has an effect on the atmospheric situation: changes in visibility absorb or reflect UV rays, participate in photochemical reactions and ageing of particles. From the environmental point of view, PM constitute a policy issue in climate sciences and air quality.

The photochemical formation processes become in the atmosphere always in presence of an oxidant and an oxizidable molecule.

The oxidant ones are produced in the atmosphere by precursors, always in presence of solar radiation that leads to the excitation of the basal state of molecules. This characteristic defines these processes as photochemical reactions.

The photochemical reactions come from the absorption of a photon by a molecule present in the atmosphere, producing, as a result, the dissociation, direct reactions with other compounds or fluorescence phenomena.

The most common molecule that takes part in these reactions is the tropospheric ozone.

- *Tropospheric ozone:*

The ozone present in the atmosphere is contained mostly in the stratosphere, but a 10% is in the troposphere.

It takes part in the chemical reactions, forming radicals that trigger the photochemical reactions in atmosphere and affect the climate due to its effect as greenhouse gas. Its presence is also increased by the photo-reactions with the particulate matter in the atmosphere.

The photochemical smog is defined as *'a mix of compounds related with the emissions of nitrogen oxides and hydrocarbons in presence of solar radiation'*. The photochemical pollution was only recognized as a problem in 1950, after a contamination event related with the irradiation of nitrogen oxides forming the so called *smog*.

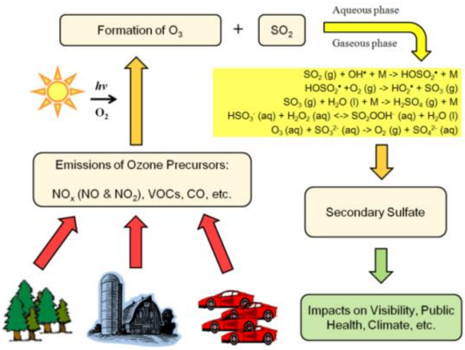


Figure 2.12.- Ozone lifecycle

The base reaction of ozone production is represented like following:

$$NO_X + hv \rightarrow O + NO \quad with\ a\ \lambda \leq 420\ nm$$

$$O + O_2 + M \rightarrow O_3 + M$$

→ *M* is a gaseous molecule that absorbs the vibrancy of the photochemical reaction. It can be a molecule of ozone or nitrogen present in the atmosphere.

Following to the previous reaction, occurs the dissociation of the new formed ozone:

$$O_3 + NO \rightarrow NO_2 + O_2$$

As will be explained in following parts, particulate matter is present in the atmosphere by the direct emissions (primary PM) and the photochemical reactions of gaseous precursors (secondary PM).

The direct emitted pollutants are mostly sulphur compounds, nitrogen compounds, organic compounds and inorganic carbon. In the other hand, the secondary PM is formed by reaction of two different emitted pollutants or with the components of the atmosphere.

There are not so many pollutants that maintain their ‘identity’ when are emitted in the atmosphere:

- *Sulphate formation:*

Between the gaseous precursors of secondary formed pollutants, sulphur dioxide constitutes almost a 95% of the anthropogenic emissions. It is emitted in the atmosphere by the oxidation of sulphur during combustion.

$$O_2 + S \rightarrow SO_2$$

Sulphur dioxide is very soluble and reactive in water, being possible to remove it in processes of rain-out , in which SO_2 act as condensation nuclei and accumulate water forming a drop; or wash out, in which is the rain that washes away the pollutants by absorbing them in the drops.

Moreover, the formation of sulphate inside drops is another of the processes that occur in the atmosphere by the photochemical action of O_3 and OH.

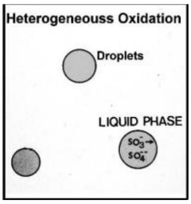
The sulphate is produced in the atmosphere by the reaction of SO_2 and H_2S, formed by the decomposition of organic matter in the soil. About half of the sulphur dioxide is oxidized during daytime, with an increasing rate when NO_x or hydrocarbons are emitted.

The photochemical formation of sulphate is done by the reaction as following:

$$SO_2 + OH^{\cdot} + M \rightarrow HOSO_2 + M$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4\ (g)$$



The inversion rate from the gaseous precursor to the sulphate is 1-10% per hour.

- *Nitrate formation:*

The nitrogen is the main constituent of the atmosphere present in the diatomic form (N_2).

Between its gaseous products present in atmosphere, the nitrous oxide is the most spread and is formed by the denitrification i.e. the reduction of nitrite and nitrate.

The ammoniac (NH_3) is one of the nitrogen compounds that is still on study the partition between natural or anthropogenic sources. The importance of it, is the capacity to give a basic pH to the atmosphere by the reaction with the acid substances.

The oxides of nitrogen (NO_x) are the most important nitrogen pollutants due to their role in the photochemical smog.

As for the sulphur oxide, the nitrous oxide reacts in the atmosphere with radicals and water to form the nitric acid. The photochemical reaction is 10 times faster than for SO_2. The peak daytime conversion rate is about 10-50% per hour.

During night-time, nitrous dioxide is oxidized by ozone and nitrate radicals.

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + OH^{\cdot} \rightarrow HNO_3$$

One of the most known cases of secondary particulate matter formation is the reaction between the ammoniac and the sulphuric acid:

$$H_2SO_3 + NH_3 \rightarrow (NH_4)_2SO_4$$

The European directives establish some threshold values to the concentration of NO_2 in the atmosphere:

Limit values *(Annex XI and XII to the European Directive 2008/50/CE)*	
Annual limit value (NO_2)	**40 µg/m^3**
Hourly limit value (NO_2) (not to be exceeded more than 18 times in a year)	**200 µg/m^3**
Annual critical level for the (NO_x) protection of vegetation and natural ecosystems	**30 µg/m^3**
Alert threshold (NO_2)	**400 µg/m^3**

Table 2.1.- Limit values of NO_2 in the atmosphere (From EU directive 2008/50/CE)

Over the last decade, the most widely studied subjects are the organic aerosol (OA) formation, new particle formation, aerosol sources and radiative forcing of aerosols *(Fuzzi et al. 2015)*.

2.2.2.3.- Sources:

Atmospheric aerosol is ubiquitous in the atmosphere and is formed from a variety of anthropogenic and natural sources, being emitted into the atmosphere directly, as primary PM or formed in the atmosphere from precursor gases, such as sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and volatile organic compounds (VOC), by physical and chemical processes, as secondary PM.

Each source produces particles with specific physical, chemical and optical characteristics.

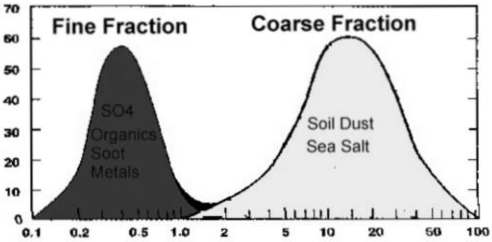


Figure 2.13.- Size distribution of pollutants based on sources

Natural sources:

Natural sources of atmospheric particulate matter include wind and wave action, volcanic activity and biogenic emissions. In general, these sources lead to suspension of coarse PM (dust and sea salt particles)

Marine sources:

Atmospheric aerosol emitted by the marine environment is one of the most important natural primary aerosols. It can scatter light; act as cloud condensation nuclei, affecting radiation budget and cloud physics; interact with anthropogenic pollution, affecting the gas phase cycles and promoting the acid depletion and halogens.

Primary marine aerosol come from breaking waves and wind action in the surface of the ocean, being this second class which gives the major amount with estimated of global emissions of 2.000-10.000 Tg/yr *(de Leeuw et al., 2011; O’Dowd et al., 1997)*.

The finest particles (0.1-1µm) have a large lifetime in the atmosphere being transported in long-range trajectories.

Aside from sea salt emissions, marine sources present organic compounds in their composition. These can be present due to two different mechanisms:

(1) Included by breaking waves

(2) Oxidation of gas-phased volatile organic compounds (VOC), such as ammines, dimethylsulfide (DMS), isoprenes and monoterpenes forming secondary organic aerosol (SOA).

Mineral dust

Mineral dust aerosol often is the predominant emission in large parts of the planet. Is estimated that the 75% is from natural origin, the rest is mainly due to agricultural emissions (*Ginoux et al. 2012*). Mineral dust contributes to the radiative forcing in two different ways: the iron particles in mineral dust absorbs radiation so contribute positively, making a warming effect on the atmosphere. The scattering of the light by the particles, leads to a negative effect, cooling the surface.

Anthropogenic sources:

The most common anthropogenic sources include traffic emissions, industrial and manufacturing processes and combustion (residential heating and use in power plants).

In general, anthropogenic sources are responsible for the formation of fine particulate matter, forming the secondary particulate matter.

Wood combustion

In residential heating has been increased the use of wood as fuel which emissions contribute to the formation of secondary organic aerosol.

Chemical and physical properties of particles emitted might vary depending on the combustion conditions and wood employed. The exposure to wood smoke carry out several effects on human health, such as reduced resistance to infections, asthma and a decreased lung functions (Boolling et al.,2009)

Road traffic

Emissions of this type of source contribute larger to total particulate matter in urban areas. It has been demonstrated that exposure to road traffic emissions have harmful effects on health. It’s important to understand some characteristics of emissions to better relate them in source apportionment.

This emissions include the contribution of exhaust, resuspension of dust (non-exhaust emissions), but also the emission of tire and brakes wear. Non-exhaust emissions contribute mainly to coarse mode of PM ($PM_{10-2.5}$) while exhaust contribute predominantly to fine particles ($PM<2.5$ µm).

Contribution of non-exhaust is becoming more important, but the information about them is unfortunately short. It’s estimated that 90% of the road emissions come from non-exhaust sources.

2.3.- Radiative forcing

The radiative forcing is defined as *'the changing in the global irradiance, measured in W/m^2, due to the variance of determined specie'*.

The aerosols have different effects on radiative forcing, changing several characteristics of the atmospheric environment. These effects can be direct, indirect and changes in the heterogenic chemistry of the atmosphere.

Direct effects: Are related with changes in the optical properties of the components of the atmosphere, such as scattering and absorbance of short and long wavelengths of radiation.

Indirect effects: Are divided in 'cloud albedo effect', 'cloud lifetime effect' and 'semi-direct effects'. The first ones are linked to the cloud condensation nuclei and the third with the absorbance of solar radiation by the aerosol, heating the air and evaporating water droplets.

→ Cloud albedo effect: Increasing the number of aerosol particles emitted, also increase the cloud condensation nuclei, forming more water droplets with a minor radio that reflect the solar radiation inhibiting the arrival to the surface, bringing to a possible cooling effect.

→ Cloud lifetime effect: A high number of little particles decrease the efficiency of rain, increasing therefore the lifetime of particles in the atmosphere.

→ Semi-direct effects: The aerosol particles absorb solar radiation, for so heating the troposphere enhancing the evaporation.

According to the molecule position that absorbs radiation, the effect in the radiative forcing can be positive or negative.

Heterogenic chemistry: It means that molecules present in the aerosol can act as catalysts or reaction sites, accelerating some reactions.

In 1988, it was created a regulatory committee to assess the aspects of climate change and its impacts, named Intergovernmental Panel on Climate Change (IPCC).

Over some years, this public entity has studied the known list of pollutants publishing a report in which are specified the effect of each group on the average temperature of the Earth.

Every year is published a report to communicate the new progresses in the accuracy of the measurements and the correct effect of the pollutants in the radiative forcing.

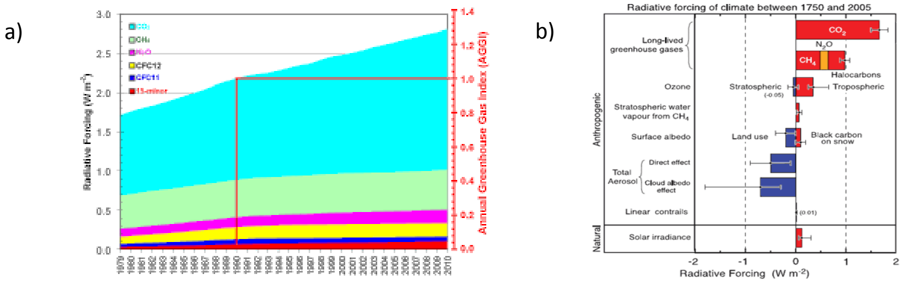


Figure 2.14.- *(a)* Contribution to radiative forcing from GHG; *(b)* Contribution to radiative forcing (Source: IPCC 2007)

Nowadays, it is still on study the effect of the each pollutant on the radiative forcing and making more accurate the measurements to reduce the uncertainty of them. There is still a lot of work to make more precise the apportionment of the pollutants.

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3. Aim of thesis

The aim of this thesis work is to make a full study of the composition of particulate matter in different types of sites. The wide range of compounds present in the atmosphere, require numerous analytical techniques in order to obtain the most complete database of the components. There are several techniques proved and standardized to analyse a huge group of molecules.

Since now, these analytical techniques available to characterize the particulate matter are focused to identify the inorganic part (ion chromatography) or groups of molecules, such as the water soluble carbon.

The organic fraction is still unknown, especially the macromolecules which suppose a risk due to their toxicology. In this PhD project, we focus our interest in make a deep study of molecular markers of this organic part in a background site in the North Italy. However, the methods used to characterize this fraction are not clearly proved in terms of recovery of extraction methods or the best analytical technique to quantify the single molecules. For this reason, we have developed a new extraction method, starting from the information found in the published articles.

The obtained data will be further used to run source apportionment models to identify and relate molecular markers with the sources of emission.

In addition, we have collaborated with a European Institute in two projects to characterize the emissions of a coastal city (France) and rural site (Switzerland) organic fraction with new online analytical techniques.

So, in this thesis were worked out:

- The analyses of inorganic part and soluble organic fraction in a background site.
- Develop an improved extraction method of the not water soluble organic fraction.
- Analysis of the molecular markers.
- Analyses of the water soluble organic compounds in two European different sites in the frame of characterization of organic fraction with new analytical techniques.

4. Identification and quantification of markers in a background site

4.1.- Introduction

The impact of particulate matter (PM) on health represents a serious scientific and policy issue. For air –quality monitoring often is interesting to know the population exposed to certain species above national and international limit values. In the other hand, for climate change related problems are more interesting see changes and trends in atmospheric composition of background air masses.

The value of identify and characterize each zone help to understand the different types of sources. Sites of study are located in areas with weak horizontal gradients of the species of interest and away from emission sources.

The definition of the site representativeness includes 2 concepts:

1) There is no difference between the concentrations of the studied species in the representative area of the site to the concentration measured at the station by more than a percentage based on the radio of the area.

2) A defined point of measurement is representative of the average in a larger area, if the probability that squared difference between the concentration in the point and area is smaller than a certain threshold, which has to be higher than the uncertainty of the measurements.

According to the previous studies carried by *Nappo et al. (1982*), the representativeness will not vary with time (season and day-to-day) but depend on species of interest.

There are some factors that influence the concentration of a certain trace species within a certain volume, such as horizontal and vertical transport, mixing, chemical transformation, surface deposition and emissions. The species with strong surface sources and with short atmospheric lifetime due to photochemistry and deposition, show stronger spatial variability and smaller areas of representativeness than species with weak surface fluxes and long lifetimes.

Based on the zone in which pollution is studied, it has been made a division based on its position: urban and suburban sites and rural and remote sites. Likewise, it has been settled the terms of:

-*Traffic site*

Are typically hot-spots located in areas of very sharp concentration gradients. The area of representativeness can be defined in terms of length of the road, 100 m or more in central areas and 1 km long or more in suburban/other areas and should be located at least 25 m street junctions to avoid influence from other streets.

This type of sites are defined by the traffic volume (accuracy: ±2,000 vehicles/day), traffic speed (accuracy: ±5 km/h, average daytime traffic) and the distance from the kerb (accuracy: ±1m)

- *Urban and suburban stations*

These types of sites are located within urban areas or agglomerations. The radio of area of representativeness is about 10 m.

-*Urban background site*

Are defined by the biogenic emissions and anthropogenic emissions referable to the short distance from the urban sites. It is located in areas with a radio between 100 m to 1 km and they have a surface from 3 km^2 to 6 km^2.

- *Near-city background site*

Is the zone located in a rural or agricultural area with a distant 3 to 10 km far from built-up areas and other major sources. The radio of the considered area of representativeness is about 1-5 km with a surface higher than 100 km^2.

- *Regional station*

Located in a rural or agricultural area with a distance from 10 to 50 km away from built-up areas. The radio of the considered representative area is between 25 and 150 km with a surface up to 10,000 km^2 with a minimum radio of 20 km.

The sub-classification of ‘near-city background site’ is to differentiate the stations influenced by nearby large agglomerations and the ‘regional stations’ affected more by the sources located in the up-wind area (long-range transport) with no possibility to distinguish the influence from a single source. Rural stations in areas with many closely located cities may be near-city background stations.

- *Remote site*

Are the stations used to monitor the base levels of pollution resulting from natural sources (‘natural background level’) and long-range transport of air pollutants. Are located in rural or agricultural areas with a minimum distance of 500 km from built-up areas and other major sources. Its representative area is about 10,000 km^2 with a radio between 200 and 500 km.

There is a high interest on the understatement of the sources of organic carbon (OC) due to the organic fraction account for a large part of the total PM mass.

Organic carbon fraction is a mixture of hundred compounds emitted directly in the atmosphere from biogenic or anthropogenic sources (primary OC) or formed by oxidation of volatile precursors (VOC), to lower volatility products (secondary OC). Some of this emitted compounds play an important role in PM health effects due to their toxicological potential impacts (e.g. PAH). In addition, certain organic compounds (organic markers) can be used for the identification of PM sources. Identification of pollution sources is essential for air quality planning.

The study will focus on methodological aspects with particular emphasis on the secondary organic aerosol (SOA) and the relationships between chemical and physical properties that confer to aerosol particles. This study's aim is perform a source apportionment of PM sources.

An overall characterization of PM composition has been carried out, paying more attention to organic substances such as levoglucosan, water soluble organic carbon (WSOC), PAHs (identified as carcinogenic by WHO), fatty acids, hopanes and some SOA markers.

The collected data will be processed using a combination of classic and advanced tools for receptor modelling.

4.2.- Sampling Campaign:

This study aims at performing source apportionment of PM sources in the background site of Ispra in Po Valley.

Aerosol sampling was performed at the Joint Research Centre station for atmospheric research in Ispra, located in the northwest edge of the Po Valley in the northern Italy. The site was previously characterized and compared with other remote and background sites and it was categorized as a typical background site (*Gilardoni et al. 2011*).

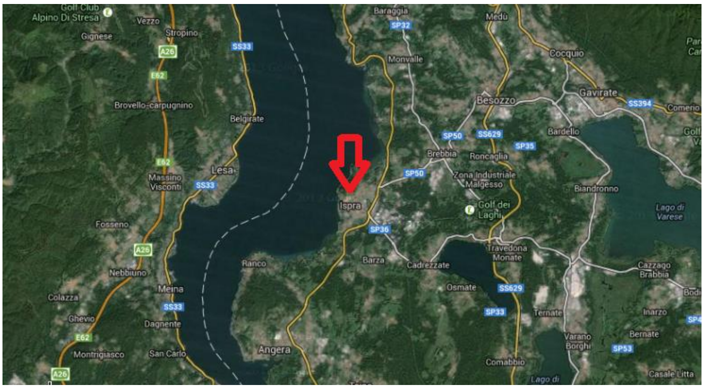


Figure 4.1.- GPS position of sampling point

The project is a part of the ABC-IS (Atmosphere, Biosphere, Climate – Integrated Station).

Sampling campaign was carried out from June 2011 to December 2012, collecting 100 samples of PM10 with a frequency of 1 each 6 days, of 24 hours sampling, using low volume samplers (*Leckel SEQ 47/50 and FAI Hydra*) in which are collected simultaneously samples in quartz and Teflon. The two samplers were settled 450 m away from the building in order to have the samples unaffected by the proximity to people.

In the Leckel SEQ 47/50, are collected the quartz samples, while in FAI Hydra, being a dual channel instrument, were made the sampling of quartz (*Pallflex tissuequartz 2055QAT*) and Teflon *(Pall Teflo ®)* samples. The filters, previously to the sampling, were pre-fired at 700 °C for 1 hour in order to remove all the organic material that could be present.

LECKEL SEQ 47/50

-Equipped with PM10 inlet according to CEN EN 12341.

-Sampling flow-rate 38.3 l/min, 1 quartz filter every six days.

FAI Hydra Sequential Gravimetric Dual Sampler.

-PM10 inlet according to CEN EN12341.

-Dual channel sequential sampling.

-Sampling flow-rate 38.3 l/min.

-Two filters contemporaneously (1 quartz filter and 1 Teflon filter) every sixth day.

Figure 4.2.- Sampling instruments

The distance from major anthropogenic emission sources is larger than 10 km. The main urban areas around the site are Varese to the East (20 km), Novara to the South (40 km) and Milan to the South-east (60 km).

Samples are subjected to different analytical techniques:

Parameter	Measuring technique	Sampling period
Total Mass	Gravimetry	06/11 - 12/12
EC/OC	TOT	Regular ABCIS
Ions	IC	Regular ABCIS
Trace elements	EDXRF	06/11 - 12/12
Aerosol Size distribution	SMPS - APS	Regular ABCIS
Aerosol Absorbance	aethalometer	Regular ABCIS
Organic markers	GC-MS	06/11 - 12/12

Table 4.1.- Analyses performed to samples.

4.3.- Experimental:

4.3.1.- Gravimetric analysis:

The gravimetric analysis of all filters has allowed to assess mass concentrations. Such analysis was carried out using the two techniques: CEN12341 and EMEP method.

- *CEN 12341:*

Previous to be weight, filters were conditioned for 48 hours in an air-controlled and temperature-controlled room. The conditions of the room were 20 ± 1 °C and relative humidity of 50 ± 3% in order to maintain in the best conditions filters to avoid the loss of material. Weighing method was carried out with an analytical balance (*METTLER TOLEDO AX26*) connected to a computer that record the measurements simultaneously. The balance is calibrated with Italian standards to assure the repeatability of the measurements assessing the weighing uncertainty.

- *EMEP method:*

For this method, filters were preconditioned for 24 hours in a temperature controlled box at 20 ± 2 °C and relative humidity 20 ± 5%. These properties were automatically regulated by a system that control the dry air input.

Filters were weighted with an analytical balance Sartorius MC5.

In order to guarantee the quality of measurements, a standard was weighted 10 times following the two explained methods.

Balance intercomp. (**10 replicates)**	**Mettler AX26**	**Sartorius MC5**
Weight mg	100	100
Standard deviation	0,000843	0,000675
Weight mg	50	50
Standard deviation	0,000632	0,000789

Table 4.1.- Balance intercomparison (From Technical report, Belis et al.,2012)

Standard deviation of both analytical balances are <1 µg, so both methods are comparable.

4.3.2.- Water Soluble Compounds:

The water soluble fraction of the aerosol emitted can absorb light in the visible and ultraviolet region, but its overall absorbing effect is almost negligible, being only important on the bright surface.

The major chemical constituents of PM are inorganic ions, mainly nitrate, sulphate, ammonium. This contributes approximately a 40% of total PM mass.

- *INORGANIC IONS:*

Their presence in the samples can be due to direct emissions or formed by photochemical reactions in the atmosphere. As explained before in *Chapter 2*, the sulphuric acid and nitric acid are formed in the atmosphere by the reaction with photochemical active molecules and with water to form the correspondent acids.

Sulphuric acid → Is mainly present in the atmosphere by the direct emission of the gaseous precursors by the anthropogenic sources (SO_2 from fossil fuel combustion or industrial processes). It is present too by the emission of marine spray, as natural source.

Nitric acid → It is one of the main secondary aerosol, formed by the oxidation and solution in water vapour of its gaseous precursors (NO_x).

Chloride → This ion is present in the atmosphere by the emissions of sea salt particles.

Sodium → It comes mainly by the biogenic emissions of sea salt particles, but its presence is also because of combustion processes. It can form soluble salts in the atmosphere with the anions present in it.

Ammonium → Is the acidic form of ammonia emitted to the atmosphere by both natural and anthropogenic sources. Is mainly related with the agricultural activities, because is one of the components of compost. Its importance is due to the capacity to turn basic the atmosphere environment when is dissolved by the humidity.

Potassium → Is the cation correlated with emissions of biomass burning and is present in the atmosphere as inorganic salts, coming from the incomplete combustions. Its presence is also a result of potassium silicate, a component of talc.

Magnesium → Comes mainly by the abrasion of rocks based on magnesium sulphate, that's why they are in the coarse fraction of particulate matter.

Calcium → Is present in natural form as a soluble salt coupled with sulphate that can be found in the air by the erosion of the rocks containing it or by the contribution of marine spray.

- *LEVOGLUCOSAN:*

The levoglucosan (1,6- anhydro-β-D-glucopyranose) is an anhydrosugar produced in the combustion of wood due to the pyrolysis of the cellulose at temperatures higher than 300 °C. Its structure is formed by a six carbon ring with an oxygen bridge.

Due to the stability of this molecule and its unilateral way of production is used as marker of wood burning. It is mostly present in winter correlated to a higher use of wood as house heating.

- *ORGANIC ACIDS:*

There is a little part of organic acids present in the atmosphere that are soluble in water due to their lower molecular weight and their polarity.

This group contains the short chain acids, such as formic acid, acetic acid, propionic acid, methansulphonic acid and oxalic acid. Those are present in the atmosphere more commonly in the gaseous phase, participating in the acid precipitation in urban and remote areas. In the ‘80s, it was estimated that organic acids may contribute up to 64% to the acid rain deposition, in the particular case of formic and acetic acid, can change the acidity of the rain from a 16% to a 35%. They can be present in the atmosphere by numerous sources, but they are not adequately explained yet. They are emitted by direct emissions but also by the transformation of precursors.

Carboxylic acids have a weak reactivity in the atmosphere, so they are not subjected to removal in the gas phase. For the specific case of formic acid, its main gaseous precursor is the formaldehyde but is also demonstrated that can be formed by the decomposition of the isoprene emissions in the reaction with the ozone present in the atmosphere (*Jacob, 1986*).

For the dicarboxylic acids, due to the presence of two carboxylic groups, they present a higher polarity and molecular weight, being less volatile.

In previous studies, was found that the most present dicarboxylic acid is the oxalic acid, followed by malonic, succinic, maleic and adipic. These acids are associated with the particle phase.

Their contribution to the total PM is about a 1-3% in urban and suburban areas and up to 10% in marine environments. *(Kawamura et al.1993)*.

Their origin is from the emissions mostly of biomass burning, fossil fuels and photo-oxidation of precursors.

Methansulphonic acid (MSA) is commonly used to consider the contribution of biogenic emissions from marine environment and it represents almost the total amount of the biogenic emissions of sulphur into the atmosphere. In the artic region, for example, the emissions from biogenic sulphur are up to a 42% of the total. *(Bates et. al., 1992)*

This acid is formed by the oxidation in the atmosphere of the dimethylsulphoxide (DMS), which is formed by the enzymatic decomposition of dimethylsulfonium propionate (DMSP) by the algae. The DMS is transferred to the atmosphere through the air/sea interface. The DMS emissions comprise over a 50% of sulphur flux in the atmosphere.

The formation process of the MSA is a photochemical oxidation reaction of the DMS with radicals present in the atmosphere, the $OH^{\cdot}$ during the day and $NO_3^{\cdot}$ during the night.

Together with the MSA, the oxidation of DMS also leads to the formation of sulphate, denominate as non-seasalt sulphate (nss-SO_4^{2-}), due to the secondary formation nature. In fact, the MSA can be considered the marker of the DMS oxidation products and, as a consequence, the marker of biogenic emissions.

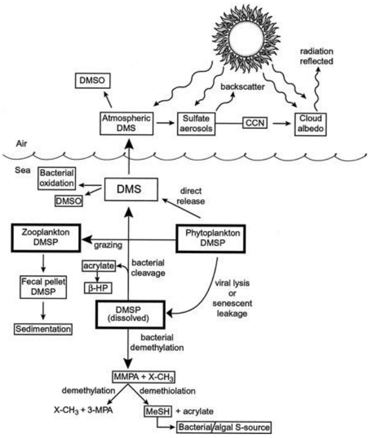


Figure 4.3.- MSA formation cycle

- *WATER SOLUBLE ORGANIC CARBON:*

The carbonaceous fraction of particulate matter consists in a mix of elemental carbon and a various types of species of organic compounds, that constitutes the organic matter fraction (OM). Due to its complex nature, the knowledge about the composition, sources and behaviour is limited.

The origin of organic carbon can be both from primary origin or secondary formation, being distinguish in primary organic aerosol (POA) and secondary aerosol (SOA). The POA is composed by the carbon containing molecules emitted that are condensed onto the particles; while SOA, are the organic compounds formed in the atmosphere by the gas-to-particle processes.

The soluble part of the organic matter can alter the hygroscopicity of the particles, changing their characteristic, making them more effective in the condensation processes, acting as nuclei and therefore changing the radiative effects of the particles.

The water soluble organic compounds (WSOC) contribute to the biomass burning emissions, the formation of secondary organic aerosol via the oxidation or organic precursors and the ageing of the PM.

4.3.2.1.- Extraction methods:

There is not a certified method to extract the PM samples. Commonly, samples are extracted with a unique step with a certain volume of water and a different time cycles in the ultrasound bath (*Chow and Watson, 1999*). In our laboratory was set-up a method to extract samples in order to obtain a high solubilisation of ions, in which the sample undergo three extraction steps helped with ultrasonic bath (*Fermo et al. 2006*).

The extraction method consists in three repeated steps in which a 1,5 cm^2 sample, contained in a plastic tube, is put in contact with approximately 2 ml of ultrapure water (*Milli-Q Merck*) and is immersed in the sonication bath (*Branson 2510*) for 20 mins. The solution is then transferred to another plastic tube, without removing filter, renewing water and repeating the first step another 2 times. Finally, the filter is also move with the last extracted solution. This procedure allows to extract quantitatively all the soluble ions, with almost 100% of recovery.

	1st step	*2nd step*	*3rd step*
Chloride	29 ± 15%	55 ± 15%	16 ± 5%
Nitrate	85 ± 3%	11 ± 3%	2 ± 1%
Sulphate	83 ± 4%	13 ± 2%	5 ± 2%
Ammonium	80 ± 6%	15 ± 4%	5 ± 3%

Table 4.1.- Recovery of three extraction steps

4.3.2.2.- Ion chromatography analysis:

The chromatography analyses allow separating the ions solubilized, commonly in water solution, by affinity with an ionic exchanger as stationary phase with opposite charge of the analyte of interest. The separation occur by how many time the ions are hold by the affinity of the analytes, based on the charge and the size of the ion: larger is the ion and higher is the charge, more time is retained.

To fulfil the separation, is necessary a mobile phase, which is a contra-ion, with certain strength and the same sign of charge of the analyte that has to be separated.

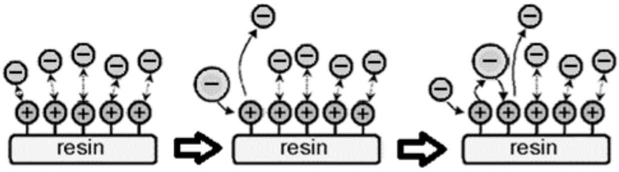


Figure 4.4.- Ion exchange principle. (From Shimadzu)

In the case of anion separation, the columns in which separation happens, the stationary phase is commonly functionalized with ammine or amide groups ($-NHR_2^+$; $-NR_3^+$) and the mobile phase is a mixture of carbonate/bicarbonate (CO_3^{2-}/HCO_3^-) or potassium hydroxide (KOH).

For the cation separation, the functionalized groups are mainly sulphonic or carboxylic, in which the solvent that acts as contra-ion is methansulphonic acid.

The detector of ionic chromatography analysis uses the changes in conductivity as detection system. Being an ionic solution, is needed an additional step before the solution enters in the detector, in order to suppress the signal of the eluent.

The suppression system, consist in a membrane connected to an electric impulse, which is variable based on the concentration of the eluent, that is capable eliminate the current charge and enhance the signal to the analytes.

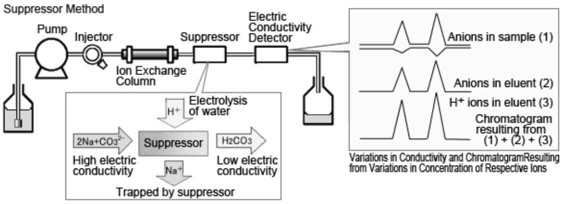


Figure 4.5.- Ionic Chromatography separation system (From Shimadzu)

The determination of the ionic part of our samples were made with an Ionic Chromatography Dionex ICS-1000 *(Sunnyvale, California 94088-3603 U.S.A.)*, equipped with an auto sampler AS40 and a conductimetric system as detector.

- Anion analysis:

For the anionic determination, it has been used a column IonPac AS11-HC 4 x 250 mm, which is hydroxide-selective column for a fast separation of short-chain inorganic acids and anions (*Dionex, specifics of column*).

The separation come about using a linear gradient of eluent KOH, helped by a Reagent Free Controller which make automatically the solution mixing a concentrate reagent with a water taken of reservoir, at a flow of 1,5 ml/min . The gradient starts from 1 mM and finish after 19 minutes at 17 mM. As suppressor system was used a Dionex ASRS-4mm suppressor with a current of 64 mA to reduce the signal of the eluent.

The analysed anions, in exiting order on chromatogram, were formate, acetate, propionate, methansulphonate, chloride, nitrite, nitrate, sulphite, sulphate and oxalate.

- Levoglucosan:

The levoglucosan is the marker of wood burning and being a carbohydrate, the separation is not made as usual. In previous studies made in our laboratory, it was developed a method to analyse the levoglucosan with ionic chromatography coupled with an amperometric detector with a gold electrode (HPAEC-PAD). Is used the same ion chromatography ICS-1000 equipped with ED50 unit, as amperometric detector.

The separation of levoglucosan and its isomers (mannosan and galactosan) was carried out with an IonPac PA10 column 4 x 250 mm, a column sensitive to mono- and disaccharides, using an 18 mM NaOH eluent in an isocratic method with a flow of 1ml/min.

4.3.2.3.- Total Organic Carbon (TOC) analysis:

There is a fraction of organic carbon that is soluble in water, mainly short chain organic acids and macromolecules containing nitrogen atoms in their structures. This technique allows the quantification of this fraction of organic carbon in water solution.

The analysis of water soluble organic fraction are carried out with a Total Organic Carbon- Total Nitrogen (*TOC-*$V_{CPH/CPN}$ *- Shimadzu Corporation, Columbia*) analyser, that works with solubilized samples, oxidizing it and using as detection system the infrared technique. This instrument allows the quantification of organic part and simultaneously, the quantification of the nitrogen in samples.

In our case, before the analysis, the sample is previously treated with an acidic gas in order to remove the inorganic carbon and obtain the so called, non-purgeable organic carbon (NPOC), that is identify as TOC. This method is recognized as valid for official test methods (EPA, ASTM, etc.).

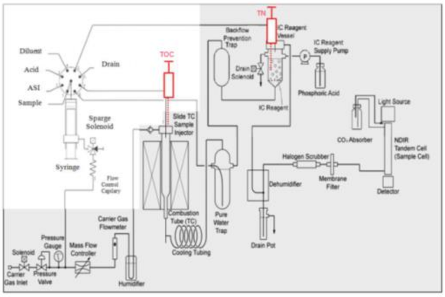


Figure 4.6.- TOC/TN analytic system.

- <u>TOC analysis:</u>

A certain volume of the sample is introduced in a chamber in which is treated with a flux of an acidic solution (HCl 2M). After a 1:30 min acidic treatment, one aliquot of about 80 µl travels helped by the carrier gas (purified air), to an oxidizing catalyst at 720 °C, that oxidize or decompose the sample to CO_2. Once the sample passes this step, goes to infrared detector, which uses the non-dispersive infrared technique to detect. The result is a chromatogram-like graph that gives a peak of NPOC. The analysis is repeated two times and the given concentration is the average of two measurements, being valid if the coefficient of variance (CV) is lower than a 10%.

The calibration of the TOC unit is made with a concentrate solution containing 100 ppm of C and N, of which are made automatically the dilutions to create a 25 ppm range calibration curve.

- TN analysis:

The total nitrogen unit works in parallel with one aliquot of previously treated sample that goes to another catalyst set at 720 °C in which the nitrogen compounds are decomposed to nitrogen monoxide that pass through an electronic dehumidifier where the NO is cooled. Then the formed NO enters in the detector, which is a chemiluminiscence gas analyser where the detected concentration gives a peak in the software, showed in the graph. As for TOC, the measurements are repeated twice and are valid if the CV is lower than 10%. If this condition is not respected, the instrument make an additional analyse and repeat the statistic controls, excluding the wrong one.

The calibrations of the TOC and TN unit are made with a concentrate solution containing 100 ppm of C+N and another concentrate one containing 100 ppm of N, respectively, of which are made automatically the dilutions to create a 25 ppm range calibration curve.

Solutions that will be analysed are prepared by the extraction of one punch of 1,5 cm^2 with approximately 6 ml of ultrapure water *(MilliQ – Merck)* in a glass tubes, previously washed with water and hydrogen peroxide to remove the possible organic residues present in them. The mix is extracted with ultrasonic bath for 90 mins without heating. After this procedure, the solution is centrifuged for 5 minutes at 2500 rpm (*Hettich Zentrifugen EBA 20*) to separate well the solid and the suspended particles.

4.3.3.- Solvent Extractable Organic Compounds (SEOC):

There is no a unique technique that permits to resolve all the organic compounds contained in particulate matter. The most used methods are those in which is necessary the extraction of compounds followed by the analysis with analytical techniques such as gas-chromatography coupled with mass spectrometry (GC-MS), gas-chromatography coupled with Fourier-transform infrared spectroscopy or liquid-chromatography mass spectrometry. Traditionally, is used the extraction with a mixture of organic solvents and the GC-MS (*Facchini et al. 1999*)

Inside the organic fraction of PM, is needed a sub-classification into *water soluble organic carbon* and *solvent extractable organic compounds*.

The extraction and analysis of the first group has been explained in the previous section. Solvent extractable compounds are the group of organic molecules for that are needed organic solvents to be able to solubilize them and use the mentioned analytical tools.

In this group are included fatty acids, alkanes, alkanols, paraffins, phthalates, terpenes, isoprenes, polycyclic aromatic hydrocarbons, hopanes and other molecules present in PM.

The difficulty of the identification of this molecules is the high molecular weight and so a lower volatility. For minimize this hitch is used the derivatization to convert them in more polar compounds, that low the vapour pressure of the molecules.

4.3.3.1.- Extraction methods:

There is not a standardized method to extract organic compounds that asses a good recovery and a reasonable ratio time/consuming solvents. In literature, are explained different methods, but almost all of them requires extraction times around 3 hours and volumes of mixture solvent of at least 30 ml. In our case, the available quantity of sample to extract is very little so is huge problem the high quantity of required solvent which would add possible sources of uncertainty and cross-contamination.

For this reason, we have set-up an extraction method reducing the consumption of solvent mixture and time. As reference, we have chosen the method explained by *Turlington et. al (2010)* in which is used as organic mixture a solution of methanol, dichloromethane and hexane (1:1:1),
but using a lower volume of solvent and not using a pressurized Soxhlet extractor.

The set-up of the extraction method was done using high-volume filters of an old campaign made in Milan in 2011, with a high load of organic compounds and spiked with a known quantity of hopane standard. Two different methods of extraction are tested:
1.- Sonication of a little portion of filter with 2 ml of solvent mixtures for 10 minutes, with n=3 steps of extraction.

2.- Percolation of filter portions with 25 ml of mixture solvent, heated until the boiling point for 4 hours.

1.- *Sonication:*

A punch of 1,5 cm^2 of filter was put in a vial and added 2 ml of mixture of solvents, sonicating for 10 minutes in ultrasonic bath (*Branson 2510*). After this, the extract was transferred in another vial and dried under purified N_2 flow. The extraction step is repeated 2 times more.

The results of the recovery repeated for 3 samples are shown in the *Section 4.5*.

2.- *Percolation:*

A similar quantity of sample, as for sonication, was put in the extracting camera chamber, using 25 ml of solvent in the reaction flask.

The solvent was heated until it reached the boiling point, following the extraction procedure for 4 hours.

Results of recovery for 3 samples are reported in the *Section 4.5*.

When the extraction procedure was finished and the sample is dried, was necessary the derivatization of the extract to render the organic molecules more volatile. The derivatization processes was carried out with 100 µl of methanol acidified with gaseous hydrochloric acid and heated for 40 minutes at 42 °C. After this step, the samples were left at room temperature and then extracted the organic fraction with 200 µl of n-hexane.

Finally, the sample is ready to be analysed, in this work, using the gas-chromatography coupled with mass spectrometry (GC-MS).

4.3.3.2.- Gas-chromatography (GC-MS):

Gas-chromatography is the most used technique to identify and quantify the volatile compounds contained in organic solvents. The separation principle is based in the difference of molecular weight and polarity, which conditions the vapour pressure of molecules and, therefore, the volatility.

The columns of GC are long with a very little thickness, covered internally with organic phases depending on the separation needed, i.e. separation of very non-polar molecules require a stationary phase of 100 % of polysiloxane (the most used base).

In this work were used two different GC-MS to analyse all the solvent extractable components, due to the different characteristics of the instruments:

-Organic compounds and hopanes:

To analyse this groups, was used a GC-MS Bruker Scion SQ - SCION SQTMARK (*Bruker Daltonix, Macerata, Italia*) equipped with a capillary column Factor four (VF-5ms: stationary phase of 5% of phenyl, 95% dimethylpolysiloxane) of length 30m; thickness: 0.25 µm; diameter: 0.25 µm. The temperature gradient was established as following:

- Initial temperature: 60 °C hold for 3 minutes
- Temperature ramp from 60 to 120 °C with an increasing of 8 °C/min (Hold for 1 min at 120°C)
- Temperature ramp from 120 to 280 °C with an increasing of 4 °C/min (Hold for 1 min at 280°C)
- Temperature ramp from 280 to 330 °C at 10 °C/min (Hold for 2,5 minutes).

The injector temperature was 250°C in a split/splitless ratio of 1:30, with 1 ml/min flow of pure Helium and 1 µl of sample injected.

The mass spectrometer was set at -70 eV of ionization using the FULL scan options for fatty acids, terpenes, phthalates, parrafins and alkanes and the SIM scan for hopanes at m/z=191, which is the major visible fragmented ion.

- Polycyclic aromatic hydrocarbons (PAH):

This group was analysed using an Agilent GC-MS 6850-5973 *(Agilent, Santa Clara, California*), equipped with a capillary column DB-XLB of length 60 m, thickness: 250 µm, film 0.25 µm (*J&W Scientific, Folson, California*).

The separation was made with a method of temperature gradient established like following:

- Temperature ramp from 80 to 150 °C with an increasing of 40 °C/min
- Temperature ramp from 150 to 300 °C with an increasing of 5 °C/min
- Isothermal hold at 300 °C for 30 min
- Temperature ramp from 300 to 330 °C at 30 °C/min
- Isothermal hold at 330 °C for 16 minutes.

The injector was set 300 °C, the flow was 1ml/min of Helium purity 99,999% and was injected 2 µl of sample in splitless mode.

The mass spectrometer used was a quadrupole MS 5973 (*Network Mass Selective Detector, Agilent Technologies*) operating at 70 eV in electron ionization mode, using a SIM detection in gradient method of m/z in increasing order of molecular weight of molecules.

Were analysed 10 PAH benzo[a]anthracene (BaA), cyclopenta[cd]pyrene (CPcdP), chrysene (CHR), benzo[b+j]fluoranthene (BbF+BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP). (*Perrone et. al, 2012*).

4.4.- Results and Discussion:

In this section will be explained all the results of all the species analysed.

4.4.1.- Gravimetric analysis:

Gravimetric analyses, such as weighing filters and calculate the concentration of PM based on the volume of air sampled, gives us an idea of which is the distributions around the year. The following table, reports the average values, in terms of concentration of PM in µg/m^3.

	Average	***Std. Dev***	***Median***	***Max. value***	***Min. value***	***n***
January	24.3	28.2	32.6	60.5	4.1	3
February	67.8	38.0	59.9	121.8	121.8	5
March	36.8	25.3	36.0	69.0	69.0	5
April	15.5	7.2	13.6	27.8	27.8	5
May	13.8	7.6	10.5	23.5	23.5	5
June	15.8	7.7	17.3	5.1	26.1	6.0
July	14.7	7.0	14.3	4.7	24.7	10.0
August	15.9	5.1	14.9	10.2	26.2	10.0
September	18.2	6.7	16.4	11.2	30.9	10.0
October	23.0	9.8	24.8	7.6	36.1	12
November	33.9	27.5	31.6	6.0	88.3	8.0
December	29.1	20.6	26.5	5.2	104.2	22.0

Table 4.3.- Distribution of concentration (µg/m^3) of PM during the year

The standard deviation (*σ*) of the group of data, explain the variability of the PM concentration during each month. For example, the high *σ* of February data, explains the difference between the 5 measurements carried out in this month, possibly due to especial events of emission or long-range transport from the cities near to the sampling point.

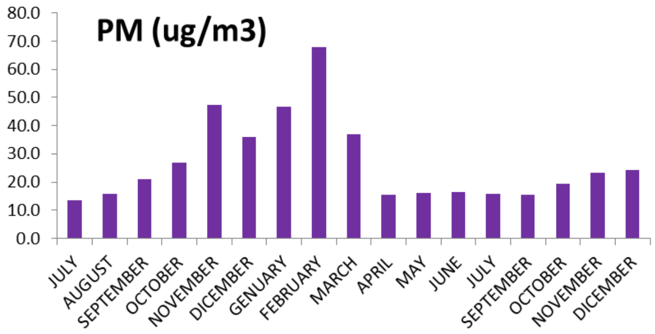


Figure 4.7.- Graphic of distribution of PM

The graphic shows a month distribution of PM concentration during the two years of study. The trend of PM concentration is higher during winter than in summer, probably due to the presence of more sources of emission.

4.4.2.- Main compounds:

As explained in the previous section, the mains compounds of the particulate matter are the inorganic ions, water soluble organic compounds and the levoglucosan, as marker of wood burning.

4.4.2.1- Ions:

The ionic fraction was analysed with Ionic Chromatography as explained in the *Section 4.3.1*.

SULPHATE:

Sulphate is the main anion present in the atmosphere and which participates mostly in the secondary organic aerosol formation.

The concentration of this ion is reported below as percentage during 2011-2012.

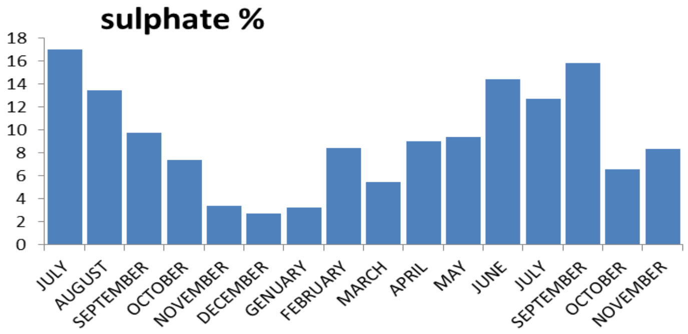


Figure 4.8.- Trend of percentage of sulphate concentration.

The higher concentration in summer is due to a higher photochemical activity based on the more presence of solar rays that form radicals $OH^{\bullet}$, which reacts homogeneously with the SO_2 emitted.

Some cases of a higher presence of % sulphate are related with a month in which there were clear days that leads to a more oxidation of gaseous precursors, i.e. in February 2012.

NITRATE:

Nitrate, as explained in the Chapter 2, is formed by the oxidation of gaseous precursors (NO_x) by ozone and OH radicals.

In the following graphic is showed the concentration in percentage of nitrate found in our samples:

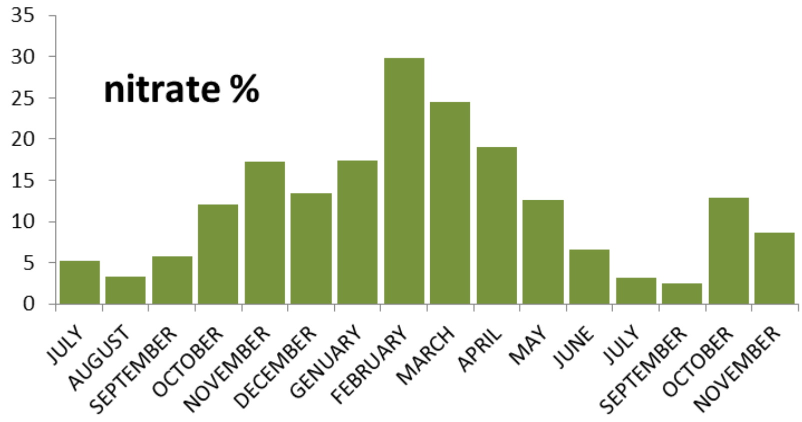


Figure 4.9.- Annual trend of nitrate formation

The higher presence of nitrate in winter than in summer can be explained by two assumptions:

1) Higher emission of NO_x by combustion of not containing sulphur fuels, such as methane or biomass burning, that leads to a higher partition factor in gas phase of ammonium nitrate at lower temperatures. In this case, the NO_2 photochemistry is greater in winter.

2) Due to higher temperatures in summer, is more favourable the reduction of NO_3^- to NO_2 being susceptible of pass to the air again, accounting for less concentration by a negative artefact of loss of material.

SHORT-CHAIN ORGANIC ACIDS:

Numerous sources of carboxylic acids are identified but they are not adequately explained yet. Both anthropogenic and biogenic sources contribute to the concentration of organic acids.

In the *Table 4.3.*are shown the average concentrations in ng/m^3 of the four found species in each season:

	Winter campaign		**Summer Campaign**	
Species	*Average ± σ*	*Range*	*Average ± σ*	*Range*
Formiate (HCOO$^-$)	281 ± 210	100-730	112 ± 147	78-760
Acetate (CH$_3$COO$^-$)	36 ± 33	16-160	12 ± 6	6-29
Oxalate ($C_2O_4^{2-}$)	80 ± 66	30-308	35 ± 35	4-29
MSA-	20 ± 24	4-65	23 ± 13	4-127

Table 4.4.- Organic acid seasonal distribution

The average concentration of each season is in accordance with results found in a previous work made in the same site *(Gilardoni et al., 2011).*

Looking the average results, the concentration of methansulphonic acid is more or less the same in winter than in summer, a trend not usually followed.

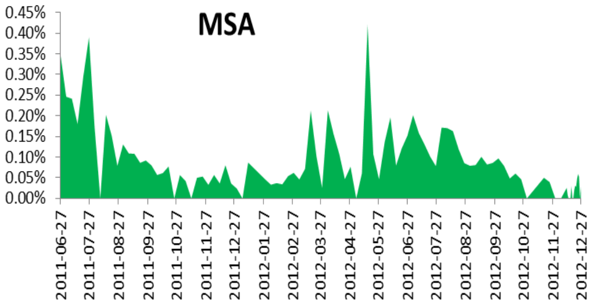


Figure 4.10.- Trend of MSA concentration during the whole campaign.

There are some peaks of high concentration of MSA in summer and in spring. Following the characteristics of the site of study (is located in a middle of the forest, in the Po Valley) and the definition of MSA, the source of emission of MSA could be another different to sea spray emissions.

As explained in literature, enhanced levels of MSA can be found in forests due to the production of dimethylsulfoxide by forest floor in early summer (*Miyazaki et al. 2012*).

A higher concentration of MSA can be also linked to the emissions from lagoon, due to the turnover of water which brings nutrients of bacteria at the top layer, producing DMS and therefore MSA (*Prodi et al., 2009*). This source is likely because of the proximity of Lake Maggiore to the sampling site.

It can be also calculate the percentage of sulphate that comes from MSA and this coming from anthropogenic sources.

As calculated by *Prodi et al. (2009)*, the ratio $MSA\text{-}SO_4^{2-}/MSA=10$. Following this definition can be calculated the percentage of sulphate coming from MSA and the coming from other sources:

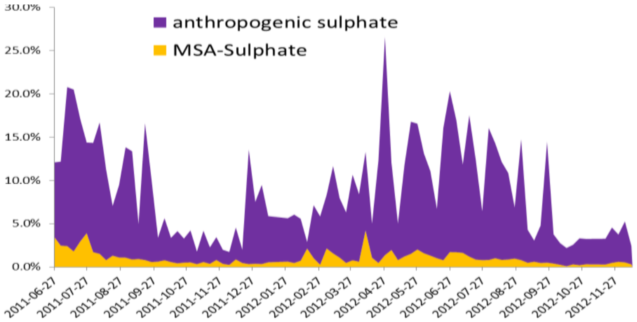


Figure 4.11.- Percentage of SO_4^{2-} from MSA and other sources

Carboxylic acids have several different sources of emission, primary and secondary, including fossil fuel emissions, biomass burning, and photo-oxidation of gaseous precursors from both biogenic and anthropogenic sources. They can be as well produced by heterogeneous in-cloud reactions.

In rural sites or, as in our case, urban background site located in a forest, the presence of carboxylic acids can be also related with the biosynthesis by insects, vegetation, bacteria, and mushrooms and emitted by pollen. (*M. Freitas et al., 2012*).

The monocarboxylic acids are commonly present in the atmosphere by the photo-oxidation of gaseous precursors in the atmosphere, being therefore higher during summer period.

Formate and acetate can be also attributed to soil dust particles. A high correlation between them, explain the hypothesis of a common source of emission.

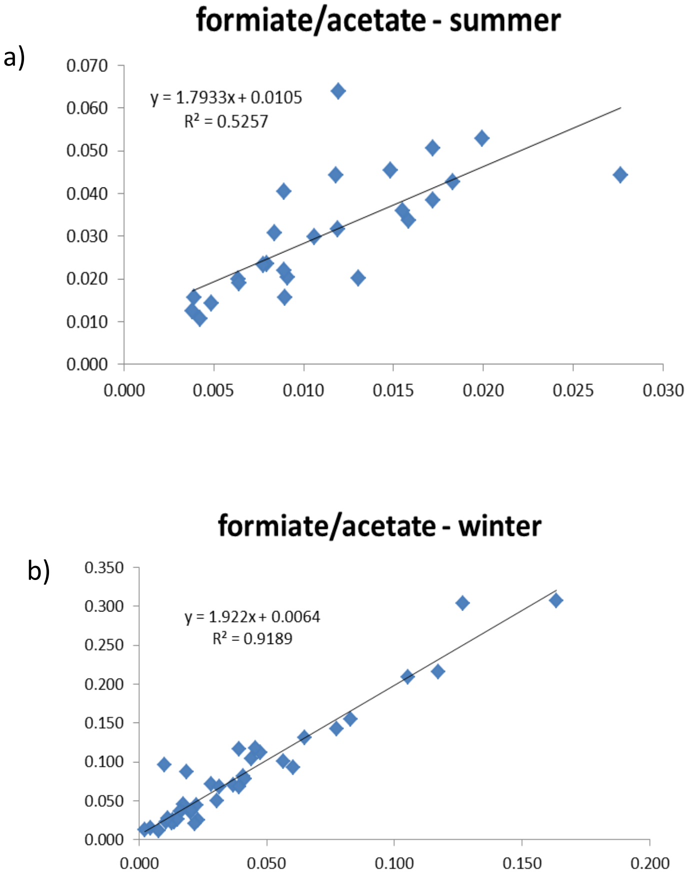


Figure 4.12.- Correlation of $HCOO^-$/$CH3COO^-$ during winter and summer

During summer, the correlation is not very clear. In winter, the correlation is almost perfect, that means the source of emission is the same for both monocarboxylic acid.

As studied in the literature, the main winter source of these compounds is the biomass burning *(Karthikeyan et a., 2006)*.

In the literature, in urban sites has been found a higher concentration of dicarboxylic acids respect to the rural site. On the other hand, in rural sites, predominate the presence of monocarboxylic acids*. (Freitas et al., 2014)*

In this case of study, the site is characterized as urban background site but sampling site is located in a middle of a forest. This fact can explain the inverse trend that follows our set of results.

Comparing data with urban sites of Brazil:

	Urban site $_{PM10}$ *(Londrina, Brazil)*	**Rural site $_{PM10}$ *(Londrina, Brazil)***	**Urban background site $_{PM10}$ *(Ispra, Italy)***
Formiate ($HCOO^-$)	68 ± 30	56 ± 14	112 ± 147
Acetate (CH_3COO^-)	70 ± 27	63 ± 17	12 ± 6
Oxalate ($C_2O_4^{2-}$)	215 ± 25	19 ± 9	35 ± 35

Table 4.5.- Data of carboxylic acids in different type of sites

The ratio between formate/acetate gives information of possible sources of emission. Based in the value of ratio, can be classified the emissions:

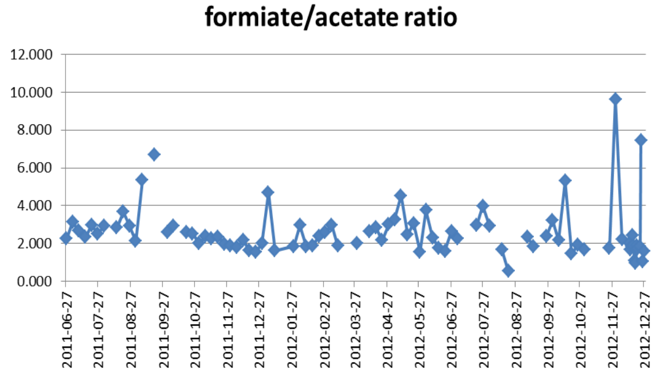


Figure 4.13.- Trend of $HCOO^-/CH3COO^-$ during the year.

As explained in a work made by *Kwaja et al.,* ratio >1 indicate that organics acids can be formed by photo-oxidation in the atmosphere. In the other hand, ratio <1, explain the direct emissions. In winter, we expect a ratio lower than 1, due to the emissions by biomass burning.

Strangely, in winter are found ratio higher than in summer. This phenomenon could be explained if acetate and formate are formed anyway by the photo-oxidation in the atmosphere of precursors.

An increasing concentration of acetate and formiate can be attributed to the ozonolysis of some alkenes derived from biogenic emissions from forest and other type of vegetation and anthropogenic sources.

4.4.2.2.- Levoglucosan:

The levoglucosan is considered the marker of wood burning, being emitted by the incomplete combustion of hemicellulose.

The trend of levoglucosan in the PM tend, usually, to be higher during winter month respect to summer ones, because of the use during winter of wood as fuel in house heating.

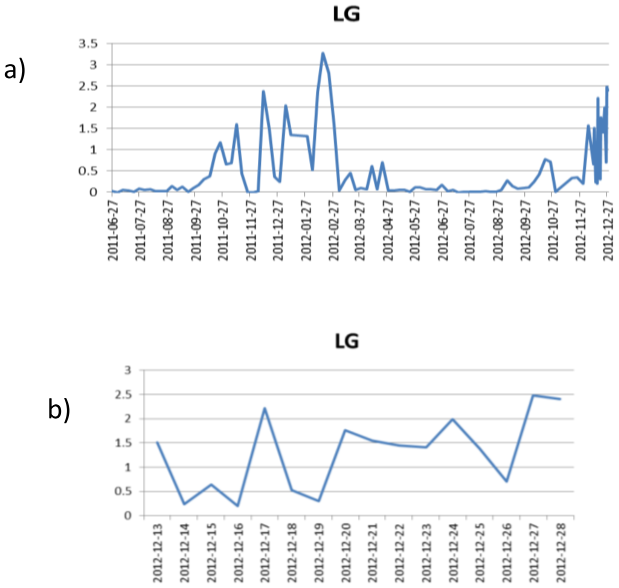


Figure 4.10.- (a) Annual trend of LG; (b) Trend LG during last days of winter

In the figure ***(a)*** is represented all of the data in µg/m^3 obtained by the HPAEC-PAD. The last points are so near because the samples are taken one by day, having more details about the emissions.

In the ***(b)*** figure can be observed the variability of the wood burning emissions in dayly cycles of the last winter days.

The range of concentrations of levoglucosan in our campaign is $1.26 \cdot 10^{-3}$ - 3.27 µg/m^3. These values are comparable with values reported in literature for an urban-background site *(Piazzalunga et al. 2010).*

The contribution of biomass burning is increased in the last few decades, due to the common thought that this type of fuel is green, not afecting the environment.

As Piazzalunga et al. quantificate, the biomass burning, and so the levoglucosan, contribute up to a 50 % to PM mass in winter months.

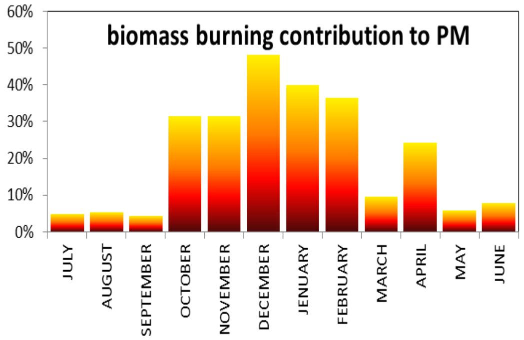


Figure 4.11.- Contribution to PM by biomass burning (BB) (Taken from Piazzalunga et al. 2010)

4.4.2.2.- Water soluble organic compounds:

Are the responsible of the changes in the hygroscopicity of particles playing an important role in the processes of cloud condensations and visibility. They generally tend to have higher values in rural or background areas.

This group of compounds often count for 20-70% of organic particulate matter (*Duarte et al., 2007*).

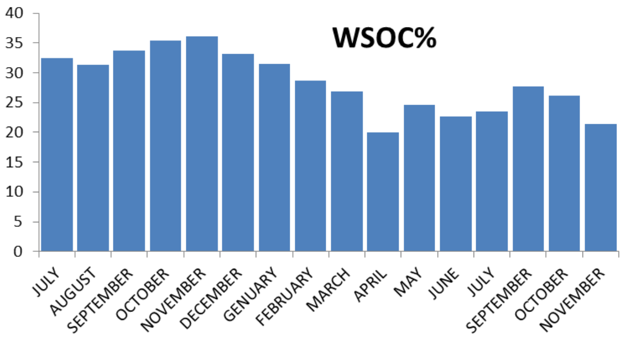


Figure 4.12.- WSOC trend during year

The absence of a seasonal variation can be attributed to the contribution of different sources to the concentration of these compounds.

WSOC have a contribution of biomass burning emissions and fossil fuels emissions, as important primary sources during winter, being also involved in the secondary aerosol formation (SOA), via oxidation of gaseous precursors and in the ageing of organic aerosols.

Making the correlation with other compounds analysed in this campaign, is possible to individuate some of these sources.

Correlation LG/WSOC:

Biomass burning (BB) is the main source of WSOC emission, being higher during winter.

In order to assess the contribution of BB, the correlation with LG has been done.

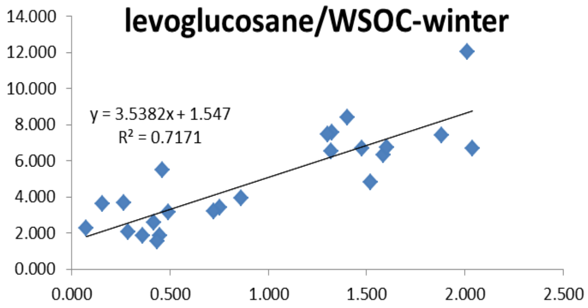


Figure 4.13.- Correlation LG/WSOC in winter

A good correlation of LG and WSOC in winter means that in this season, WSOC present in the atmosphere contribute to biomass burning emissions.

As explained in *Gilardoni et al. 2011*, a work made in the same site of study, the contribution of biomass burning in winter is 64 % of total carbon, while during summer the contribution of secondary organic aerosol account for a 50 % of total carbon.

The secondary organic aerosol contribution is significant during the year, being attributed to biogenic emissions during summer and to biomass burning and fossil fuels during winter.

Correlation Short chain organic acids/WSOC:

Several studies have shown a high correlation of presence of oxalic acid with the emissions from fossil fuels combustion. This source is one of the main contributions to the formation in the atmosphere of water soluble organic compounds.

The presence of oxalate is more likely to be from the photo-oxidation of gaseous precursor emitted by fossil fuel combustion, such as SO_2 that leads to the formation of sulphate in the atmosphere.

In order to prove this possible correlation, it has been plotted the concentration of sulphate in summer and in winter:

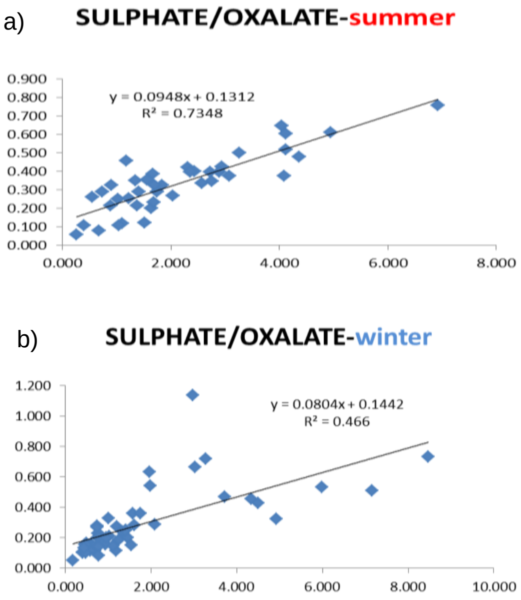


Figure 4.14.- Correlation of sulphate and oxalate in two seasons.

The high correlation of sulphate and oxalate in summer (R_2=*0.7348*), confirm that in this season, the source of oxalate is the photo-oxidation of SO_2, a process highly favoured by the more presence of radicals in the atmosphere produced by solar radiation

Correlation MSA/WSOC:

The distribution during the year of the ratio of MSA and WSOC shows a high contribution of methansulphonic acid to the water soluble compounds during warm months.

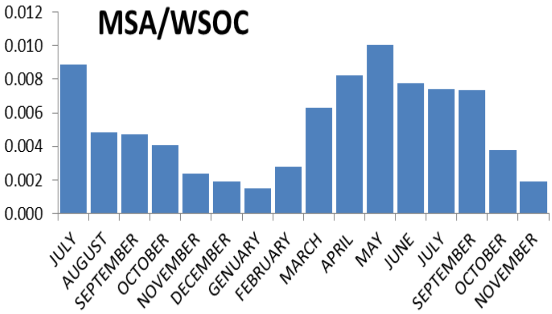


Figure 4.14.- Distribution in time of ratio MSA/WSOC

TOTAL NITROGEN:

Apart from short chain organic acids (formate, acetate, oxalate), methansulphonic acid and levoglucosan, water soluble organic compounds include also macromolecules that are soluble due to the presence of nitrogen and oxygen in their structures. These kinds of molecules are the humic and fulvic acids that are typical components of soil near coastal areas or of the surroundings of rivers and lakes and are formed by the decomposition by bacteria of dead organic matter. These acids pass to the atmosphere by the interface soil-air unaltered due to a so stable structure.

Measurements of nitrogen content in our samples help to understand if there is a high contribution of these macromolecules.

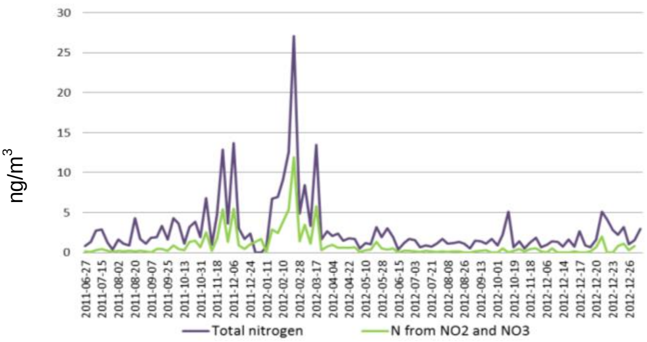


Figure 4.15.- Trend during year of total nitrogen and N from ionic fraction

Total nitrogen is during whole year higher than the sum of inorganic fraction. This fact indicates that there is a high presence of organic compounds that contain nitrogen in their structures, especially during winter where we found a huge peak of nitrogen, possibly related with wood burning emissions that are likely to release in the atmosphere fulvic-like compounds.

During summer, as for the MSA, the presence of these macromolecules could be related with the turnover of lake or the decomposition of the forest floor.

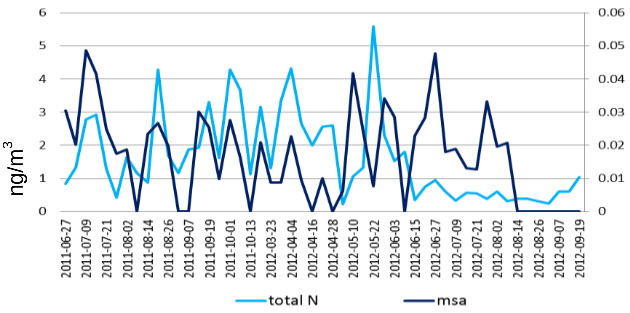


Figure 4.16.- Trend of Total N and MSA during summer.

The shown trend uphold the hypothesis that nitrogen containing macromolecules have the same sources of emission of MSA and corroborate also the proposed sources for MSA, such as decomposition of forest floor and the turnover of the lake.

4.4.3.- Set-up of extraction method for Solvent Extractable Organic Compounds:

In the *Section 4.3.3.1*, have been explained the requirement of an extraction method, because of the availability of small sample amount.

To assess the recovery of extraction method by two explained techniques (sonication and percolation), have been repeated the procedure using both techniques three times.

- Sonication:

To calculate the yield of the extraction method, were taken and treated 3 blank filters spiked with a known quantity of hopanes (12.5, 40 and 50 ng/µl).

Filters were extracted as explained in *Section 4.3.3.1* with 2 ml of organic solution mix. 1 µl of extract were injected in the GC-MS, using SIM method of spectrometer to detect.

- Percolation:

To calculate the yield of the extraction method, were taken and treated 3 blank filters spiked with a known quantity of hopanes (12.5, 40 and 50 ng/µl).

Filters were extracted as explained in *Section 4.3.3.1* with 30 ml of organic solution mix heated in reflux for 4 hours. 1 µl of extract were injected in the GC-MS, using SIM method of spectrometer to detect.

We have chosen hopanes as spiker, because of the low quantity in atmosphere, in the range of ng/m^3.

In the following table, are shown the area of the standard, the theoretical area of peak and the recovery.

Hopane	**Theoretical area**	**Area of peak (Percolation, n=3)**	**%R**	**Area of peak (Sonication, n=3)**	**%R**
12,5	$1,20\cdot10^{8}$ ± $4,12\cdot10^{6}$	$8,32\cdot10^{7}$ ± $5,87\cdot10^{6}$	69,33 ± 0,75	$9,67\cdot10^{7}$ ± $1,75\cdot10^{6}$	80,40 ± 1,45
40	$2,20\cdot10^{9}$ ± $1,05\cdot10^{7}$	$1,33\cdot10^{9}$ ± $2,45\cdot10^{7}$	60,45 ± 1,64	$1,90\cdot10^{8}$ ± $1,31\cdot10^{7}$	86,45 ± 0,59
50	$2,79\cdot10^{9}$ ± $7,96\cdot10^{7}$	$1,81\cdot10^{9}$ ± $3,48\cdot10^{7}$	67,03 ± 4,33	$2,28\cdot10^{8}$ ± $6,78\cdot10^{8}$	84,49 ± 2,51

Table 4.6.- Recoveries of two techniques.

Looking the recovery percentages, can be assumed that the sonication is better than percolation, having an average recovery of %R=*83.78.* Therefore, the extraction technique that has been applied to this project is the sonication.

4.4.4.- Trace compounds:

This group is classified as 'trace' due to the lower concentration in the atmosphere compared with inorganic compounds.

4.4.4.1.- Fatty acids:

Fatty acids are the so called long-chain organic acids, with a high number of carbons in their aliphatic structure. The sources of this kind of molecules are different and each organic acid can have more than one, being meat cooking the most common source. Are in a very low concentration in the atmosphere, with ranges of concentration of few ng/m^3 to a hundred ng/m^3, the most abundant ones.

Based on the length of carbon chain and number of unsaturation in their structure can be done a classification of possible sources of emission:

- Saturated fatty acids with number of carbons from n_C-22 to n_C-28 are commonly from biological sources, i.e. higher plant waxes through reactions of elongation and decarboxylation of lower size fatty acids (C_{16}, C_{18}) *(Rogge et al. 1993e)*
- The unsaturated homologues with carbon number lower than 20, are related with emissions from microbial sources. *(Simoneit et al., 1990)*

- The alkanoic acids with n_C<18 are emitted by petroleum-based sources such as gasoline and diesel vehicles or distillation of fuel oil. *(Rogge et al., 1993a)*

The most present unsaturated fatty acids are myristic acid (C_{14}), palmitic acid (C_{16}), stearic acid (C_{18}), eicosanoic acid (C_{20}), docosanoic (C_{22}) and tetracosanoic (C_{40}).

Biomass burning is one of anthropogenic sources that emit fatty acids, especially palmitic and stearic acids.

- Unsaturated fatty acids are found in the atmosphere coming from the emissions of microbial sources and processing of plant and animal constituents, such as meat cooking *(Rogge et al., 1993)*. This source is so important in the emission of alkenoic acids, such as oleic ($C_{18:1}$) and palmitoleic (C-16:1) *(Rogge et al., 1991)*.

When these molecules are emitted in the atmosphere, are likely to be photo-oxidised by ozone radicals or other oxidants, producing saturated fatty acids with lower number of carbons. The presence of alkenoic acids indicates a 'freshly' emitted particulate matter and which is an indicator of recent biogenesis of these molecules. This characteristic makes possible to calculate the so called 'age of the PM', that is the ratio between concentration of an unsaturated fatty acid and its homologous saturated one.

Based in the concentration and number of carbons that predominate during year, can be made an approximation of which are the sources that contribute more to particulate matter in this urban background site.

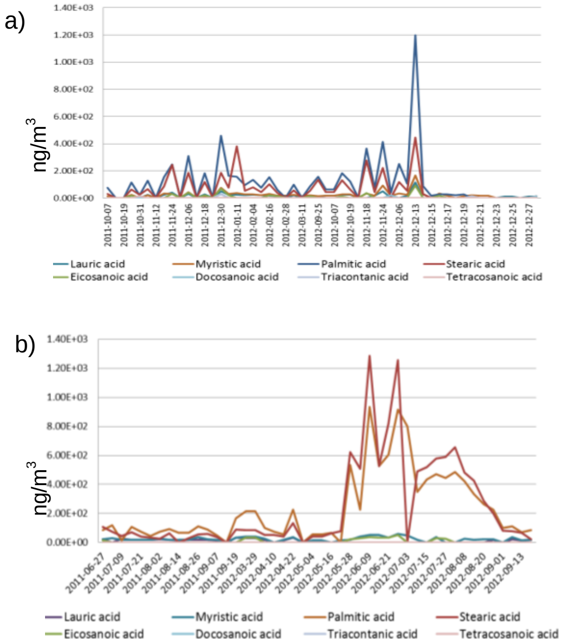


Figure 4.17.- Trend of concentration of saturated fatty acids in (a) winter and (b) summer.

During winter, the concentration trends are equilibrated, there is not a molecule that has a huge different concentration than others, but homologues with carbon number lower than 20 are more present. This fact is explained by the predominance of emissions from anthropogenic sources (fossil fuel emissions, biomass burning) during this season.

On the other hand, in summer the homologues with C_{16} and C_{18} are the most present. This higher presence of C_{16} and C_{18} is explained by the more photochemical activity during this season, more radicals are formed, higher is the oxidation of unsaturated fatty acids.

To confirm this hypothesis, we have plot the ratio between oleic acid ($C_{18:1}$) and stearic acid ($C_{18:0}$).

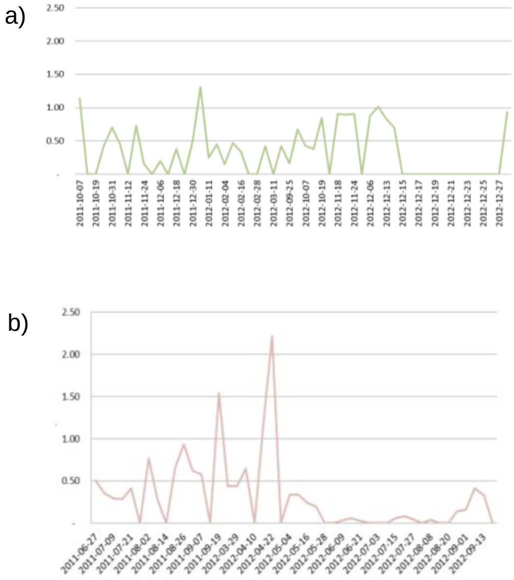


Figure 4.18.- Ratio oleic/stearic during (a) winter and (b) summer

During summer, ratio has a big fluctuation, probably due to the emission and aging of PM in a short time. The episodes with ratio higher than 1, means that particulate matter present in the atmosphere is freshly emitted an event that occurs in autumn of 2011 and 2012, probably because of the restart working of canteen in the Joint Research Centre.

On the other hand, in winter the ratio oleic/stearic is less than 1 for almost all the season. Only one episode have a ratio value near 1.5, in 5th January of 2012, maybe for the same reason that happened in summer, a high load of work in the canteen of JRC.

There is another ratio that is used in source apportionment to relate the concentration of some fatty acids with their source of emission.

Palmitic (C_{16}) and stearic acid (C_{18}), alone, cannot be used as markers of emission, due to the different sources to which can be attributed, but the ratio between them is unique.

Different ranges of values of C_{18}/C_{16} determine the source of emission:

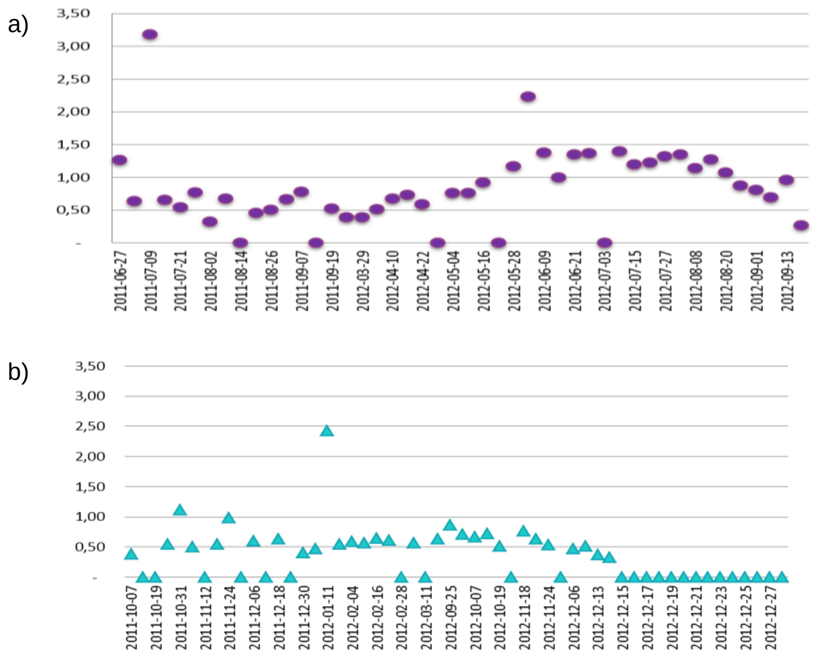


Figure 4.19.- Stearic/palmitic ratio in (a) summer and (b) winter

Values in the range of 0.17-0.71 of stearic/palmitic ratio are attributable to the major contributors of PM.

Ratio C18/C16 values	***Source of emission***
<0.5	Wood smoke, car exhaust
0.5-1	Dust from roads, agricultural activity and meat cooking
2-3	Open dairy farms and dust from them

Table 4.7.- Correlation between C_{18}/C_{16} value and sources

In winter, C_{18}/C_{16} ratio is below one in almost all the cases, that means the sources of stearic and palmitic acid are probably meat cooking and agricultural fields. In one episode, the ratio value arrives to 2.5 that could be the emission from two sources, meat cooking from the JRC canteen and emission biomass burning that release in the atmosphere these two fatty acids.

In summer, all the values are included between 0.5-1 which is an evidence of emissions from agricultural sources and meat cooking.

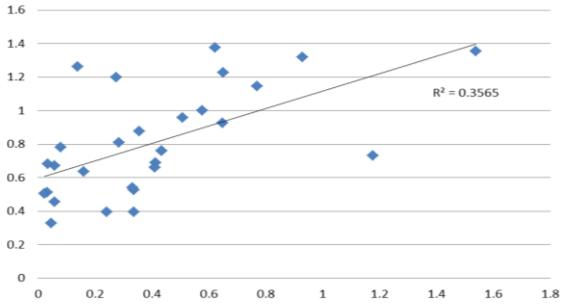


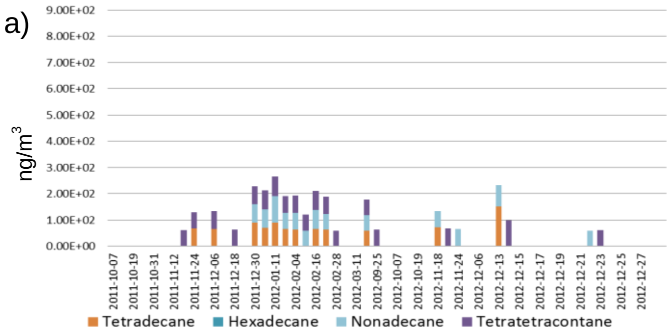
Figure 4.20.- Correlation between ratio $C_{18:1}/C_{18}$ and C_{18}/C_{16}

A slight correlation between these two ratios indicates that the source of emission meat cooking is the main in this period of the year.

4.4.4.2.- Alkanes:

Aliphatic hydrocarbons are ubiquitous organic compounds emitted by many sources, being difficult to assign them to an specific one. Alkanes present in atmospheric aerosol are in the range of C_{12} to C_{40}, with higher carbon number homologues are from biogenic origin while low number of carbon are from anthropogenic sources.

The most common biogenic source is the emission from plant waxes by the wind abrasion of leafs, which is related with high odd number carbon alkanes.



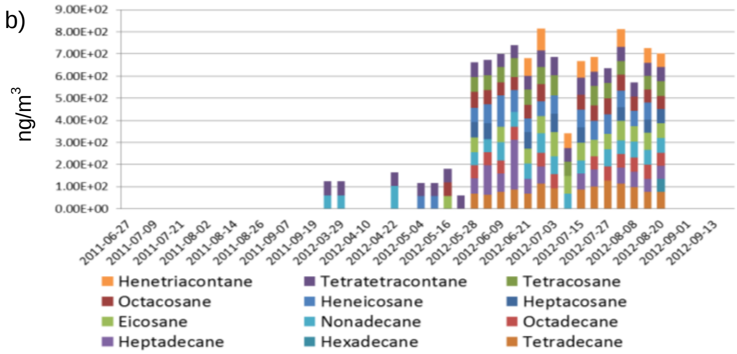


Figure 4.21.- Alkanes in (a) winter and (b) summer

During winter, the presence of alkanes is reduced with predominance of even homologues of lower nuber of carbons (C_{14}, C_{16} and C_{19}), specific of antrhopogenic sources.

Alkanes with number of carbons higher than 35 are typical from road abrassion and vehicle exhaust.

In summer, alkanes are more present, with an increasing number of species. Odd hydrocarbons outnumber in this season, which confirm the contribution of plant waxes emitted alkanes to the PM both from direct emission that for biomass burning. The predominat species are C_{27} (heptacosane) and C_{31} (henetriacontane).

Is also present the contribution of lower number of carbon alkanes, from anthropogenic emissions and those with a carbon number over 35.

Even carbon number alkanes can be from the plastic exposure to heat, as we will see in the next section.

4.4.4.2.- Phthalates:

Plastic is one of the most used materials nowadays, their use is increased to 3 million tons in 2001 *(Teil et al., 2006)*. Its impact is important both in soil contamination that in water pollution, due to the dumping and a long time to degrade them.

Atmospheric pollution is another way that plastics impact the environment by their combustion even if there is the purpose or not, being a common practice in some discarding processes.

Plastics are formed mostly of alkanes of high even number, as a result of ethylene polymerisation, that is the fabrication process, phthalates that are used as plasticisers and antioxidants. Smoke coming by plastic burning is harmful to human and is emitted into the atmosphere together with particles of combustion.

The principal plasticisers are the phthalates which are spread widely into the environment, mainly the bis(2-ethylhexyl)phthalate (DEHP), together with a minor quantity of other phthalates (dibutyl, diisobutyl, diisooctil, dioctyl).

Their release into the atmosphere, besides combustion, is the exposure of plastics to heat in summer, because of their low vapour pressure that allow this molecules to be found in the atmosphere. Near to our site of study there is a plastic packaging company, far from sampling point 3.6 km.

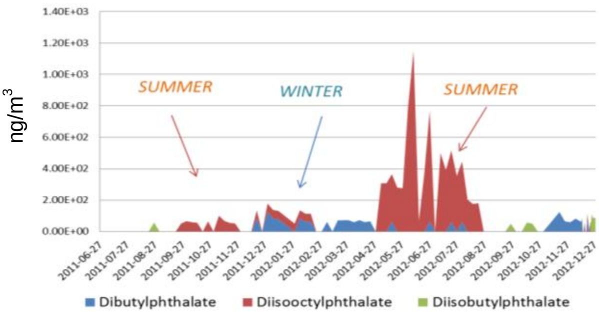


Figure 4.22.- Annual trend of phthalates concentration (ng/m^3)

The average values of three shown phthalates are shown in the following table:

	Average concentration (ng/m^3)
Diisobutyl phthalate	64.1
Diisooctyl phthalate	110
Dibutyl phthalate	73.1

Table 4.8.- Plasticisers average concentration (ng/m^3) during whole year

These results are comparable with those found by *Teil et al.* in Paris, in which the range of concentration was from 0.3 to 77 ng/m^3.

Taking into account that phthalates are ubiquitous in the atmosphere, their quantification and use as markers of plastic burning is important to make regulation in air quality policies.

In our samples, we have found another molecule, the 2,4-di-*tert*-butylphenol, used as antioxidant in plastic production processes. This molecule is also released into the atmosphere, together with phthalates.

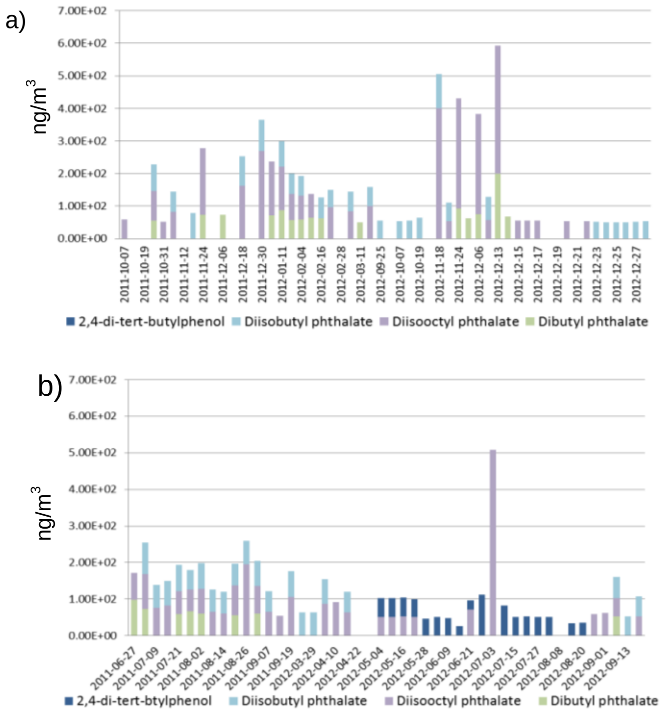


Figure 4.23.- Emissions of phthlates and antioxidant during (a) winter and (b) summer

During winter, the 2,4-di-tert-butylphenol is not present due to the lower temperatures, that leads to an absence of evaporation of this molecule. In summer, instead of winter, the antioxidant is evolved to the gaseous phase due to higher temperatures, like phthalates.

Concentration of phthalates is higher during winter than in summer, maybe due to the ongoing production of plastics in the surroundings.

4.4.4.3.- Terpenes:

The terpenes are biogenic emitted compounds via different mechanisms as response to attacks of insects or changes in the weather conditions (humidity, temperature). In 1960, *Went et al*. made a study in which discovered the formation of organic aerosol from biogenic emitted volatile organic compounds (VOC).

The most commonly reported terpenes are α and β-pinene, limonene, caryophyllene, copaene and eucalyptol. These are emitted in gas-phase and they participate in photoreactions with radicals to form secondary organic aerosol (SOA).

The terpenes are classified depending on their number of units of isoprene (C_5H_8) which is the skeleton of all of them. The most found in atmospheric environment are the monoterpenes (limonene, α and β-pinene) and sesquiterpenes (caryophyllene). Plants release also terpenes with one or more cyclic structures, such as limonene or eucalyptol.

Recent studies in Spain for orange trees and in Amazonian forest have shown that sesquiterpenes participate actively in SOA formation by oxidation of VOC near the ground (*Ciccioli et al., 1999; Jardine et al., 2001*).

Oxygenated terpenes are likely to undergo solubilisation reactions from relative humidity, being depleted from the surface of emitting sources.

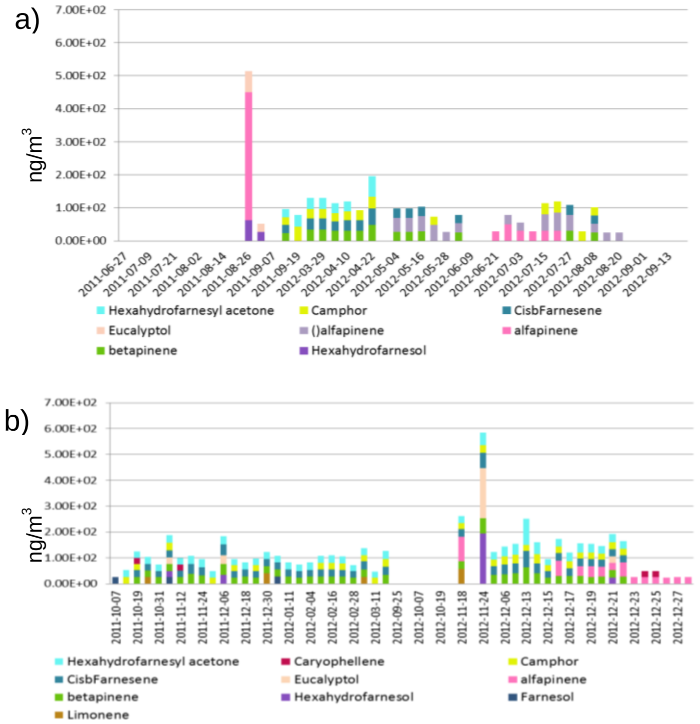


Figure 4.24.- Concentration of terpenes during a) summer and b) winter.

During summer, the most present terpenes are α and β-pinene, VOCs coming from trees and ferns that enclose sampling point. Unlike to sesquiterpenes, these terpenes are not soluble in water, not being subjected to removal from canopy by humidity or rain *(Jaoui et al. 2013).*

Cis-β-farnesene is a linear sesquiterpene related with the green apple odour, coming from gardenia or potato. The notable presence during spring and autumn (April, May and September) of this molecule is referable to the presence of Magnolia tree (*Magnolia grandiflora L.*) in the forest, which belongs to the same family of Gardenia *(Gardenia jasminoides L.*), that blossom in this period.

Among found terpenes, hexahydro farnesyl acetone is one of the compounds released by of fern, highly present in JRC sampling point. It presence is mainly in the spring period, when all plants grow.

In winter, there are a higher number of terpenes that are released in the atmosphere. Cis-β-farnesene e hexahydrofarnesylacetone are emitted when plants and fruits dead. There is a slight presence of limonene and caryophyllene, probably due to a lower humidity during October and December when they do not suffer from the suppression by solubilisation.

4.4.4.4.- Hopanes:

Hopanes are a natural pentacyclictriterpanes commonly containing 27-35 atoms in a naphthenic structure composed of four six-membered carbon rings and one of five-membered. These structures were firstly found in bacteria, where they change properties of the lipid membrane. Their structure is similar to cholesterol.

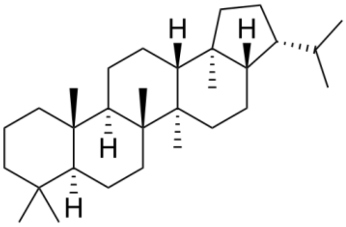


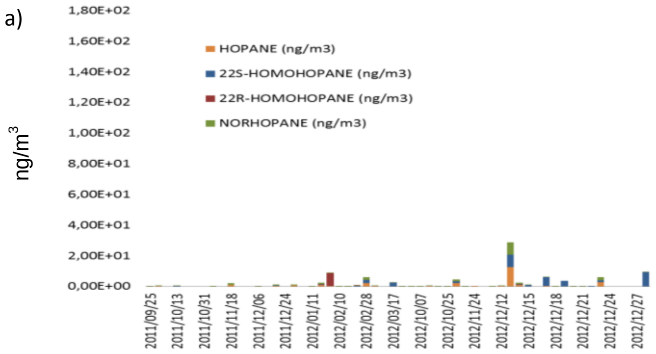
Figure 4.25.- Hopanes structure.

Living organisms synthetize hopanes with ββ configuration, which when increasing maturity, the less stability of this configuration leads to αβ or βα configurations.

Hopanes with configuration 17α(H),21β(H) are the most common in the nature of which in the range of 27-35 number of carbons are typical of petroleum derivates.

This structure make them so thermodynamically stable and so, are among the most useful molecular markers for diagnostic tracer of automobile exhaust, which is one of major sources of emission in urban environment.

The most stable and abundant hopanes are 17α(H), 21β(H)-hopane (C_{30}), 17α(H), 21β(H)-30-norhopane (C_{29}), 22R-17α(H), 21β(H)-homohopane (C_{31}), 22S-17α(H), 21β(H)-homohopane (C_{31}). The difference between these four hopanes resides in their structures, with one more side chain methyl (homopane) or the absence of this (norhopane) respect to the Hopane structure (*Figure 4.25*)



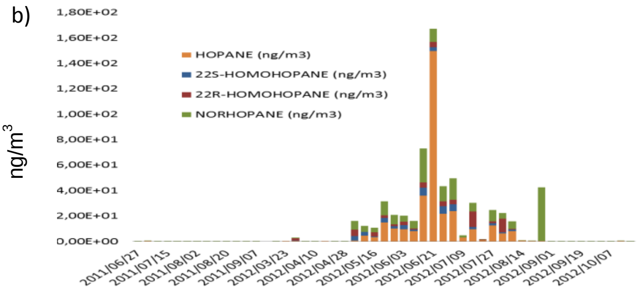


Figure 4.26.- Annual trend of hopanes (ng/m^3), (a) winter, (b) summer

In various studies, were found that hopanes are emitted from unburned lubricating oils rather than from fuel combustion (*El Haddad et al. 2009*). Around the year, the most present hopanes are 30-norhopane and hopane, being those related with vehicle exhaust.

Several studies had determine that during summer, the concentration of hopane is higher than 30-norhopane, being inverted during winter especially in urban and suburban areas (*Hang et al., 2015*).

	Average (ng/m^3)	**Average (ng/m^3) in Ausburg (Germany)**
17α(H), 21β(H)-hopane	1.99	0.92
17α(H),21β(H)-30-norhopane	3.45	0.63
22R-17α(H),21β(H)-homohopane	0.78	0.26
22S-17α(H),21β(H)-homohopane	0.67	0.75

***Table 4.9.- Comparison of average concentration of hopanes (Data from Schnelle-Kreis et al., 2007*)**

30-norhopane is especially present in pyrolysis products being therefore correlated with coal burning, particularly from ashes produced (*Subroto et. al, 1991*). Where, in summer its presence could be explained by barbecue activities during holidays near Lago Maggiore that could be transported by air masses to the sampling point. During winter, the coal as fuel in house heating is still in use which would confirm the presence of this hopane.

Calculating the ratio between the 30-norhopane ($C_{29}\alpha\beta$) and hopane ($C_{31}\alpha\beta$) can be determined the possible origin of emission, because of it has been set range of values for which the origin of these two hopanes is coal combustion *(Alves et al. 2007).*

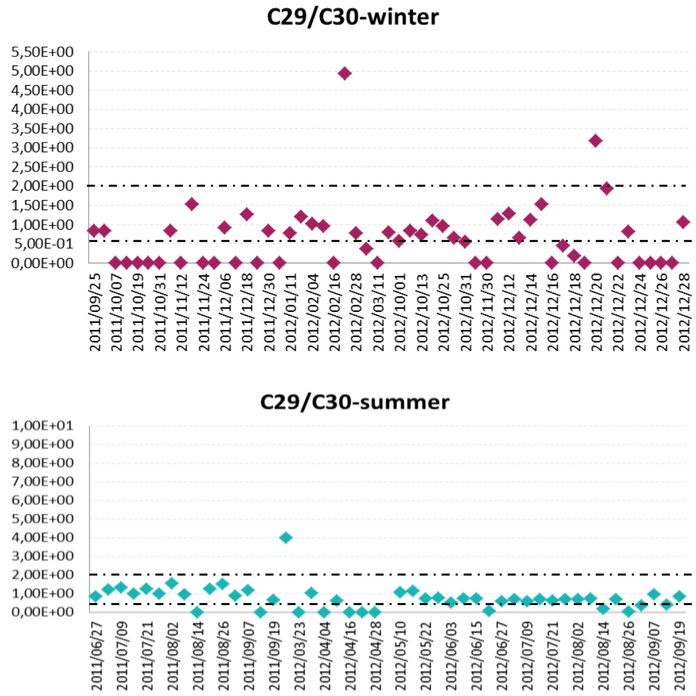
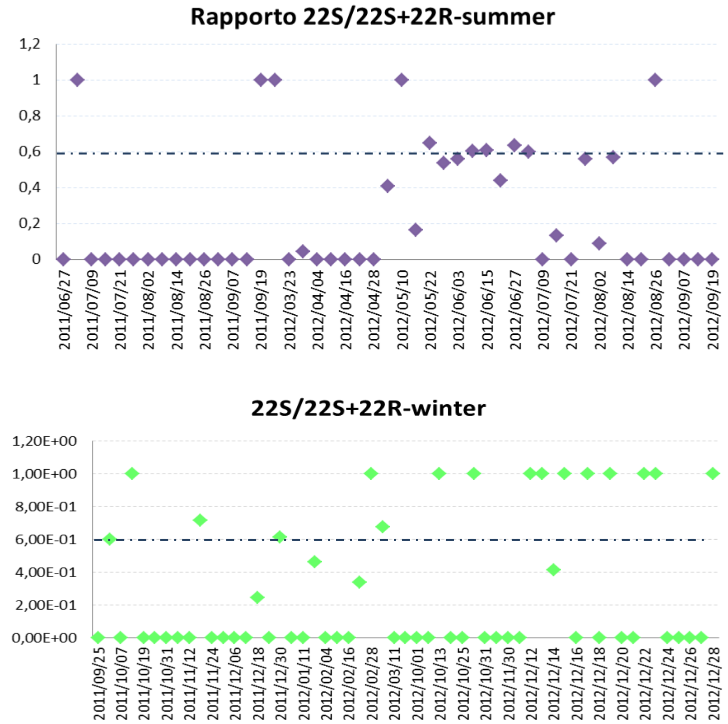


Figure 4.27.- Ratio $C_{29}\alpha\beta/C_{30}\alpha\beta$ during year

The values between the signed ranges (0.6-2.0) are indicators of biomass combustion. During winter are more common emissions from this source than in summer, but are also present. This is added evidence that hopanes emissions in summer are due to coal combustion.

The other two found hopanes, 22R and 22S-homopane are from prokaryotic origin, being the 22R-homopane the footprint of coal and biogenic emissions. A ratio between them is used in source apportionment models as marker of coal burning or gas natural in household heating


Rapporto 22S/22S+22R-summer

22S/22S+22R-winter

Figure 4.28.- Ratio 22S/22R in summer and winter

The values of the homopane index (22S/22S+22R) between 0.1 and 0.4 are due to the coal combustion. During summer 2012, sometimes the value of this ratio is less than 0.4 which means that in those days the emission of hopanes is due to the coal combustion.

During winter, the values are higher, but in some points the homopane index is between the aforementioned values bearing out that the emissions are coming from biogenic sources.

A correlation of this homopane with levoglucosan could clear furthermore the origin of this molecule in the surroundings of the sampling area.

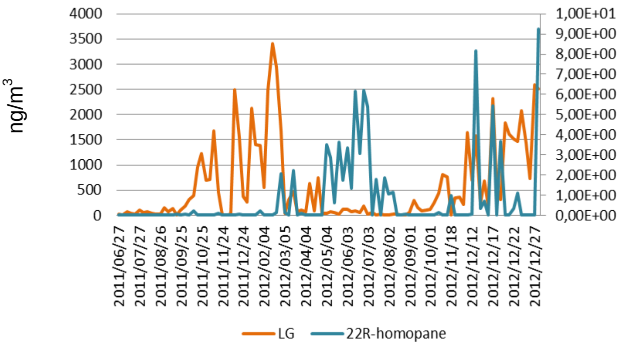


Figure 4.29.- Trend of levoglucosan and 22R-homopane.

A similar trend during some days in winter (March, December), corroborate the hypothesis that the origin of the 22R homopane is biomass burning.

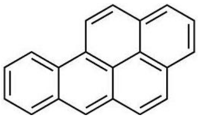
4.4.4.5.- Polycyclic aromatic hydrocarbons:

PAHs are composed by different number of aromatic rings, are non-polar, so non water soluble, and because of their high molecular weight, some of them are not volatile, being ubiquitous pollutants and neutral when released in the atmosphere, due to the high stability to degradation by photoreactions. They are formed by natural chemical reactions from steroids being part of coal or natural crude oils (*Roy G. M., 1995*). The most simple PAH is the anthracene.

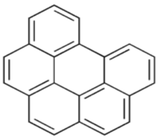
PAHs are found in the atmosphere by the incomplete combustion of fuels due to insufficient oxygen and are present deposited in tar.
They have been signed by the World Health Organization as one of the problems of air quality due to their toxicity and carcinogenic potential.

The classification is made by the number of fused aromatic rings.

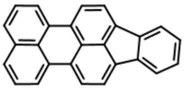
- Five members: The most representative of this group is the benzo[a]pyrene; the first studied and signed in the list of risk pollutants



- Six rings: One example is the Benzo[ghi]perylene



- Seven members: This group is the most important due to their toxically effects.



The origin of PAHs and where they are found, leads to hypothesize that sources of emission are therefore biomass burning and vehicle exhaust. These two sources have predominance during the coldest season, when house heating and vehicles are mostly used. Following, it is shown the trend of PAH in our site:

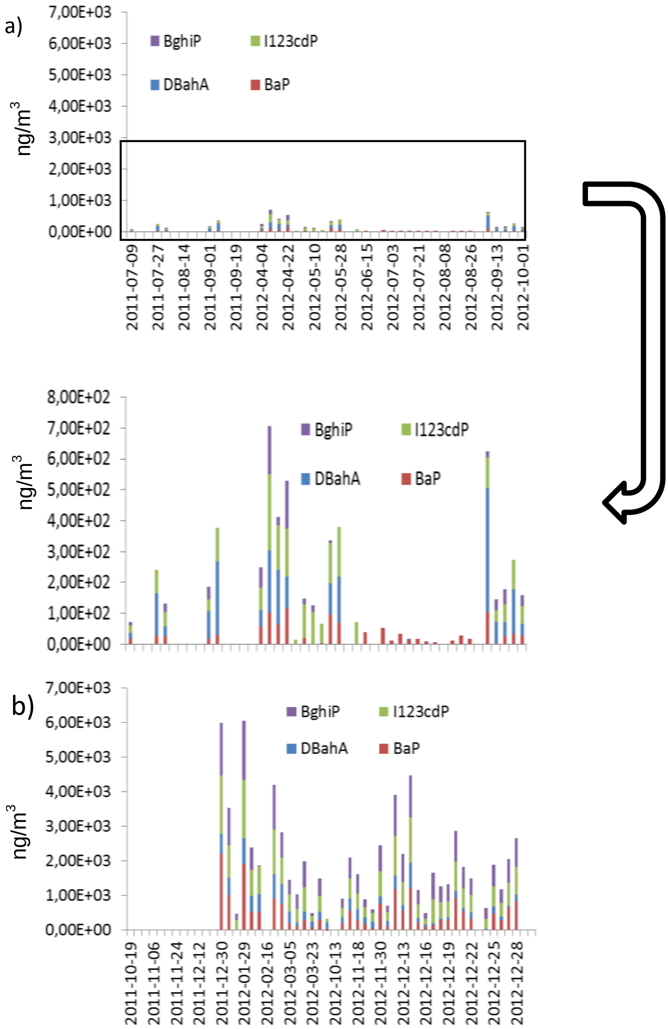


Figure 4.30.- Annual trend of PAH divided in two seasons, a) summer and b) winter

In the graphics are represented the most important species of PAH, Benzo[a]pyrene *(BaP*), signed as carcinogenic by WHO; Dibenzo[ah]anthracene *(DBahA)*, with 6 rings in its structure; Indene[123,cd]perylene *(I123cdP)* and Benzo[ghi]perylene *(BghiP)*, which have 7 rings making them the most dangerous.

As told before, the predominance of PAH is during winter, giving more signs that the possible sources of emission are biomass burning and vehicle exhaust.

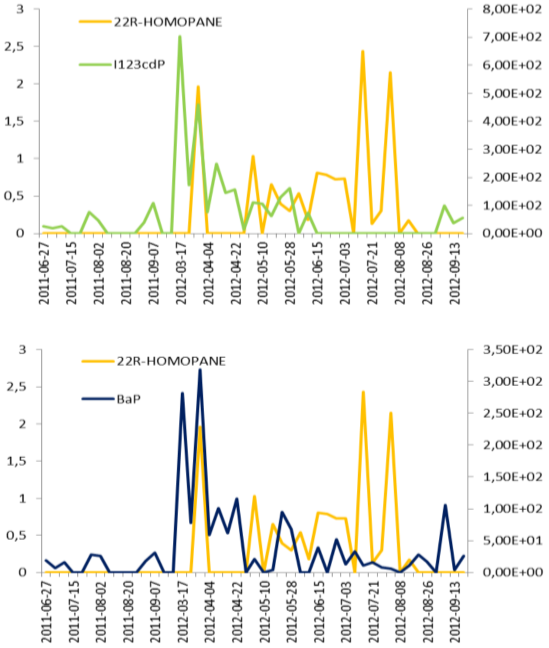


Figure 4.31.- Correlation between 22R-homopane and PAH during summer

During summer, the *BaP* and *I123cdP* are correlated with 22R-homopane, marker of carbon burning, being borne out that the origin of PAH in this period is the biomass burning.

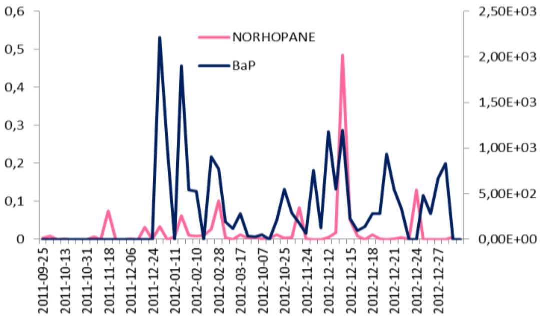


Figure 4.32.- Correlation 30-Norhopane with BaP

In the other hand, during winter 30-Norhopane and BaP follow almost the same trend along the season which could mean that the BaP is from unburnt products of the vechicle exhaust and from the pyrolisis of coal or other type of crude oil derivated fuels, such as kerosene.

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5. Identification and quantification of the contribution of organic aerosol to each size fraction

5.1.- Introduction:

The relevance of the biological organic aerosol (BOA) has been studied for decades to understand the effect of this unknown fraction into health and the contribution of this subgroup to organic aerosol.

The organic aerosol, for its difficulty to be characterized, it has been the goal of several studies made in the last century due to the role in atmospheric processes of cloud condensation, acting as nuclei also for ice formation.

After being emitted, the biological aerosol undergo different physical and aging processes into the atmosphere, where depending on their surface can serve as condensation nuclei being removed via wet or dry deposition. Once is removed, the BOA can interact with water and soil ecosystems, bringing to another emissions, closing a cycle.

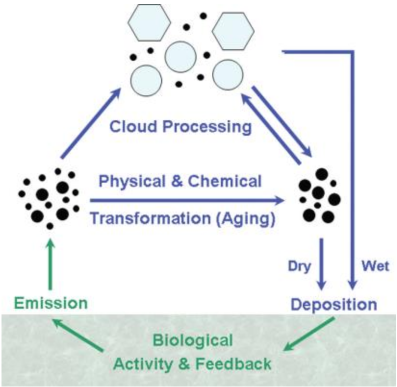


Figure 5.1.- Emission/Deposition cycle of BOA (From: Després et al, 2011)

In spite of the importance of the biological aerosol, it has not been the aim of studies may be owing to the absence of techniques capable to study deeply the characteristics and sources. The further knowledge of BOA will help to better understand processes and sources of emission and, therefore, develop climatic models more accurate.

In this work, has been made a brief study of the water soluble primary organic aerosol using a wide range of techniques which permit a full characterization of this, nowadays, unattended particulate matter fraction. In particular we have centred our attention in the water soluble organic compounds group and the characterization of the total nitrogen quantification in collaboration with the Paul Scherrer Institute which have designed the project of study.

Traditional analytical techniques to study this fraction of aerosol are, among all those used, cultivation of cells to identify the bacteria, fungi and spores that are emitted by the biogenic sources. Newer techniques are classified as molecular techniques, such as the analysis of chemical tracer determination or non-optical techniques, i.e. Raman spectroscopy or fluorescent spectroscopy, being non-destructive techniques.

Together with these newer techniques, classic chemical techniques are used, such as the ionic characterization with ionic chromatography, the analysis of specific markers or the elemental and organic carbon through thermal-optical techniques (TOT).

Despite the range of analytical techniques available, the characterization of primary biological aerosol remains an unknown by the differences between the previous studies and models.

To permit the accurate characterization of this organic fraction has been used a recent technique, the Aerodyne Time-of-flight Aerosol Mass Spectrometry (ToF-AMS), in which aerosol is sampled and analysed online by a mass-spectrometer. The online analysis help to understand exactly what is in this moment in the atmosphere in order to avoid losses of material with the storage of filters.

Were analysed the three particulate matter fractions, PM_1, $PM_{2,5}$ and PM_{10} due to the broad range of size that present the biological organic aerosol, being able to belong to the three distribution modes (accumulation, fine and coarse). Simultaneously was made a common sampling in the rural site of Payerne (Switzerland).

5.2.- Experimental:

The sampling campaign contain one different batch of samples, the Batch A .

The Batch A is composed by 87 samples of 24 hours sampling, during the periods of June-July 2012 and January-February 2013. Were sampled the three fractions, using three parallel high-volume samplers which collect aerosol in quartz fibre filters (*Total filter area*:153.94 cm^2 ; *Air volume*: 500l/min).

During summer campaign were collected 15 samples for each fraction and during winter 14 for each one.

All the samples have been subjected to different analytical techniques.

Analytical Method	Property measured	Batch A
Gravimetric measurements	Mass of sampled aerosol	All filters
Aerodyne Mass Spectrometer Off-line	Organic matter soluble in water environment	All filters
Thermally evolved carbon by Optical Technique (TOT)	Organic, pyrolytic and black carbon	All filters
Ion exchange chromatography	Anions + Cations	All filters
Total organic carbon + TN	Water soluble organic compounds + total nitrogen	All filters
Conversion of enzymatic cellulose to D-glucose and detect photometrically	Cellulose	32 filters (9 summer PM_{10} filters, 4 winter PM_{10}, 5 summer $PM_{2.5}$, 9 summer PM_1, and 5 summer PM_1)
In-Situ Derivatization of compounds and Thermal Desorption coupled with Gas Chromatography-Mass Spectrometry of TOF	Molecules that act as markers	40 samples (15 summer PM_1, 15 summer PM_{10}, 5 winter PM_1, 5 winter PM_{10})
Spectroscopy of X-Ray	C1s, N1s Binding energies	6 samples (3 summer PM_{10}, 3 summer PM_1)
Genomic analysis of Chain reaction from Polymerase	DNA from bacteria and fungi	58 samples (all summer PM_1, $PM_{2.5}$, and PM_{10}, all winter PM_1 and PM_{10})
High Performance Anion Exchange Chromatography with Amperometric Detector (HPAEC-PAD)	Sugars and polyalcohol	All samples

Table 5.1.- Techniques applied to Batch A (From Bozzetti et al. 2015, submitted)

Samples collected in the Batch B are only be subjected to online-AMS analysis.

All this analyses were carried out in Paul Scherrer Institute (PSI) in collaboration with other European institutes to develop all the analysis. We collaborate in this project performing the tests to obtain the data of water soluble organic compounds.

5.2.1.- Water soluble organic compounds:

The primary organic aerosol is composed by carbon containing molecules that are condensed onto the particles present in the atmosphere. Water soluble organic compounds can change the properties of aerosol of absorbing or reflecting the UV rays.

EXTRACTION METHOD:

The PSI have provided us two circular portions of high volume filters of 1,1 cm of diameter. These two portions were extracted in 5 ml of ultrapure water *(MilliQ – Merck)* in plastic tubes. Previously were made different tests to prove that plastic does not release anything that can contaminate samples. The tubes were immersed in the ultrasonic bath (*Branson 2510*) for 90 minutes without heating and, after extraction process, solutions were centrifuged (*Hettich Zentrifugen EBA 20*) for 5 minutes at 2500 rpm to separate the solid particles.

WSOC ANALYSES:

The analyses were carried out with a Total Organic Carbon- Total Nitrogen (*TOC-V*$_{CPH/CPN}$ *- Shimadzu Corporation, Columbia*) which uses the non-dispersive infrared (ND-IR) technique as detector.

A certain volume, automatically set, of the sample is sparkled with an acidic solution (HCl, 2M) for 1:30 minutes to remove inorganic carbon and the remaining solution pass through a catalyst to oxidize the organic molecules to CO_2 that is detected with ND-IR. Together with the analyses of the WSOC, the total nitrogen is also detected. Two aliquots of 80 µl are analysed by the TN unit after passing through a catalyst where all the nitrogen containing molecules are oxidize to NO_2, quantified by a chemiluminiscence detector.

5.3.- Results:

The data obtained by before listed techniques are published in the work published by *Bozzetti et al*. In this section, are only shown the results of water soluble organic compounds (WSOC) and total nitrogen (TN) analyses, because of are those develop in our structure.

The analyses were carried out in 29 samples, 14 of the summer campaign in 2012 and 15 of winter campaign in 2013 of PM_1, $PM_{2.5}$ and PM_{10} fractions. The WSOC have been used in the source apportionment comparison with molecular tracers obtained by other techniques. They were included as water soluble organic matter (WSOM), calculated with the ratio of organic carbon/organic matter (OC/OM) obtained by the offline-AMS.

WATER SOLUBLE ORGANIC COMPOUNDS:

The distribution of WSOC in the three particulate matter fractions helps to elucidate the possible sources of emission of these soluble compounds. Based on the distribution of water soluble organic compounds in size fractions, different sources are related with them, i.e. during winter the water soluble primary biological organic aerosol remains in the $PM_{2.5}$ fraction (fine fraction). All this data is explained briefly in the article *Bozzetti et al (2015, submitted).*

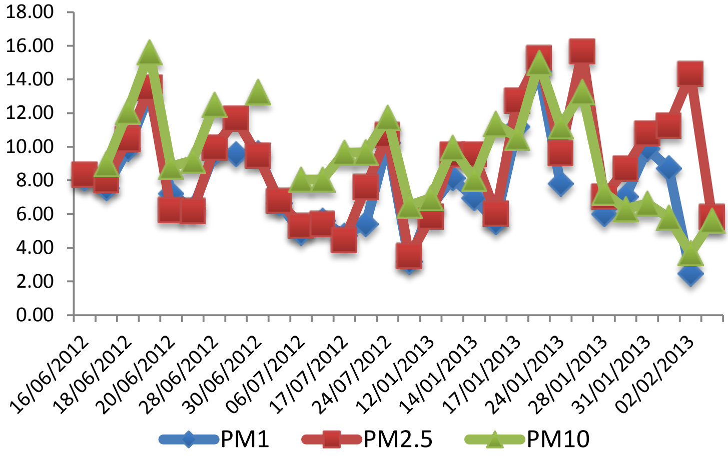


Figure 5.2.- Distribution of WSOC in the three PM fractions

In all the cases the organic fraction is equal or higher in the fractions with higher size fraction of PM. Those cases in which the WSOC is lower in the PM_{10} than in the other fractions are attributable to a second analysis of extracted samples for recalculate total nitrogen data, made four months after the first analyses. These have been repeated due to a problem with the TOC instrument, which had evinced a malfunction of TN detector.

Those samples reanalysed show a good agreement between first WSOC data and the reanalysed ones.

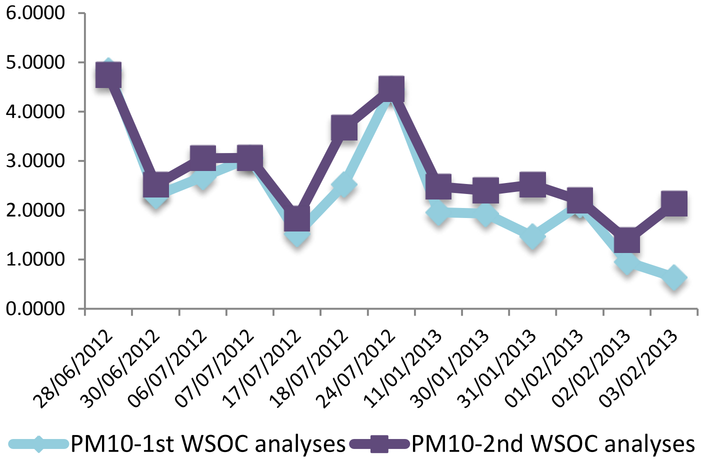


Figure 5.3.- Accordance of PM10 data of two analysis

The WSOC data obtained are compared with the organic matter results acquired with offline-AMS results.

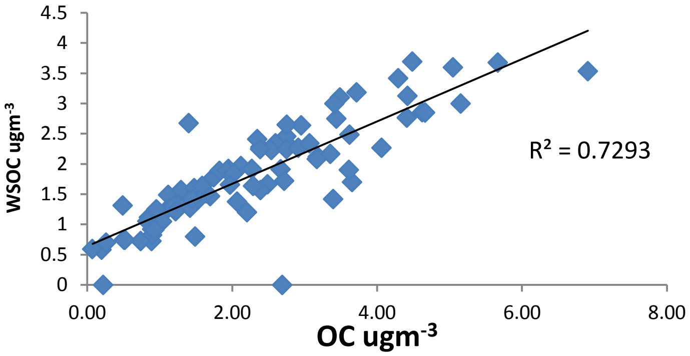


Figure 5.4.- Correlation between organic carbon (OC) and the WSOC

A good correlation between them means that a great part of organic carbon detected in samples is soluble in water.

TOTAL NITROGEN:

The total nitrogen data has been correlated with ionic fraction of NO_3^- and NH_4^+ to determine the portion of nitrogen found in samples is referable to macromolecules containing it.

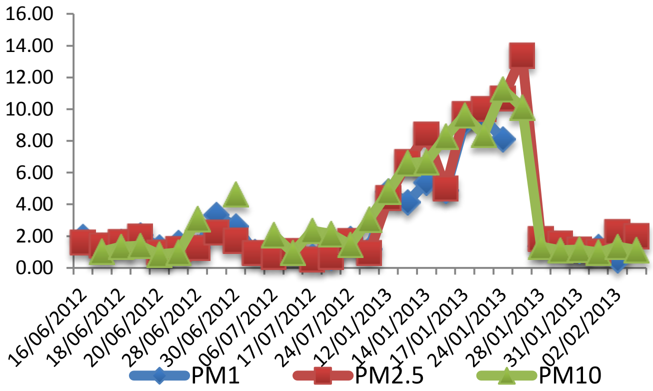


Figure 5.5.- Trend of TN during whole campaigns.

Also in this case, the data lower in PM_{10} than in $PM_{2.5}$ or PM_1 are due to different data in which are analysed samples, 4 months later than the other ones.

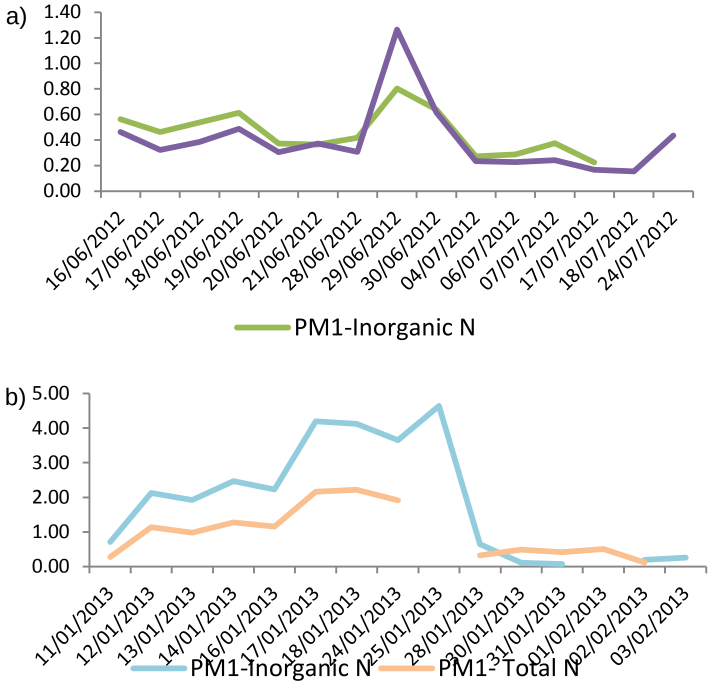


Figure 5.6.- (a) Summer and (b) winter comparison of TN and inorganic N in PM_1

In the PM_1, in summer and winter, inorganic N is higher than total nitrogen. This may be due to loss of material or a problem with the TOC instrument when analyse the nitrogen fraction.

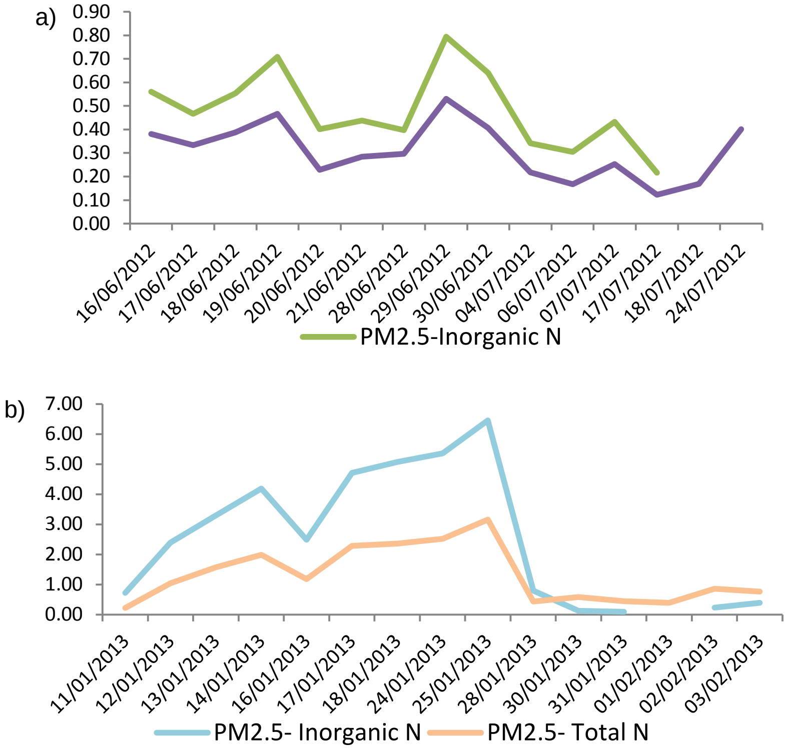
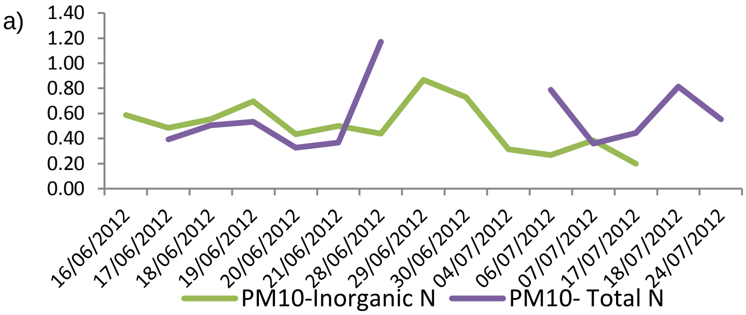


Figure 5.7.- (a) Summer and (b) winter comparison of TN and inorganic N in $PM_{2.5}$



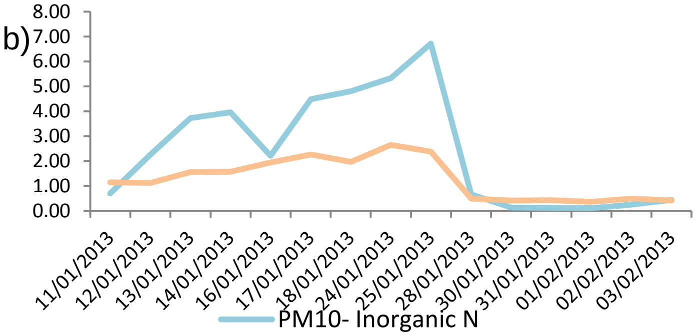


Figure 5.8.- (a) Summer and (b) winter comparison of TN and inorganic N in PM_{10}

For $PM_{2.5}$ and PM_{10}, the trend of inorganic and total nitrogen is the same for the PM_1, may be by an overestimation of NO_3^- and NH_4^+ in samples or a loss of total nitrogen during analyses of WSOC or a problem with the instrument.

All data and source apportionment and consideration of sources are explained in the article *Bozzetti et al. (2015, Submitted)*

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6. Characterization of organic aerosol in coastal city of Marseille

6.1.- Introduction:

The organic fraction of particulate matter is nowadays a challenge in atmospheric studies, due to the many different processes of formation and sources of emission. The distribution of these molecules in particulate matter fractions sampled commonly is widely, being the aim of studies in this decade.

The importance of determine the size distribution of pollutants and above all the organic compounds resides in the ability of particles to enter and pass through body barriers being able to go beyond the soft tissues and arrive to blood, therefore spread in all the organs.

The use of different analytical techniques is helpful to identify several classes of molecules, but they have a lack on offline methods because of the possibility of loss of material before the analysis or the cross contamination overestimating the concentration of compounds present. The employment of online techniques improve the determination of real-time concentrations avoiding the before mentioned lacks. Despite the noticeable advantages, the complexity and high cost of maintenance of these instruments limit the sampling and the spatial coverage especially for long-term monitoring.

One of the newest techniques to analyse real-time concentrations is the Aerodyne Aerosol Mass Spectrometer (AMS), which have improved the analyses of different size fractions with very good results avoiding the positive and negative bias. This technique has been applied for one year in the coastal city of Marseille to determine the PM_1 fraction, particularly, the organic fraction.

It has been applied this technique due to the special conditions of the city with several sources of emission and long-range transported aerosol.

However, the high costs to use the online technique have prompted the development of an offline use of the AMS that includes a water extraction of quartz fibre sampled filters via ultra-sonication.

This project has been mapped out by the Paul Scherrer Institute (PSI-Switzerland) in collaboration with the University of Marseille, particularly the Laboratorie Chemie.

6.2.- Experimental:

It has been made a year study of the aerosol in the coastal city of Marseille. This city is important because it is the main port of Mediterranean sea and the 3rd harbour of crude oil treatment, which make the sampling site very interesting from the huge quantity of sources and the special features point of view. These characteristics of the city make the sampling point interesting to understand the influence of the big ports in city air quality.

Previous studies made in this city have revealed a complex range of anthropogenic sources influencing the city air quality, together with photochemical reactions and a very strong influence of marine wind patterns during the daytime *(El Haddad et al. 2013)*.

The sampling campaign was carried out between 2011 and 2012 in an urban background site in the city of Marseille.

It was collected the fraction under 2.5 µm ($PM_{2.5}$), for a total amount of 216 high volume samples, that were subjected to different analytical techniques to obtain the major characterization of the contained compounds,

Analytical Method	Property measured
Gravimetry	PM mass
Off-line AMS	Water soluble organic matter
Thermal Optical Transmitance (TOT)	Elemental and organic carbon
Ion chromatography	Ionic fraction
Water soluble organic carbon analysis + total nitrogen	WSOC
In-Situ Derivatization Thermal Desorption- Gas Chromatography Time-of-Flight Mass Spectrometry	Molecular markers
X-Ray Photoelectron Spectroscopy	C1s, N1s Binding energies
IC coupled to a Mass Spectrometer (IC-PAD)	Trace elements

Table 6.1.- Analytical techniques to characterize samples

After being obtained all the data, those were used to run source apportionment of the organic fraction using a multilinear engine algorithm (*Canonaco et al., 2013)*. All the analyses are performed in the PSI or Marseille University, supported by the A.P.I.C.E project.

We have collaborated with this project developing the water soluble organic compounds and total nitrogen analyses.

6.2.1.- Water soluble compounds:

Together with the soluble fraction, the characterization of the total amount of nitrogen is also analysed to identify the fraction that corresponds to the organic nitrogen, maybe contained in macromolecules.

EXTRACTION METHOD:

PSI have provided us a 1/8 portion of a high volume filter (*total area*: 153.94 cm^2; *air volume sampled*: 740 m^3). From this portion of provided filter, a punch of 1,5 cm^2 area was taken and extracted in plastic tubes with 5 ml of ultrapure water (*MilliQ – Merck)* for 90 minutes helped by a ultrasonic bath. After ultrasonic cycle, samples are centrifuged and analyse within 24 hours of extraction, to avoid the deterioration of samples.

The data was obtained analysing the solubilized samples with a Total Organic Carbon analyser (*TOC-$V_{CPH/CPN}$ - Shimadzu Corporation)* with a

TN unit that works with a chemiluminiscence detector to quantify nitrogen.

6.3.- Results:

Samples were taken in sets of composite, which were analysed separately to obtain a full characterization of each one.

To determine the organic fraction of the nitrogen, the inorganic fraction of nitrate and ammonium is compared with data of total nitrogen.

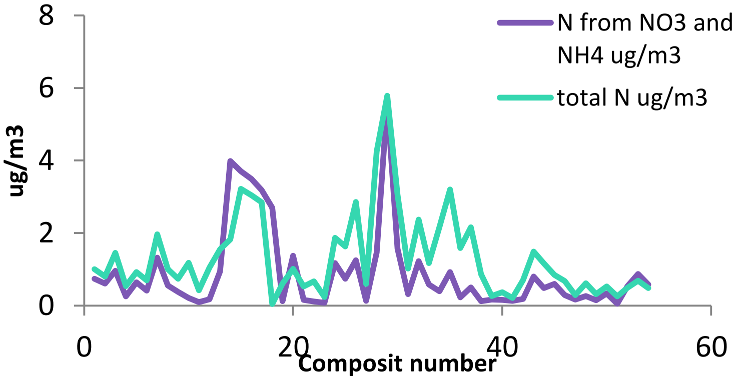

Figure 6.1.- Trend in µg/m^3 of inorganic and organic N.

For whole set of samples the organic nitrogen is higher than inorganic one, except in composites 13 to 17, possibly due to a loss of material during sampling or an overestimation of inorganic part by a positive bias of the analytical technique.

The data of water soluble organic part has been used in source apportionment, being compared to the organic matter analysed by the other techniques.

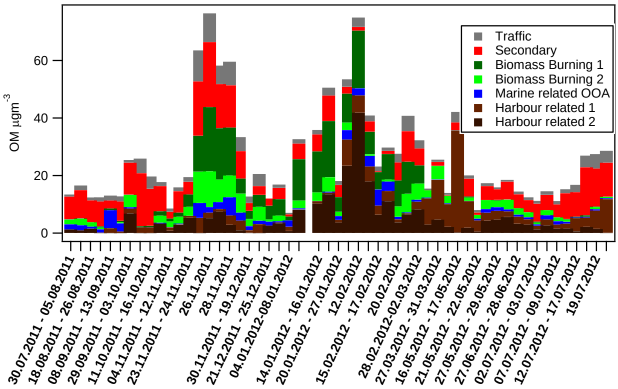

Figure 6.2.- Graphic of source apportionment of organic matter

From the *Figure 6.2* can be observed that the high contribution or anthropogenic sources, in particulate the biomass burning, that account for up to 40% on average during wintertime. During summer, the secondary organic aerosol account for 47% of the organic matter which is consistently with the data reported by *El haddad et al*. in the 2013 made campaign.

From the graphic is also shown that the organic matter from the harbour (*Harbour related OM*) that is ~20% of the total fraction.

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7. Conclusions

Aerosol particles and their composition are the central issue of study of atmospheric physics and analytical chemistry, due to their effect on environment, changing the climate in terms of temperature, cloud formation and rain. These changes have an effect in public health.

Is important to better understand the particulate matter in order to regulate the direct emissions and make the policies to protect the public health and our environment.

In this work, we have make a full characterization and classification of components of the aerosol in an urban background site. This deep investigation has led us to realize that the contribution to the pollution in this background sites can be majorly by the transport of suspended particles to the site of study from the nearest cities rather than direct emission from local sources.

The organic fraction of atmospheric aerosol is still a riddle because of the huge amount of sources of emission and their high possibility to be present as secondary product of the oxidation of precursors in the atmosphere. Is an interesting topic from the high percentage that account for the total concentration of particulate matter.

The secondary origin of the organic fraction, involves a problem of making policies to regulate the emissions because even if the anthropogenic emissions (traffic, industry, house heating) are reduced, the precursors emitted contribute alike to the formation of particulate matter.

The soluble part of the organic aerosol, has been studied for decades and their components are partially recognized. The water insoluble part is still an unknown fraction, but is the most dangerous because the removal mechanisms of deposition are mostly in water environment.

In this work, we have pay more attention to this fraction for its toxicity and the ability of these molecules to attach to the finest size fraction of the particulate matter (PM_1). The absence of an standardized method, make the characterization more difficult since the recovery of the material from the sampled filter is not proved to be the best.

In the *chapter 4*, we have developed a new extraction method for the solvent-extractable organic compounds with a minor time and solvent consumption, which makes the extraction technique more environmental friendly.

This technique has given a good recovery for the hopanes (marker of vehicle exhaust), that are present in the atmosphere in a concentration range of a few ng/m^3.

This extraction method has been used with the urban background site characterization, which is explained in all the *chapter 4*. All the data obtained of solvent-extractable compounds have been a help to come to know of a new group of compounds that are present in our atmosphere. These data, will be used to run mathematical models to assign each compound of emission to a source and calculate the contribution of each one to the pollution in whole the period of study campaign. The source apportionment will be performed in the Joint Research Centre located in Ispra (VA).

The collaboration projects have been useful to understand the difference on the contribution of different sources to the organic fraction in two different sites.

In a rural site as the Swiss city of Payerne, the characterization has been made in the three size fractions of the particulate matter, to better understand the contribution to each mode of most common sources, helped by source apportionment and the characterization of aerosol components with new analytical techniques, such as the Aerodyne Mass Spectrometer (AMS) and genomic analysis, to identify the bacterial and fungal contribution.
The goal of this project was the identification of the primary biological organic aerosol, that account for a large percent of the coarse fraction of particulate matter.

The project in the coastal city of Marseille, have been performed to identify the organic fraction in an important site as one of the main harbours of the world. The characterization of this city's aerosol gives a clue of the consequences of the emissions from the harbour in the city air quality.

Source apportionment tools help to correlate the found molecules with sources of emission and calculate the contribution of each one to the organic aerosol fraction. During whole year, the harbour activities represent approximately a 20% of the total organic aerosol.

8. Acknowledgments

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Despues de 3 interminables años, ha llegado tambien a su fin esta etapa...

Como no, gracias a toda la family que me ha oido quejarme todo este tiempo y me ha entendido hasta cuando no habia que entender...

El 'gracias' mas grande y mas especial va a ti, por 3 años de consejos interminables, por soportarme lo insoportable, por cambiar lo que hasta hacia 3 años no sabia que queria cambiar, por abrirme un mundo desconocido y hacerme entender que no es oro todo lo que reluce...

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