

## Chapter 1 – Introduction

The current interest in atmospheric particulate matter (PM) is mainly due to its effect on human health [1-7] and its role in climate change [8]. Atmospheric PM is a complex mixture of elemental and organic carbon, ammonium, nitrates, sulphates, mineral dust, trace elements and water.

Carbonaceous compounds are the largest contributor to the particulate matter in the atmosphere of both urban and rural areas (20-50%). However, relatively little is known about the composition, seasonal patterns and source/receptor relationships, and concentrations that govern the individual compounds present in this complex matrix. Existing environmental data that describe organic aerosol composition are limited to certain compound classes (e.g. polycyclic aromatic hydrocarbons, alkanes). Even the secondary organic aerosol (SOA), formed in atmosphere by oxidation of gaseous precursor is still poorly understood. About 50% of SOA come from aromatic oxidation and are composed of polymers [9]. Many studies carry on the identification of organic compounds in both aerosol phase and particulate matter matrix: n-alkanes, n-alkanoic acids, n-alkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic ketones, polycyclic aromatic quinones (PAQ), diterpenoid acids and some nitrogen containing compounds, are found in samples collected only for fine particulate matter. Another study [10] proposed the identification *in vitro* of molecular traces in organic aerosol from biomass burning. N- Alkanes, n-Alkenes, Alkanoid Acids, n-Alkanones, n-Alkenols, n-Alkanoids, Wax Esters, Glycols, Steroids, Triterpenoids, Lignin Pyrolysis Products (syringols and substituted syringols; guaiacol and substituted guaiacol; lignans), Cellulose Pyrolysis Products, PAH, Volatile Organic Carbon are found.

When the biomass fuel is heated, its constituents start to hydrolyze, to oxidize, to dehydrate and to pyrolyze. Interstitial compounds and decomposition products of cellulose, hemicellulose and lignin, together with water vapour, are stripped and then undergo partial to complete combustion in the flaming zone. These studies are very interesting and are a model of *in vitro* oxidation process. But they have only the low molecular weight identified products that can lead to the identification of markers in a real sample of particulate matter, but not of compounds only partially pyrolyzed that could compose (with some oxidative differences) an important part of the unknown PM's organic fraction.

Detailed investigations of the chemical characteristics of atmospheric PM are important for both, elucidating the particle toxicity and its role in climate change. As a consequence, the atmospheric pollution develops mainly near the urban and industrialized areas. However, the meteorology and the morphology also act to favour or hinder an atmospheric pollution condition. In fact, the air quality is not only a function of the quantity and quality of the anthropogenic compounds emitted into the atmosphere, but also a function of the atmospheric ability to dilute and scatter these pollutants.

PM<sub>2.5</sub> is most clearly associated with adverse health effects in a number of epidemiological studies, and it has been shown to have a more robust association with mortality in most studies than other fine particle metrics [5]. An example of critical area is the Po valley (north of Italy), where the morphological and meteorological conditions [11], together with the high urbanization and industrialization, determine frequent high air pollution situations. The air pollution is more serious during the winter season, when the frequent low mixing layer causes the stagnation of the air masses over the Po valley (called the “dirty Po Valley”), and the air pollutant concentration, (fig.1).

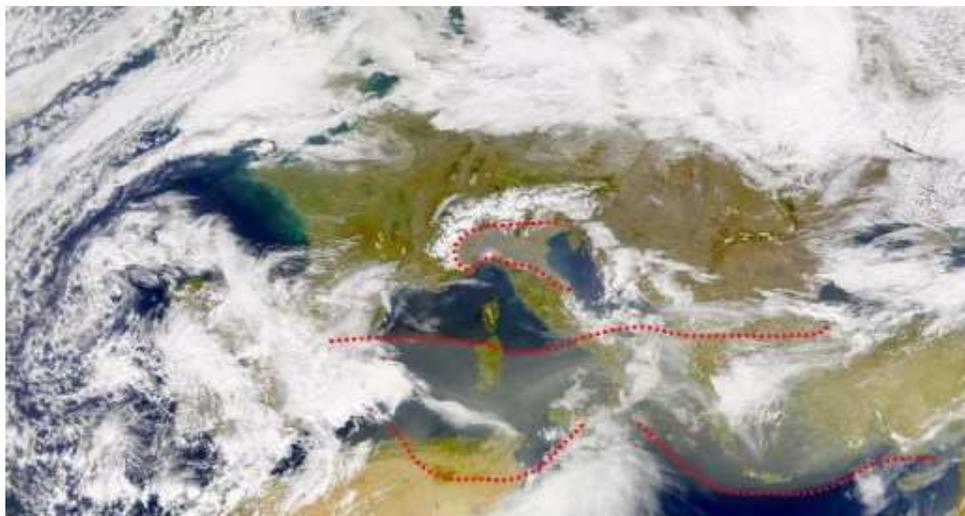


Fig. 1 - The satellite image shows in the red dashed area a big cloud of desert dust moving towards Europe. In Northern Italy, however, emissions from the industrialised Po valley pollute the air, (“Atmospheric Composition Change” – European Network of Excellence).

The new Directive, 2008/50/EC (that could be acknowledged in two years), comes near to the WHO quality guidelines for the Particulate Matter, (tab.1) [12]:

Particulate Matter	24-hour average PM10	Annual Average PM10	24-hour average PM2,5	Annual Average PM2,5
2008/50/EC Upper assessment threshold	35 $\mu\text{g}/\text{m}^3$ , not more than 35 times/year	28 $\mu\text{g}/\text{m}^3$	none	17 $\mu\text{g}/\text{m}^3$
2008/50/EC Lower assessment threshold	25 $\mu\text{g}/\text{m}^3$ , not more than 35 times/year	20 $\mu\text{g}/\text{m}^3$	none	12 $\mu\text{g}/\text{m}^3$
WHO limit value	50 $\mu\text{g}/\text{m}^3$	20 $\mu\text{g}/\text{m}^3$	25 $\mu\text{g}/\text{m}^3$	10 $\mu\text{g}/\text{m}^3$

Tab.1 - Directive 2008/50/EC for the Particulate Matter Emissions.

The values of particulate matter, as could be seen in the fig.2, and the monitored biological effects, in the area object of study, explain the interest in the presented research.

The present paper will study the atmospheric concentration and behaviour of specific organic compounds in the Lombardy Region, a critical area for atmospheric pollution. The attention will be focused on compounds that can give information on the polymeric fraction of particulate matter, the important toxicological pollutants and their mechanism of action on human health.

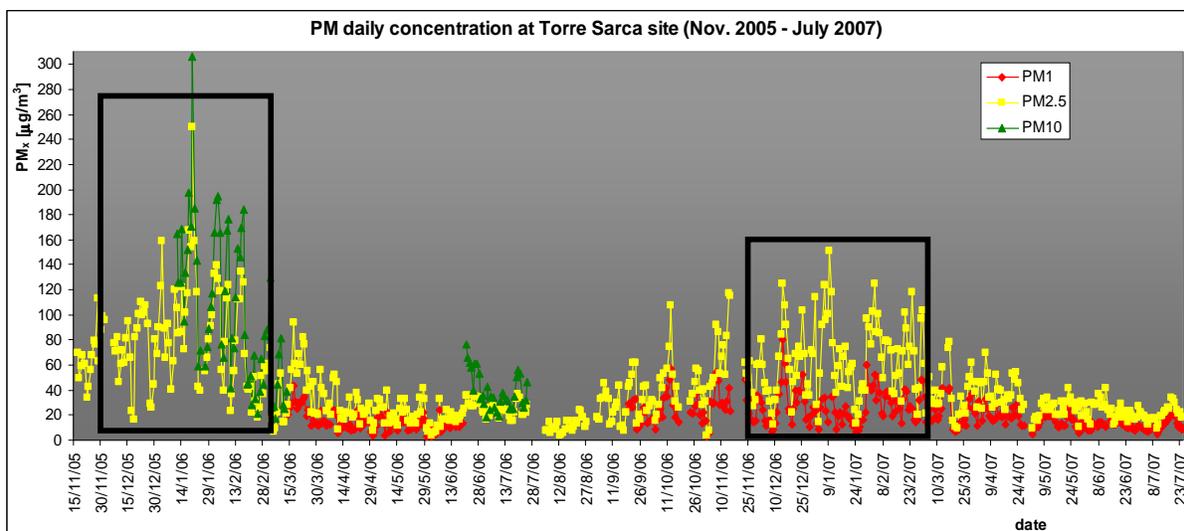


Fig.2 – Concentration of Particulate Matter in the Urban City of Milan.

Organic matter in the tropospheric aerosol derives from two major sources and is admixed depending on the geographic area. These sources are biogenic detritus and anthropogenic emissions. Moreover the bibliographic research showed how the biogenic material is one of the most important constituents of the complex environmental matrix as atmospheric particulate matter [9]. In fact, there was a close molar balance between organic matter production and the total polymeric content, which could contribute to many important atmospheric process. In particular, the study of lignin was treated, the second most important natural biopolymer [13]. Its structure is like a net of unstructured, branched and randomly sorted polymers, with some interactive inter-unity bonds [14]. So, the research method employed for the lignin compounds could be extended (with appropriate changes) to other polymeric components like cellulose, pectin, hemicellulose, etc.

Information on emission sources of trace anthropogenic organic compounds is also obtained to evaluate the abundances in different sites (urban; rural and remote), which represent different pollution levels and quality, and the particulate toxicity depends on the chemical composition. In fact a pollutant emitted in the atmosphere could react or not, near or far from the local emission in the gaseous or particulate phase, with the production of other toxic or more toxic compounds. The studies of Oxygenated Polycyclic Aromatic Hydrocarbons, secondary products of Polycyclic Aromatic Hydrocarbons, are good markers for the long range study of sources and fate of pollutants.

Another pollutant of new interest in the particulate matter study is Bisphenol A (BPA). The molecule was originally tested as synthetic estrogen, then abandoned for the Diethylstilbestrol (DES) [15, 16]. Currently, it constitutes the monomer in the synthesis of polycarbonate plastic, used, among other things, like raw material for food and drink containers. The high amounts industrially supplied every year, have produced contamination of the different environmental compartments [17]. Moreover, it is present in the urban particulate matter and combustion emissions [18]. The released BPA, especially at the high temperature, from food containers and from parts of electrical material, is assumed respectively by food's ingestion and inhalation of the atmospheric particulate matter. Therefore people turn out subordinated to a high exposure: the xenobiotic is concentrated in nano-molar level concentrations in serum, maternal milk, urines and amniotic fluid.

Close to the study of chemical composition of particulate matter, there is a high interest on the research concerning the matrix biological effects on human health and its toxic components. A logical temporal relationship exists, with exposure (e.g. daily peaks in PM), followed by effects (e.g. increased mortality and hospitalizations), although the rapidity with which mortality has been observed following incidents of high exposure remains a puzzle in terms of the particles' mechanism of action. Also the study of biological mechanism of action of the same pollutants is necessary in order to understand the possible common structure of these molecules and to predict the pathways involved. The practice could be due to predictive results and address the *in vivo* and *in vitro* studies.

Therefore a protocol was settled for the molecular docking study of environmental pollutant focused on Bisphenol A, as a case study, because of the abundant bibliographic references on its toxic effect.

### 1.1 Particulate Matter: Dimensional Characterization

Particles emitted from air pollution sources and formed by natural processes have a number of different shapes and densities, [19-21]. The particle size definition for spherical particles is the diameter of the particle, but some particles aren't spherical and others have different composition, i.e. different densities. The necessity to use an international particle size definition was instituted, the "aerodynamic equivalent diameter", (AED;  $d_{ae}$ ), the "diameter of a spherical particle having a density of 1 g/cm<sup>3</sup> that has the same inertial properties (terminal settling velocity) in the gas as the particle of interest".

Particles that appear to have different physical sizes and shapes can have the same aerodynamic diameter and conversely some particles that appear to be visually similar can have different aerodynamic diameters. Since in the atmosphere and in the respiratory system the particles of different sizes behave differently, it is necessary to divide the particulate matter in different categories. The EPA has defined four terms for categorizing particles of different sizes. Figure 3 displays the EPA terminology along with the corresponding particle sizes.

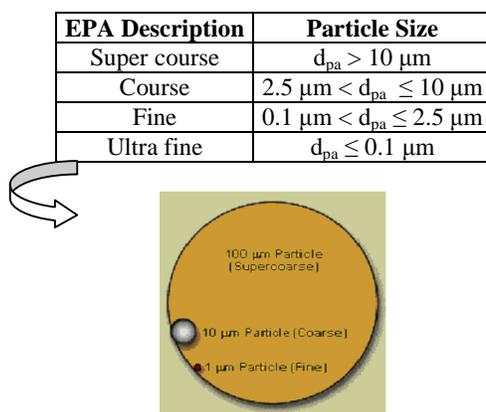


Fig. 3 – EPA particle size classes of distribution and the image description of a fine, coarse and super coarse particle [19].

In addition to the terminology provided in fig. 3, the EPA (setting the National Ambient Air Quality Standard – NAAQS) categorizes particles as follows:

- Total Suspended Particulate Matter (TSP)
- $PM_{10}$
- $PM_{2.5}$
- Particles less than  $0.1 \mu\text{m}$
- Condensable Particulate Matter

These particle categories are important because particulate matter is regulated and tested under these categories. Figure 4 displays a typical size distribution of ambient particulate matter that combines the discussed classification schemes.

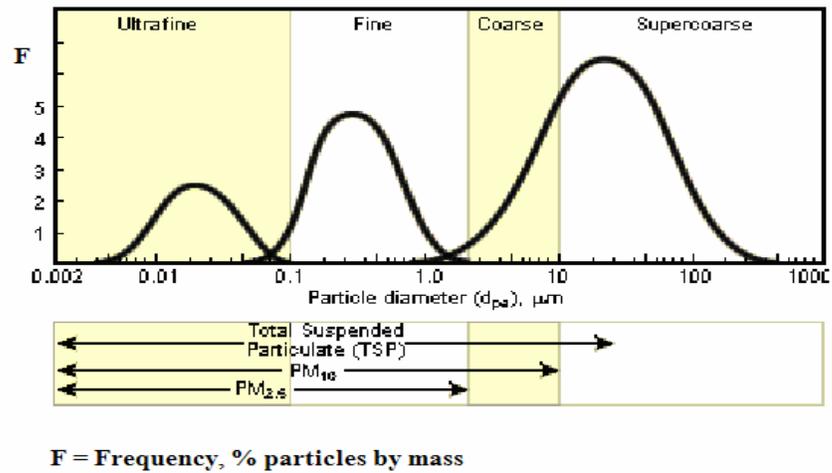


Fig. 4 – Correlation between the particulate matter’s particle size distribution and the EPA tested categories [19].

The U.S. EPA defines  $PM_{10}$  as “particulate matter with a diameter of  $10 \mu\text{m}$  collected with 50% efficiency by a  $PM_{10}$  sampling collection device” [19].

As with  $PM_{10}$ , EPA defines  $PM_{2.5}$  as “particulate matter with a diameter of  $2.5 \mu\text{m}$  collected with 48% efficiency by a  $PM_{2.5}$  sampling collection device” [19].

Normal weather patterns can keep  $PM_{2.5}$  particles airborne for several hours to several days and enable these particles to cover hundreds of miles. Particles  $< 1 \mu\text{m}$  in diameter are termed **sub micrometer**: particles in the range of **0.2 to 0.5  $\mu\text{m}$**  are common in many types of combustion, waste incineration, and metallurgical sources. Particles in the range of **0.1 to 1.0  $\mu\text{m}$**  are important because they can represent a significant fraction of the particulate emissions from some types of industrial sources (tab. 1). Particles composed of as little as 20 to 50 molecules clustered together can exist in a stable form. Some industrial processes such as combustion and metallurgical sources generate particles in the range of 0.01 to 0.1  $\mu\text{m}$ . These sizes are approaching the size of individual gas molecules, which are in the range of 0.0002 to 0.001  $\mu\text{m}$ . However, particles in the size range of 0.01 to 0.1  $\mu\text{m}$  tend to agglomerate rapidly to yield particles in the greater than 0.1  $\mu\text{m}$  range.

Particulate matter formed by condensing gas or vapours is referred to as **condensable particulate matter**. Condensable particulate matter formed by chemical reactions as well as by physical phenomena, (tab. 2).

For many anthropogenic sources, the observed particulate matter distribution approximates a lognormal distribution. Therefore, it is often beneficial to work with particle size distributions on a logarithmic basis.

<i>TYPE</i>	<i>Dimensional Composition</i>	<i>Main Sources</i>	<i>Behaviour</i>
TPS	Total suspended Particulate matter: ultra fine; fine; coarse; partly super coarse fractions	Traffic; domestic; industrial; bacteria; pollen; biogenic and anthropogenic fibres; mechanical forces such as crushing and abrasion of soil or dust	Short retention time in air for the super coarse and coarse component. Long retention time in air (from hour to several days) for fine and ultra fine component.
PM 10	Coarse; Fine and Ultra fine fractions	Traffic; domestic; industrial; bacteria; anthropogenic and biogenic crushing and abrasion of soil and dust	Medium permanence in air for the coarse fraction; long for the fine and ultra fine components.
PM 2.5	Fine and Ultra fine fractions	Traffic; domestic; industrial emission	High permanence in air and possibility of transport for hundred of miles.
Sub micrometer Particles	Partly Fine and Ultra fine fractions	Industrial sources combustion; waste incineration; metallurgical sources	High permanence in air and possibility of transport for hundred of miles.
Particles less than 0.1 $\mu\text{m}$	Ultra fine fraction of 20-50 molecules clustered together	Combustion; metallurgical sources	Rapid aggregation in particles greater than 0.1 $\mu\text{m}$ .
Condensable Particulate Matter	Condensed gases or vapours formed	Industrial and traffic stacks	Condensation or reaction in air (in about a few seconds) upon cooling and dilution.

Tab. 2 – Description of the different particulate matter fraction for their dimension, composition, sources and behaviours.

## 1.2 Particulate Matter: Sources

Atmospheric aerosol particles can be divided into two classes according to their formation mechanism: **primary** particles have been emitted directly from sources into the atmosphere, whereas **secondary** particles are those produced in the atmosphere [22]. The sources' contributions depend on the geographical location, season and meteorology. The major sources are presented below.

Primary sources. The primary aerosol particles in urban air originate from a wide variety of sources, which can be classified according to the particle size. The main sources of *Fine particles* ( $D_p < 1 \mu\text{m}$ ) are various combustion processes, including diesel and gasoline vehicles, biomass burning, industrial activities, energy production and special activities. *Coarse particles* ( $D_p > 1 \mu\text{m}$ ) are emitted from different mechanical processes; the main sources are soil-related dust, sea salt and biogenic particles including bacteria, fungal spores and pollen. In general, primary fine particles in the urban atmosphere result mainly from anthropogenic activities, whereas both natural and anthropogenic sources make a significant contribution to the primary coarse particles present in urban air [23].

Secondary sources. A significant fraction of the particulate mass in the atmosphere is formed principally through gas-to-particle conversion but also through condensation, evaporation and coagulation with other particles or activation in condition of super saturation [24]. The gases producing secondary particles originate from both natural and anthropogenic sources.

*Industrial sources.*

Physical attrition occurs when two surfaces rub together. The compositions and densities of these particles are identical to the parent materials. The dust particles formed range from less than 10 to almost 1000  $\mu\text{m}$ . Most industrial scale combustion processes (for example, coal-fired boilers and oil-fired boilers) use physical attrition in order to prepare or to introduce their fuel into the furnace (fig.5).

Combustion Particle Burnout occurs when fuel particles are injected into the hot furnace, like in fossil-fuel-fired boilers, the fuel particles, which started as 10 to 1000  $\mu\text{m}$  particles, are reduced to ash and char particles that are primarily in the 1 to 100  $\mu\text{m}$  range.

Homogeneous nucleation and heterogeneous nucleation involve the conversion of vapour phase materials to particulate when the vapour-containing gas streams cools to the dew point. Homogeneous nucleation is composed entirely by the vapour phase material that involves only one compound. Heterogeneous nucleation is the accumulation of material on the surfaces of existing particles, involving more than one compound. The vapour phase material contributors are: (1) organic compounds, and (2) inorganic metals and metal compounds. In a waste incinerator, waste that turns into organic vapour and is generally oxidized completely to carbon dioxide and water. However, if there is an upset in the combustion process organic compounds, volatile metals and metal compounds or their partial oxidation products remain in the gas stream as it leaves the incinerator and can condense homogeneously or heterogeneously. Homogeneous and heterogeneous nucleation create small particles, between 0.1 and 1.0  $\mu\text{m}$  with the enrichment in the sub micrometer size range (fig.5). The involved industrial processes are fossil fuel combustion, incineration, industrial furnaces and metallurgical processes. Consequently, very small particles have more potentially toxic materials than large particles leaving the processes. During heterogeneous nucleation, small quantities of metals are deposited on the surface of many small particles. In this form, the metals are available to participate in catalytic reactions with gases or other vapour phase materials that are continuing to nucleate.

Droplet Evaporation Some air pollution control systems use solid-containing water recycled from wet scrubbers to cool the gas streams. The water streams are atomized during injection into the hot gas streams. As these small droplets evaporate to dryness, the suspended and dissolved solids are released as small particles that probably creates particles that range in size from 0.1 to 20  $\mu\text{m}$  (fig.5).

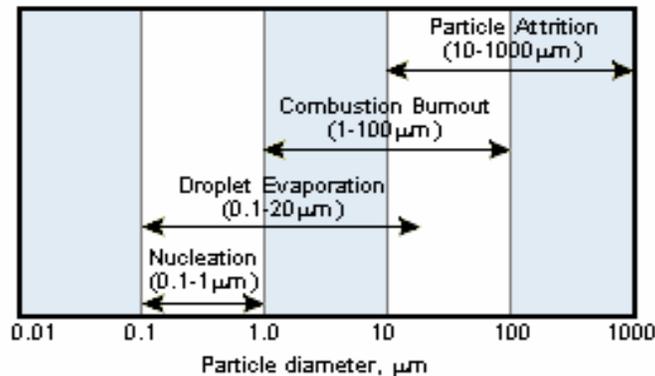


Fig. 5– Particle size range for formation mechanism directly correlated with the smaller industrial and household emissions.

### 1.3 Particulate Matter: Evolution

The atmospheric aerosol encounters evolution by coagulation, chemical reaction and activation. The *coagulation* process occurs with two particles for thermal agitation with formation of a bigger particle. Globally there is a particle number loss, but the mass concentration of atmospheric aerosol remains unchanged. Only the particles with a  $d_{ae} < 10\text{nm}$  grow by coagulation: so, these fine particles are observed only near their sources. In the *condensation* process, the chemical semivolatil compounds (ex.  $\text{NH}_4\text{NO}_3$ ) pass through the gaseous state to a major density state, liquid or solid. It can occur when the thermodynamic equilibrium of the chemical compound moves from the gaseous to the particulate phase because of external conditions. The main inorganic gaseous species involved in the condensation and growth of aerosol particles are  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ .

In opposition to the condensation process we could have *evaporation*. In fig. 6 the different atmospheric transformations of particulate matter [24] are presented.

The activation of aerosol's particles to form small drops (of fog or clouds) occurs when, in super saturation condition of watery vapour (Relative Humidity –  $\text{RH} > 100\%$ ), the particles grow quickly because of the condensation of the watery vapour itself. The critic super saturation value, in order that activation could happen, depends (Köler's theory) on the soluble material (inorganic salts and organic soluble compounds) contained in the Cloud Condensation Nucleus and on its hygroscopic capacity (the material's tendency, by then dissolved, to lower equilibrium pressure of the watery vapour on the solution) [24]. Besides the watery vapour, some soluble gas (ex.  $\text{HNO}_3$ ) can condense during the activation process, increasing the solutes content in the aqueous phase and decreasing therefore the critic super saturation vapour. The aerosol is removed from the atmosphere with wet and dry deposition. The bigger particles ( $d_{ae} > 1\mu\text{m}$ ), leave a sediment, while the particles with a  $d_{ae} < 1\mu\text{m}$  are removed for permeation head toward the earth's surface, mainly through a wet deposition process, as a consequence of activation in the clouds and subsequent precipitation. Among the several chemical-physical phenomenon concerning the compound dispersed in the atmosphere, the photochemical processes in some occasion could lead to the formation of photochemical smog, characterized of a high production of secondary pollutants as  $\text{O}_3$ ,  $\text{HNO}_3$ , and resulting organic compounds as PAN, particulate phase compounds as  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . A lot of these organic compounds are subsequently absorbed on the aerosol surface, affecting the chemical-physical characteristic of the particulate matter itself.

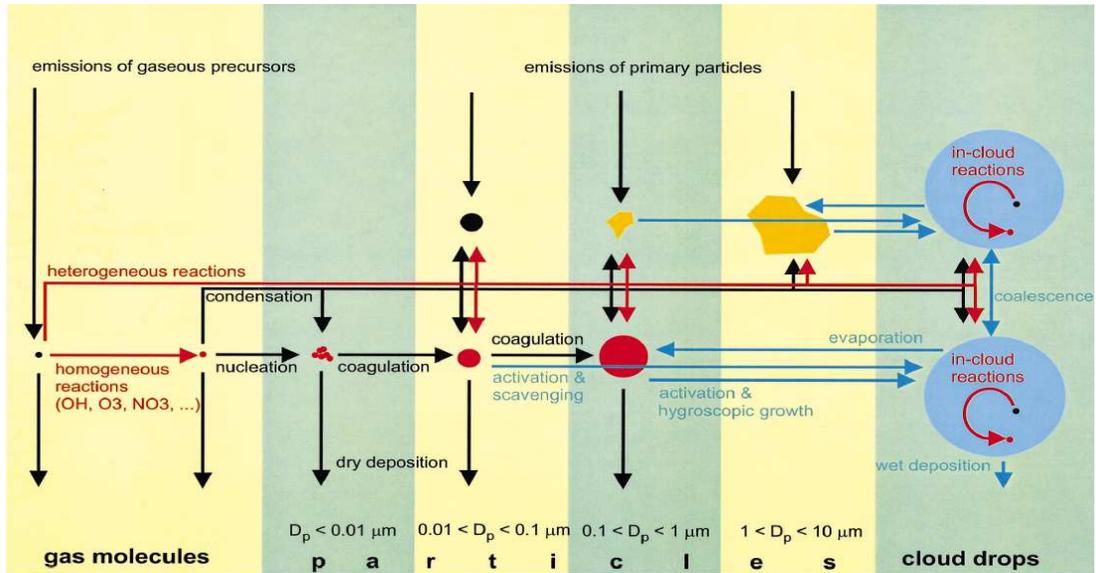


Fig.6 – Microphysical processes influencing size distribution and chemical composition of atmospheric aerosol, [24].

The particles are named in correlation with their coagulation capacity and diameter size as:

- **Coarse mode particles**  $D_p > 1000 \text{ nm}$ ;
- **Accumulation mode particles**  $100 < D_p < 1000 \text{ nm}$ ;
- **Aitken mode particles**  $10 < D_p < 100 \text{ nm}$ ;
- **Nucleation mode particles**  $D_p < 10 \text{ nm}$ , [25].

*For an Urban environment (city of Milan).* Emissions from traffic and industrial sources are linked with the Nucleation mode (maximum diameter size 15 nm). The Accumulation mode particles, however present, come from a more aged aerosol with a regional scale circulation and are formed by cloud processing and condensation [25]

*Sub-Urban Environment (semi-urban area 50 Km far from Milan).* This area is majorly influenced from an instable Aitken mode (because of it is freshly formed by coagulation and growth of the Nucleation mode). The Accumulation mode is also present, partly coming from the coagulation and growth of the Nucleation mode and partly coming from aged particles, formed by cloud processing and coagulation [25].

#### 1.4 The lignin [26-28].

The foremost support of overland plant is grounded on the rigidity of the tissues thanks to the presence of specialized cell walls: this kind of support is the wood. It's the frame established of the lignin walls that sustains a tree. The gymnosperm plants (conifer) have a simple structure (homogenous and regular wood), while the angiosperm (broad-leaved) has a specialized element that leads to a complex composition and a heterogeneous system. The vegetal cell has a wall rather fine but mechanically strong: the primary cell wall is framed of hemicellulose absorbed in a polysaccharide matrix and pectin plus some structural proteins, not very specialized and similar in all types of plants;

the secondary cell wall is framed of lignin and hemicellulose, more strong and thick. Between a primary and a secondary cell there is a median layer rich on pectin (colloid carbohydrates) and on different protein composition.

The hemicellulose is a polysaccharide plant that is bound with a cellulose that compounded a slippery shell. The pectins shape a gel in which the cellulose and the hemicellulose are dipped to preserve the cell aggregation. The structural proteins add mechanical strength.

The *cellulose*, fig.7, is a polymer compounded of  $\beta$ -D-glucose's linear chains condensed through  $\beta$  (1-4) glycoside bonds present in starch and other carbohydrates: because of the bond's conformation, the polymer's repetitive unite is the dimer (cellobiose).

Cellulose is a straight chain polymer: the molecule adopts an extended rod-like conformation. In microfibrils, the multiple hydroxyl groups on the glucose residues hydrogen bond with each other, holding the chains firmly together and contributing to their high tensile strength. This strength is important in cell walls, where they are mashed into a carbohydrate matrix, conferring rigidity to plant cells. The lateral width of the cellulose microfibril has been estimated as 4-10 nm. The ability to break down cellulose directly is possessed only by certain bacteria (which have specific enzymes) like or by fungi. The enzymes cleave the glycoside linkage in cellulose. Many cellulolytic bacteria, fungi or enzymes break down cellulose into shorter linked chains.

The cellulose is insoluble and doesn't chemically attack unless with the required enzymes; the hemicellulose is chemically attacked by caustic solutions (NaOH 0.1-4 M). In the primary cell's wall the hemicellulose is compounded of xyloglucane, a polysaccharide with a frame like the cellulose one's with a short lateral chains that give a planar configuration. Depending on the growth and the species, the hemicellulose fraction of the cell wall contains even *xylane*, figure 8, (the xylane is principal constituent of the hemicellulose of the secondary cell wall) and *glucomannan*.

Although the backbone xylane structure is similar to that occurring in cellulose there is little driving force to produce crystalline type structures as the intra and inter-molecular hydrogen bonds associated with the 6-hydroxyl groups are necessarily absent. For example the *arabinoxylane* (present in grasses), consist of 1500 - 5000 residues.

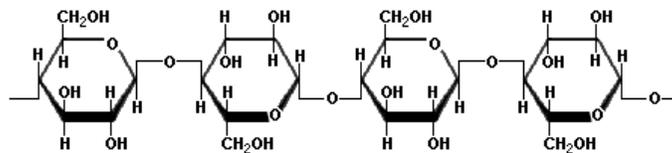


Fig. 7 – Structure of cellulose.

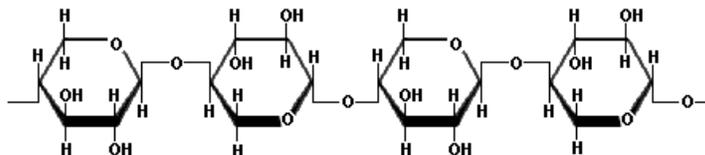


Fig. 8 – Structure of xylane.

Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plant tissues. Pectin is the methylated ester of polygalacturonic acid, which consists of chains of 300 to 1000 **galacturonic acid** units joined with  $1\alpha\rightarrow4$  linkages. The Degree of Esterification (DE) affects the pectin gelling properties. The structure shown in fig. 9, has three methyl ester forms ( $-\text{COOCH}_3$ ) for every two carboxyl groups ( $-\text{COOH}$ ), hence it has a 60% degree of esterification, normally called a DE-60 pectin. It is the cell wall most soluble polysaccharide: they can be extracted in hot water.

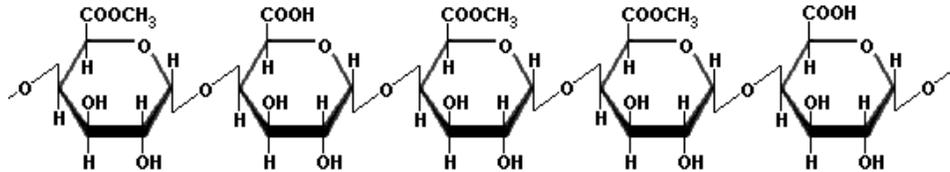


Fig. 9 – Structure of pectin.

All the plant's shares open to the atmosphere are covered by macromolecules or long chains of fatty acids hydroxylates, mixture of lipids, alcohols, alkanes ( $\text{C}_{21-37}$ ), esters and carboxylic acids.

Finally Amino acids, chlorophyll and nucleotide are primary metabolites; the terpenes, phenols and alkaloids (for example the cyanogen glycoside) are secondary metabolites.

For the study of lignin polymers, *tannins and flavonoids* (15 carbon atoms compounds two aromatic ring bond with a C3 bridge), are more important as precursors. They include simple phenylpropanes (like trans-cinnamic acid; para-cumaric acid and derivatives); cumarines (phenylpropanoic lactones); benzoic acids derivatives (fig.10). The tannins can show themselves as a condensation of different unit of flavonoids to form a polymer that could be hydrolysed with strong acids or as a condensation of gallic acid polymer, simple sugars and phenolic acids (fig.11). The last ones have a smaller dimension than the first ones, that's the reason why they can hydrolyse with diluted solutions of acids.

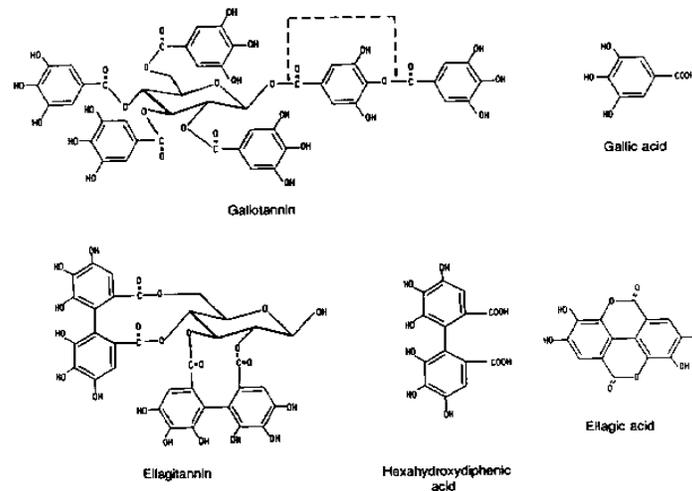


Fig. 10 – Structure of some tannins.

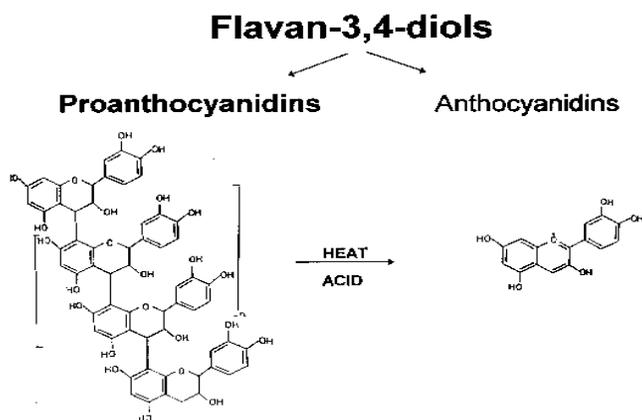


Fig. 11 – Hydrolysis of tannins.

Lignin is the most abundant plant polymer after cellulose. Lignin is a large, cross-linked and racemic [14] macromolecule with molecular masses in excess of 10,000 Dalton. It is relatively hydrophobic and aromatic in nature. The degree of polymerization in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures, which appear to repeat in a haphazard manner.

There are three **monolignol** monomers, methoxylated to various degrees: **p-coumaryl alcohol (not methoxylated)**; **coniferyl alcohol (a methoxyle content)** and **sinapyl alcohol (two methoxyle content)**, (fig. 12).

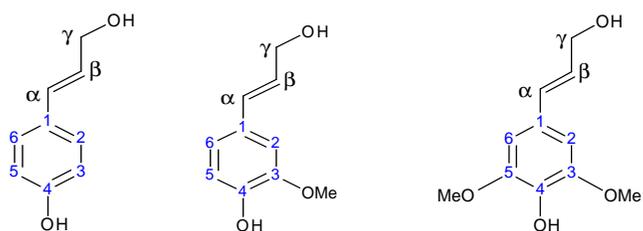


Fig. 12 – Precursor lignin monomers.

These are incorporated into lignin in the form of the phenylpropanoids **p-hydroxyphenyl (H)**, **guaiacyl (G)**, and **syngyl (S)** respectively, (fig.13).

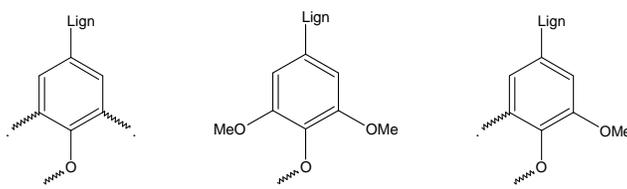


Fig.13 – Respectively H; G; S units.

**Gymnosperms (conifer or softwoods)** have a lignin that consists almost entirely of **G** with small quantities of H. That of **Angiosperms (broad-leaved or hardwoods)** is more often a mixture of **G and S** (with very little H), and **Monocotyledon lignin** is a mixture of all three **GSH** (come from **grass and palms**). That is the fundamental distinction based on the number of methoxylic groups.

All lignins contain small amounts of incomplete or modified monolignols, and other monomers are prominent in non-woody plants.

Lignin biosynthesis begins with the synthesis of glycosylated monolignols from the amino acid phenylalanine.

The polymerisation step, which is a radical-radical coupling, is catalysed by oxidative enzymes (both peroxidase and laccase). The oxidative enzyme catalyses the formation of monolignol radicals.

It's a polymer characterised from the presence of different functional groups (hydroxylic; methoxylic; carbonylic) positioned on the aromatic rings and on the lateral chains that affect the chemist property and reactivity.

The lignin content is major in the softwoods (25-33%) than in the hardwoods (20-25%); the amount of each monomer, the shape and dimension of the macromolecule differ from one specie to another; from different parts of the plants (shave; trunk); in the same cell wall.

Because of the polymerization of monolignol, monomers can't be studied *in vivo*, many theories concerning the structure and biosynthesis studies of lignin are developed with experimental data obtained *in vitro*.

From the Freudenberg study (1959), based on the polymerisation of conyferyl alcohol to a dehydrogenated polymer (DHP), similar to the lignin obtained on catalytic way via laccase, we got to the fundamental structural units [14; 29-34]. Only the radicalisation of conyferyl alcohol was investigated to simplify the final products characterisation. In the figure 10 it is shown that the dehydrogenation of monomer with the loss of phenolic hydrogen leads to the phenoxy radical stabilized for resonance.

Pairing of two of these mesomeric radicals to give a dilignol carries on the reaction. At least the reaction carries on a radical and/or ionic way to form an order superior lignols.

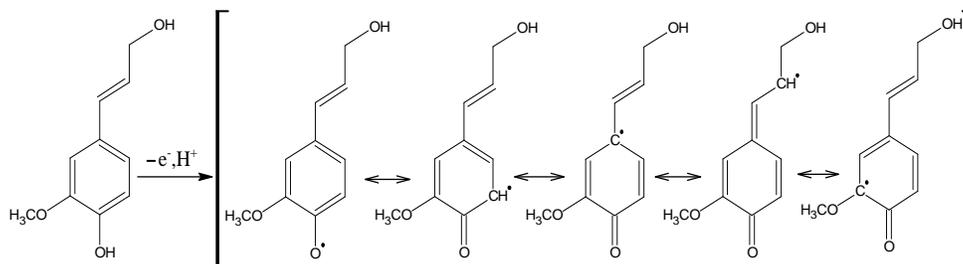


Fig. 14 – Conyferyl Alcohol dehydrogenation.

Between the mesomeric radical forms of fig.14, the five do not take part in the synthesis since they are not thermodynamically promoted and too much sterically cluttered. All possibility of pairing of the phenoxy radicals are presented in the following table, (tab.3):

	I	II	III	IV
I	Provisional peroxide 4-O-O-4	4-O-5	1-O-4	$\beta$ -O-4
II	4-O-5	5-5	5-1	$\beta$ -5
III	1-O-4	5-1	1-1	$\beta$ -1
IV	$\beta$ -O-4	$\beta$ -5	$\beta$ -1	$\beta$ - $\beta$

Tab.3 - Possibility of pairing of the phenoxy radicals shown in fig. 14.

The formation of 4-O-O-4 compounds is not allowed because of the strong instability of the final products; even the formation of 1-O-4; 5-1; 1-1;  $\beta$ -1 (III) are infrequent because of their sterical clutter. Figure 15 shows the conyferyl alcohol dimerisation reaction. The following stages of conyferyl alcohol polymerisation, carry on a way common knowledge like “end - wise”, i.e. the coupling of monolignol radicals with the oligolignols’s final phenolic groups that come from the first step (fig. 15); or the coupling of two radicals groups to the formation of a polymer (fig. 16).

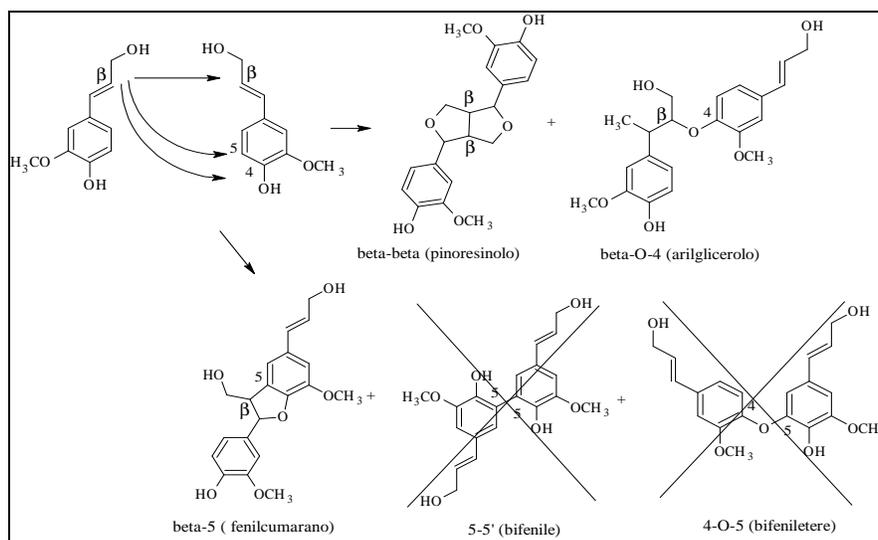


Fig. 15 – Conyferyl Alcohol Radical Dimerisation.

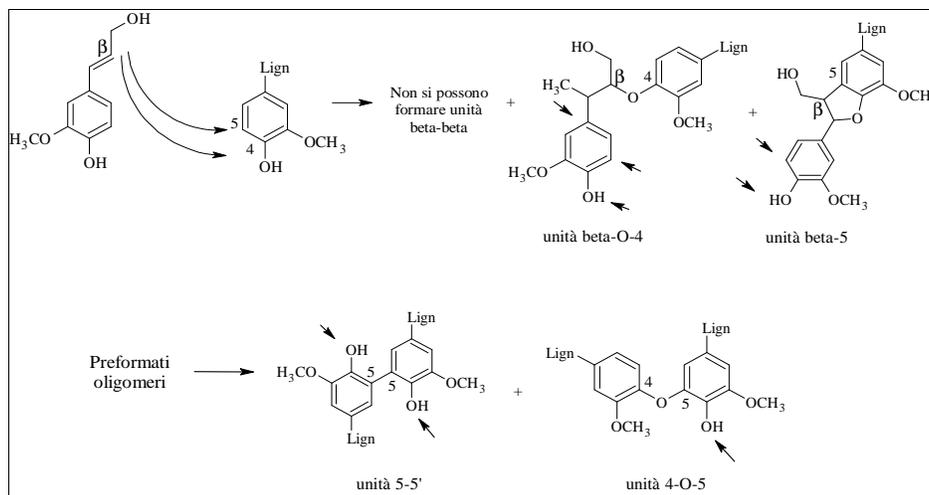


Fig. 16 – Conyferyl Alcohol radical Polymerisation.

In spite of the number of the dragged attack points, the coupling is not random; it depends on the reagent's nature; the solvent, temperature and pressure conditions. The *in vitro* lignin has a minor contribution of  $\beta$ -O-4 linkages and minor other differences.

The real lignification is a more complex process in which a radical monolignol or an oligomeric radical reacts with a preformed lignin with a cross coupling reaction in some established sites of nucleation.

In fig. 17 it is shown how the  $\beta$ -O-4 bonds are favourite in the formation of *in vivo* lignin: there are only two possibilities of coupling to an hydroxycinnamil alcohol and a guaiacyl unit (in four or five position), rather than the two possibilities carried on by the dehydrogenation. The distinction between the *in vivo* and *in vitro* polymerisation is appreciable from the two figures: the coupling that carries on the formation of  $\beta$ - $\beta$  linkages, predominant in the DHP, is not allowed because a radical delocalisation in  $\beta$  position is not promoted. Now it becomes clear the reason why the lignin with an high syringic unit content is particularly rich in  $\beta$ -etereous bonds: it's allowed only one synthetic view for the coupling with monolignols and syringic units that lead at the formation of  $\beta$ -O-4 linkages.

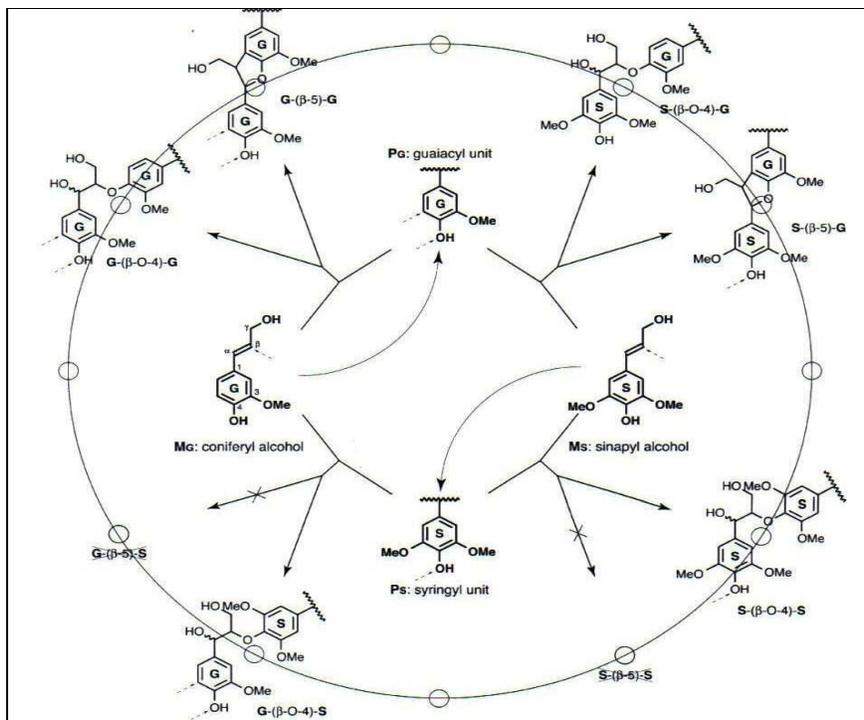


Fig. 17 – *In vivo* lignin polymerisation.

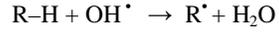
For purpose of particular matter's studies, the wood had to be in air, first as microparticles and then like nanoparticles presented in aggregation form with the particulate matter substrate. But the chemical and physical wood degradation is difficult because of its low nitrogen content, needed for the production of adapt enzymes. Rather the wood contains fungicide compounds like tannins, flavonoids, terpenes and stilbenzenes. In spite of this, there are some mushrooms that can carry on the degradation of vegetal polymers. The saprophytes ones can hydrolyse the cellulose and lignin. Rather the "rot fungi" excrete particular enzymes that break the cell wall: the "white rot fungi" are able to debase completely lignin, cellulose and hemicellulose; the "soft rot fungi" are able to debase cellulose, hemicellulose and only partially lignin; the "brown rot fungi" are able to debase cellulose and hemicellulose, but not lignin; the "dry rot fungi" remove the water around wood, supported the other fungi action. The "rot fungi" product non selective oxydases able to attack lignin: Lignin Modifying Enzyme (LME); Lignin Peroxydase (LiP); Manganese Peroxydase (MnP); Laccase (Lac). The LiP oxydises the methoxylic groups of aromatic rings; the MnP oxydises the phenolic substrate (it's less oxydative than LiP); the Lac can oxydise phenolic compounds firstly in quinones radicals and at last in quinones.

The bacteria don't have wood enzymes, but endoenzymes that carry on the degradation on the fungi's final products.

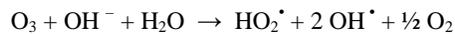
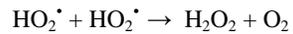
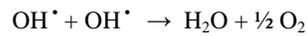
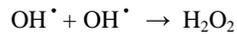
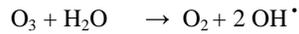
At last the xylophages insects (like termites or woodworms) can attack wood.

From a chemical point of view, the ozone is an atmosphere oxydative agent able to break the double and triple bonds C-C. the degradative *in vitro* studies show that lignin is more reactive with ozone even at room temperature leading low molecular weight compounds, while the cellulose is more refused [35-37]. In particular, the lignin ozonization breaks the aromatic rings, leaving unchanged the intermonomeric linkages.

Ozone is a strong capture of hydrogen atoms (H·), even from non activated bonds. These radicals can capture O<sub>2</sub> and arise peroxyradicals that can extract other hydrogen atoms with a chain reaction:



The finished hydroxy peroxyde at last, reduces itself to the final products. The degradation process are favourite by a water medium with the formation of hydroxylic ions:



From the pyrolysis technique for the study of lignin degradation the major thermal reduced products are known. The results of the studies show that during the pyrolysis the molecules break down only in the low bond energy points: the products are stable and volatile.

The lignin pyrolysis carries on at constant temperature leading to a characteristic phenol: the lateral chains are completely removed or contract to one or two carbon atoms; new double bounds C-C are found in the lateral chains because of pyrolysis dehydrogenation. *In vivo*, the conditions of temperature are not stabilised, so the final products change. There are some environmental studies of wood markers coming from biomass burning.

The following tab. 4 shows the investigated compounds in both a controlled pyrolysis of pure lignin and a sample of biomass burning.

Pyrolysis of a pure lignin	Aerosol from Biomass burning	Aerosol from Biomass burning additional compounds
Phenol		Veratric acid
Phenol, 2-methyl-		Vanillyl ethanol
Phenol, 3+4-methyl		Methyl vanillate
Guaiacol (G)	Guaiacol (G)	3-guaiacylpropanal
Phenol, dimethyl-		Guaiacylacetone
Guaiacol, 4-methyl		4-methoxycinnamic acid
Catechol		Vanillic acid
Phenol, 4-vinyl-		3-Guaiacylpropane
Phenol, 4-allyl-		Acetovanillone
Catechol, 3-methyl-		Vanillyl alcohol
Catechol, 3-methoxy-		3-Hydroxyguaiacol
Guaiacol, 4-ethyl		Methyl syringylpropionate
Catechol, 4-methyl		Methyl sinapate
Phenol, 4-propenyl-(cis)		Methyl syringate
Guaiacol, 4-vinyl-	Guaiacol, 4-vinyl-	Homosyringic acid
Phenol, 4-propenyl-(trans)		3-Syringylpropanal
Syringol (S)	Syringol (S)	Homosyringil alcohol
Eugenol		Syringic acid
Guaiacol, 4-propyl-		Syringylprop-2-ene
Benzaldehyde, 4-hydroxy-		3,5-Dimethoxyphenol
Vanillin	Vanillin	
Isoeugenol	Isoeugenol	
Syringol, 4-methyl-		
Homovanillin		
Acetoguaiacone		
Syringol, 4-ethyl-guaiacyl acetone		
Syringol, 4-vinyl-		
Propioguaiacone		
G-CO-CH=CH <sub>2</sub>		
Syringol, 4-allyl		
Syringol, 4-propyl		
Syringol, 4-propenyl-(cis)		
Dihydroconiferyl alcohol		
Syringaldehyde	Syringaldehyde	
Coniferyl alcohol	Coniferyl alcohol	
Syringol, 4-propenyl-(trans)		
Homosyringaldehyde	Homosyringaldehyde	
Coniferaldehyde	Coniferaldehyde	
Acetosyringone	Acetosyringone	
Syringylacetone	Syringylacetone	
Propiosyringone		
S-CO-CH=CH <sub>2</sub>		
Dihydrosinapyl alcohol		
Sinapyl alcohol	Sinapyl alcohol	
Sinapaldehyde		

Tab.4 - Investigated compound in both a controlled pyrolysis of pure lignin and a sample of biomass burning.

### 1.5 The atmospheric products of Polycyclic Aromatic Hydrocarbons: Oxygenated and Nitrated Polycyclic Aromatic Hydrocarbons.

Carbonaceous compounds are the largest contributor to the particulate matter in the atmosphere of both urban and rural areas (20-50%). However, relatively little is known about the composition, seasonal patterns and source/receptor relationships, concentrations that govern the individual compounds present in this complex matrix.

The resolved organic matter is composed by a 5% of n-alkanes; 20% of Aliphatic Dicarboxylic Acids and of a 10% of Aromatic Polycarboxylic Acids. The other constituents are less than 5% of the total and the latest 20% are unidentified organics. But the so called micro pollutants, i.e. the organic compounds present in the concentration <1ppm and that have a toxic effect on human safety, constitute less than 5% of the organic fraction, [38].

Apart from their concentration level, these compounds are monitored to understand their behaviour; source and fate in the atmosphere (fig.18). At that time many efforts were made in order to investigate new important compounds in the PM in the eyes of toxicologist and quantify them in different samples.

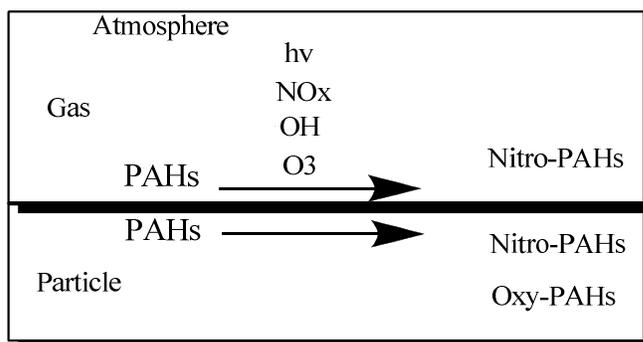


Fig.18 – Behaviour, source and fate in the atmosphere of PAHs [15].

#### 1.5.1 Polycyclic Aromatic Hydrocarbons (PAHs)

The PAH are compounds containing two or more aromatic rings fused together that do not contain heteroatoms or substituents. The simplest PAHs, as defined by the International Union on Pure and Applied Chemistry (IUPAC) [39], are Phenanthrene and anthracene. In fig.19 are presented some PAHs' structures.

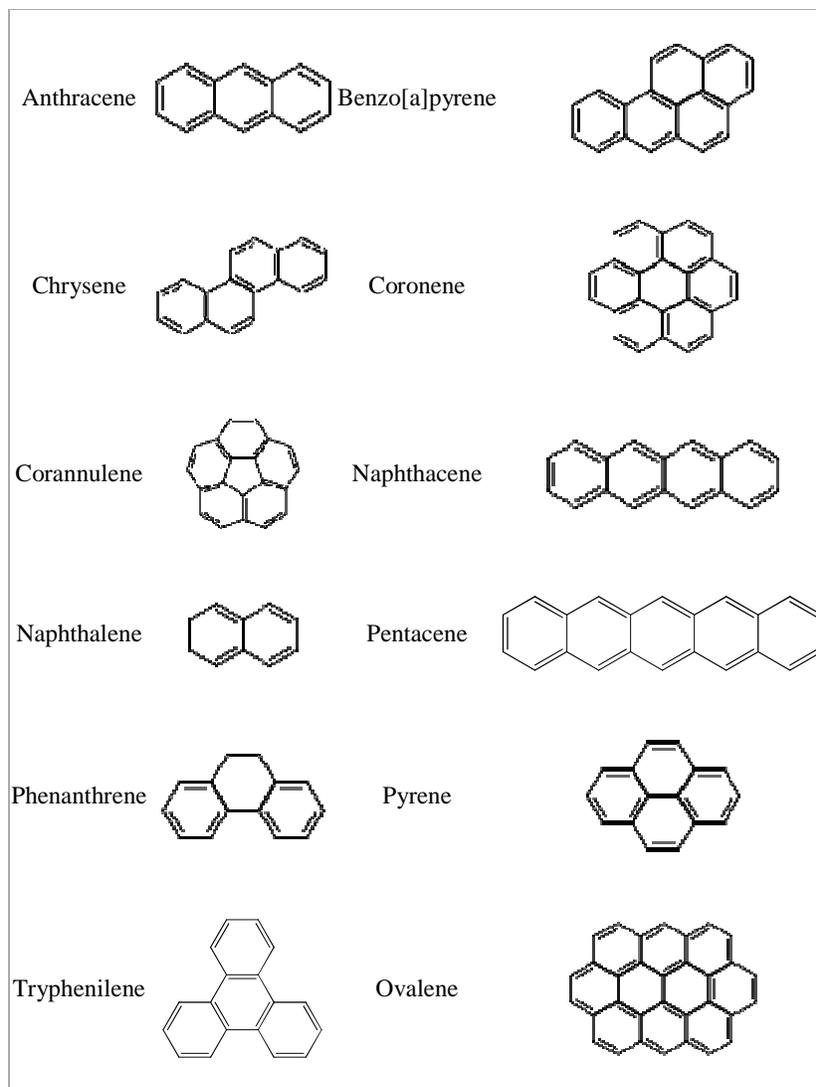


Fig.19 – Chemical structures of some Polycyclic Aromatic Hydrocarbons.

Aromatic  $\pi$ -sextets are defined as six  $\pi$ -electrons localized in a single benzene – like rings separated from adjacent rings by formal CC single bonds.

In the Phenanthrene, the molecules with the most disjoint aromatic  $\pi$ -sextets - i.e. benzene like moieties – that have a more aromatic outer ring than the central one, less aromatic, are more reactive, (fig.20), [17]. In general, aromatic  $\pi$ -sextets rings are considered to be the most aromatic centres, in the PAH. The other rings are less aromatic and are chemically more reactive [41-43]. In the figure the Clar aromatic  $\pi$ -sextets is indicated with a circle. The structure with the largest number of aromatic  $\pi$ -sextets is the so-called Clar structure. So the resonance structure 2, is more important than the resonance structure 1 (fig.20).

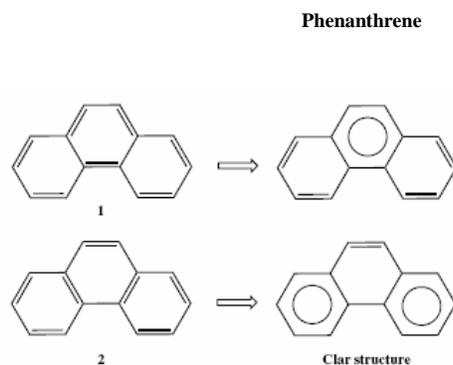


Fig.20 – Two of five Kekulé resonance structures of Phenanthrene and the individuated Clar structure with two aromatic  $\pi$ -sextets.

In contrast, in the anthracene, the number of sextets is just one and aromaticity spreads out. Three Clar structures with two sextets are present in chrysene and the aromaticity in the outer ring is larger than in the inner ring (fig.21).

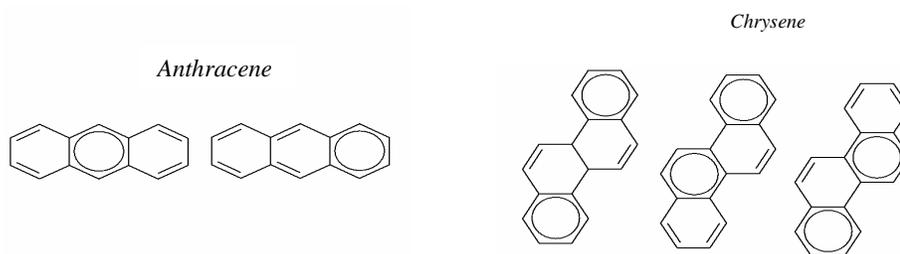


Fig.21 – Clar's structure formulas for Anthracene and Chrysene respectively [42, 43].

In general, a PAH with a given number of aromatic  $\pi$ -sextets is kinetically more stable than its isomers with fewer aromatic  $\pi$ -sextets [42-45].

There are PAHs that present a unique Clar structure (e.g. Phenanthrene), whereas other PAHs have more than one Clar structure [41, 44, 46].

Because of these considerations the PAHs were classified into Peri Condensed PAHs with a mass range of 202-276 amu: examples are pyrene, benzopyrenes, perylene; and Cata Condensed PAHs: examples are anthracene; chrysene, benzo[a]anthracene, dibenzo[a, h] anthracene.

Peri fused PAHs have internal fused carbons that are different than those in Cata fused structures: the additional condensation in the Peri fused structures makes them more rigid (less prone to molecular movements).

The boiling point ( $B_p$  values see in tab. 5), follows the number of benzene rings: for 2-3 rings  $B_p \leq 340^\circ\text{C}$ ; for four rings  $393^\circ\text{C} < B_p < 450^\circ\text{C}$ ; for five rings  $493 < B_p < 535^\circ\text{C}$ . Also the octanol water partition coefficient ( $K_{ow}$ ) follows the number of benzene rings: the less the number of ring, the more is the migration capacity of these dissolved hydrophobic organic compounds [47]. Vapour pressure, i.e. the pressure of the vapour that is formed above its liquid or solid,

decreases at the increase of ring number. So the Anthracene, for example is more volatile than the Benzo[g,h,i]perylene for example: these properties reflect the capacity of condensation from the gas phase to particulate. Also Henry's constant, H (air/water partition coefficient), is presented for some compounds in the table.

Lammel's recent study [48], presents degradation and deposition processes (radical and O<sub>3</sub> reaction, wet and dry deposition) of Benzo[a]pyrene and Fluoranthene, two different PAHs with very different vapour pressure and Henry constant values (tab.5). The multicompartamental model used shows how a very low burdens of the two considered PHAs was degraded in the particulate phase, in particular the Benzo[a]pyrene. Even the concentration of the degraded compound, as could be seen in tab.7 is very low.

Tab. 2 – Chemical-Physical Parameters for some PAHs, [24].

Name	Chemical formula	MW	Colour	Physical state	Melting point (°C)	Boiling point (°C)	Density (g/cm <sup>3</sup> )	Solubility in H <sub>2</sub> O (mg/l)	Solubility in organic solvents	Log K <sub>ow</sub>	Vapour pressure (mm Hg 25°C)	Henry's low constant (atm·m <sup>3</sup> /mol)
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178.2	Colorless	Solid	100	340	0.980	1.20	Acetic acid; Benzene; Carbon tetrachloride; Carbon disulphide; Diethyl ether; Toluene; Ethanol	4.45	6.8 10 <sup>-4</sup>	2.6 10 <sup>-5</sup>
Anthracene	C <sub>14</sub> H <sub>10</sub>	178.2	Colorless with violet fluorescence ; yellow with green fluorescence when impure	Solid	218	342	No data	0.076	Acetone; C <sub>6</sub> H <sub>6</sub> ; CS <sub>2</sub> ; CCl <sub>4</sub> ; CHCl <sub>3</sub> ; Ether; CH <sub>3</sub> CH <sub>2</sub> OH; MeOH; Toluene	4.45	1.7 10 <sup>-5</sup>	1.8 10 <sup>-5</sup>
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	202.3	Pale yellow	Solid	111	375	No data	0.23	Alcohol; Ether; Benzene; Acetic Acid	4.90	5.0 10 <sup>-6</sup>	6.5 10 <sup>-6</sup>
Pyrene	C <sub>16</sub> H <sub>10</sub>	202.3	Colourless	Solid	156	393	1.271	0.077	Benzene; Carbon Disulphide; Diethyl Ether; Alcohol; Petroleum ether; Toluene	4.88	2.5 10 <sup>-6</sup>	1.1 10 <sup>-5</sup>
B[a]anthra	C <sub>18</sub> H <sub>12</sub>	228.3	Yellow-blue fluorescence	Solid	162	400	1.274	0.010	Benzene; Diethyl ether; Acetone; slightly soluble in Acetic acid and hot Ethanol	6.61	2.2 10 <sup>-8</sup>	1.0 10 <sup>-6</sup>
Ciclop[c,d]py	C <sub>18</sub> H <sub>10</sub>	226.3										
Chrysene	C <sub>18</sub> H <sub>12</sub>	228.3	Colorless with blue or red-blue fluorescence	Solid	255	448	No data	6.76 10 <sup>-3</sup>	Slightly soluble in alcohol and Acetic Acid; Soluble in Hydrogen Sulphide on heating	6.12	1.50 10 <sup>-8</sup>	1.0 10 <sup>-6</sup>
B[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.3	Colourless	Solid	168.3	No data	No data	1.2 10 <sup>-3</sup>	Slightly soluble in Benzene and Acetone	6.04	5.0 10 <sup>-7</sup>	1.2 10 <sup>-5</sup>
B[j]fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.3	Yellow or orange	Solid	166	No data	No data	6.76 10 <sup>-3</sup>	Hydrogen Sulphide on heating; slightly soluble in Alcohol and Acetic Acid	6.12	15 10 <sup>-8</sup>	1.0 10 <sup>-6</sup>
B[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.3	Pale yellow	Solid	215.7	480	No data	7.6 10 <sup>-4</sup>	Benzene; Acetic Acid; Ethanol	6.06	9.6 10 <sup>-11</sup>	3.9 10 <sup>-5</sup>
Benzo[e]py	C <sub>20</sub> H <sub>12</sub>	252.3	Colourless	Solid	181.2	493.0	No data	6.3 10 <sup>-3</sup>	Acetone	5.68	5.7 10 <sup>-9</sup>	No data
Benzo[a]py	C <sub>20</sub> H <sub>12</sub>	252.3	Pale yellow	Solid	179.3	495	1.351	2.3 10 <sup>-3</sup>	Benzene; Toluene; Xylene; Ether. Sparingly soluble in Ethanol and Methanol	6.06	5.6 10 <sup>-9</sup>	4.9 10 <sup>-7</sup>
Dibenz[a,h]a	C <sub>22</sub> H <sub>14</sub>	278.4	Colourless	Solid	266.6	535	1.282	5 10 <sup>-4</sup>	Acetone; Acetic Acid; Benzene; Toluene; Xylene. Slightly soluble in Ethyl alcohol	6.84	1 10 <sup>-10</sup>	7.3 10 <sup>-8</sup>
I[1,2,3-c,d]py	C <sub>22</sub> H <sub>12</sub>	276.3	Yellow with a greenish-yellow fluorescence	Solid	163.6	530	No data	0.062	Organic Solvents	6.58	No data	6.95 10 <sup>-8</sup>
B[g,h,i]p	C <sub>22</sub> H <sub>12</sub>	276.3	Pale yellow-green	Solid	273	550	No data	2.6 10 <sup>-4</sup>	Benzene; Dichloromethane; Acetone	6.50	1.03 10 <sup>-10</sup>	1.44 10 <sup>-7</sup>

### 1.5.2 Oxygenated Polycyclic Aromatic Hydrocarbons (Oxi-PAHs).

Oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) are the second important compound class identified in the exhaust emissions of the natural gas-fired combustion sources [49]. Because OPA are more oxidized and less volatile than PAHs, they are generally adsorbed on the surface particles. In condition of high humidity, temperature and sunlight, the PAHs half-life is in the order of one hour: this effect is correlated with the presence of ozone; OH and  $N_{ox}$  [50, 51]. Besides PAHs rates of decay are faster at low pollutants concentration than at the higher concentration because of the competition on the particle surface with the other compounds. If PAHs react in the liquid water phase of the particle, then the rate at which they move on the surface and their solubility becomes important. So, homogeneous reactions with oxidants govern the fate of gas-phase distribution, whereas the heterogeneous reactions between surface-bound PAHs and gas phase atmospheric oxidants govern the fate of particle-bound PAHs.

Between sources the metalwork furnaces could be remembered; motorway's tunnel [52, 53]; smoke wood combustion [54]; vehicle waste pipe. In fig.22 some example of Oxy-PAHs are presented.

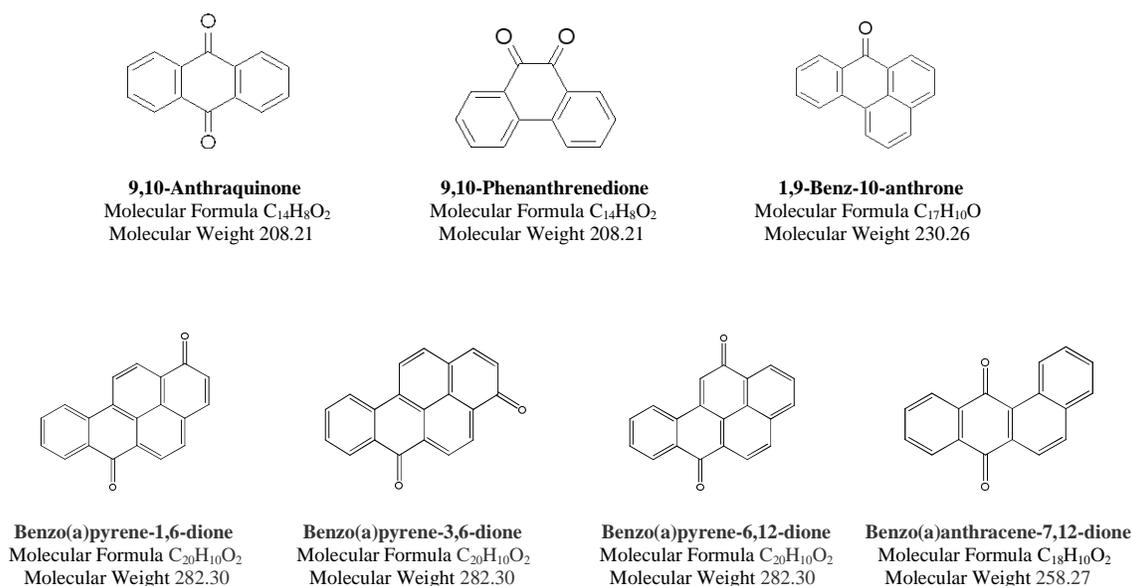


Fig. 22 – Some oxy-PAHs and their Molecular formula and weight.

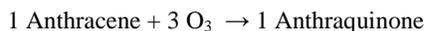
The sources of these pollutants could be biogenic or anthropogenic; primary (for example from diesel oil) or secondary as oxidative products of the correspondent PAHs depending on the single oxy-PAHs monitored and the site of sampling. For example the Anthraquinone could come from Anthracene. But Anthraquinone also naturally occurs in some plants, lichens and insects, where it serves as a basic skeleton for their pigments; it is used in the production of dyes as a catalyst in the production of wood pulp and paper industry and as a bird repellent on seeds and in the production of exhaust diesel emission. In the study of Kwamena (2006) [55], the surface-bound reaction mechanism of anthracene and ozone was investigated. The study focused on 9,10-Anthraquinone because it has been identified in atmospheric air and particulate matter. The result of the study reflects that at the high concentration of anthracene over

the 75% of the pollutant remain inreacted after long exposure to high ozone concentrations; but at low concentration, all the anthracene reacted, with a Langmuir-Hinshelwood kinetics:

$$K_{obs} = k_{max} K_{O_3} [O_3(g)] / 1 + K_{O_3} [O_3(g)]$$

Where:  $K_{obs}$  is the rate reaction coefficient observed;  $k_{max}$  is the maximum rate coefficient observed: the product results of the second order surface rate coefficient and the number of surface sites of the gas phase reactant (ozone);  $K_{O_3}$  is the ozone adsorption coefficient.

The kinetics were unchanged with ozone at high relative humidity (RH). The quantitative examination of the 9,10-Anthraquinone has a nonlinear correlation with ozone concentration: the dependence shows an increase since a plateau: the ozone is directly involved in the rate-limiting step. It is a second order surface rate coefficient mechanism reaction. The Anthraquinone yields directly by ozonolysis is about the 30%:



In the figure below are presented the Bayley reaction mechanism (1982) adopted also by Kwamena [56, 57].

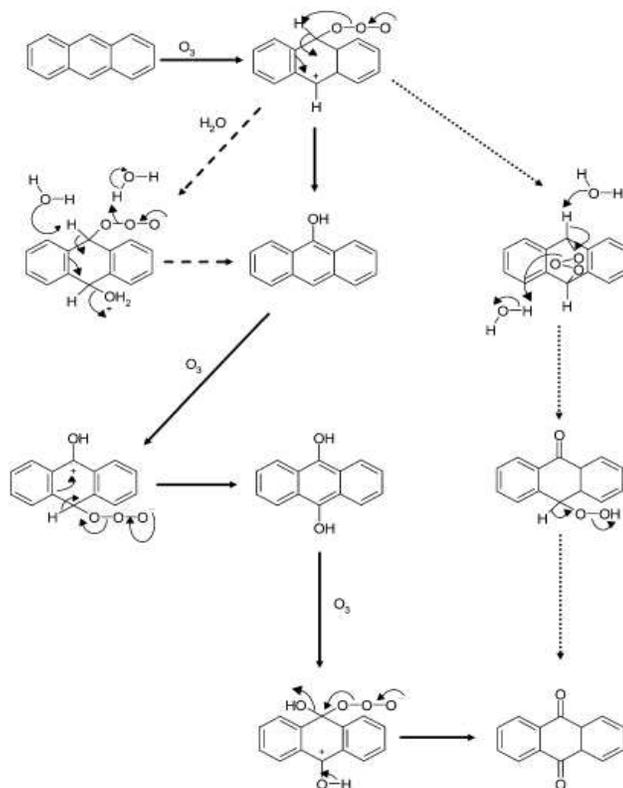


Fig.23 – Bailey’s reaction mechanism for the ozonization of anthracene to yield Anthraquinone.

Particular attention had been put towards the Benzo[a]pyrene diones for their particular health effects and their correlation to the benzo(a)pyrene concentration.

Instead the oxidative reaction of Benzo(a)pyrene is a first order rate coefficient on ozone concentration of Langmuir – Hinshelwood model:

$$K_{\text{obs}} = K_{\text{max}} K_{\text{O}_3} (\text{O}_3)$$

The reaction has a two step process: the absorption of gas-phase species and then the surface reaction. So the rate of the reaction deepens for both the surface and gas-phase species. In this case the humidity conditions affect the rate of reaction: on dry condition the BaP life-time of surface-bound is 84 min; at the 72% of RH the life-time is reduced to 28 min. With the increasing of RH, the  $K_{\text{O}_3}$  increase of the 230%; the  $K_{\text{max}}$  by only 25% (considering the  $K_{\text{max}} = K^{\text{II}} [\text{SS}]$  where  $K^{\text{II}}$  is the second order superficial rate coefficient and  $[\text{SS}]$  is the number of surface sites,  $K_{\text{O}_3}$  is the ozone gas to surface equilibrium constant;  $[\text{O}_3]_{\text{g}}$  is the gas-phase ozone concentration). Moriconi in 1961 suggested an oxidation mechanism of BaP under ozone. The reactant that unreacted was about 60-65%. This reflects the benzo(a)pyrene stability. He could also isolate the mixture of quinones among which the benzo(a)pyrene-3,6-dione; benzo(a)pyrene-1,6-dione were in a ratio of 1:3 (with trace amount of benzo(a)pyrene-4,5-dione). Moriconi didn't find the stoichiometry of the reaction but suggested the predominant attack at position 1; 3; 6 by more than one ozone molecules with a yield of about 30% (fig.24).

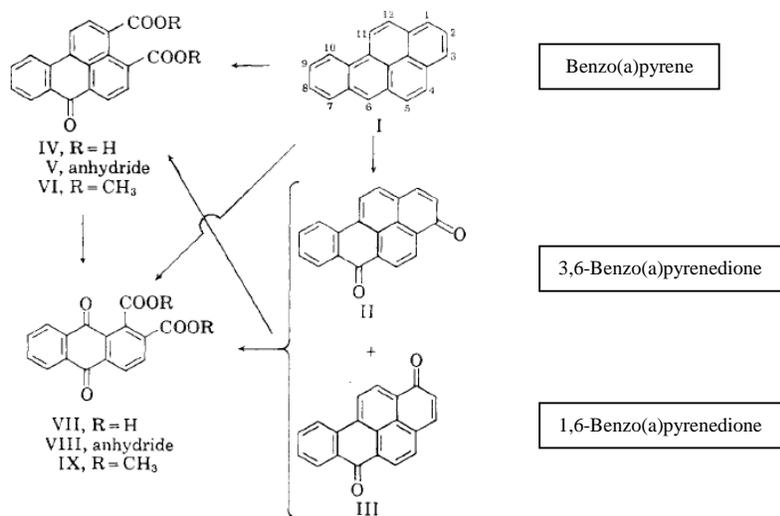
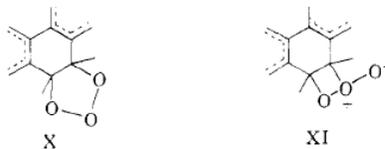


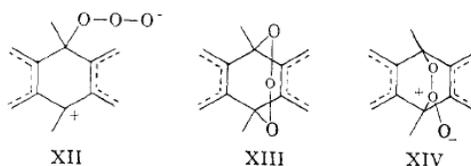
Fig.24 – Ozonolysis products of Benzo(a)pyrene, [57].

The ozone can attack not substituted carboxylic aromatics predominantly in two ways:

- 1) as double bound reactant, in one step or nearly simultaneous electrophilic – nucleophilic four centres attack on the most olefinic bond with the **X** and **XI** intermediates (fig. 10), [57].



- 2) as an electrophilic reactant assuming a two-step attack at the most reactive centers (the carbons with the lowest carbon localization energies) with the XII XIII and XIV intermediates and thence to p-quinones, [57].



As example, in subsequence fig.25 shows the view of reaction of the 6,12-Benzo(a)pyrenedione: the same view of reaction of all benzo(a)pyrenediones (1,6; 3,6; 6,12-Benzo(a)pyrenedione), [58].

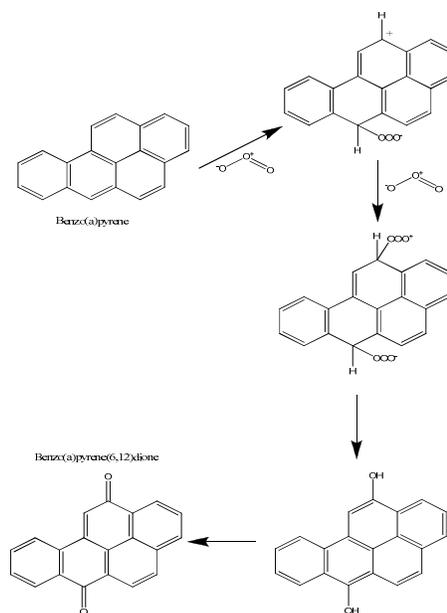


Fig. 25 – Karel and Van Cauwenberghe propose ozonolysis mechanism of Benzo(a)pyrene reaction [34].

The proposed mechanism of reaction reflected Moriconi's hypothesis of the XII intermediate, even he didn't find in in the separated mixture of diones, the Benzo(a)pyrene-6,12-dione, maybe for the lowest yield. The preferred ozonization position depends on the molar ratio of ozone/PAH after oxidative workup [58].

As we said, there are also other oxidant species: the OH and NO<sub>x</sub> radicals.

The OH major reactant is the addition to the aromatic ring with the formation of cresols that are more reactive themselves toward OH and sub sequentially with nitrogen oxides.

Like PAHs, for Oxy-PAHs the chemical-physical constants, well describe the different behaviour of single compound in relation with its chemical structure: in tab.6 these data are described.

Tab. 6 – Chemical physical constant of Oxy-PAHs (for the explanations see tab.5) [59].

Name	NCI Catalogue No.	Chemical formula	MW	Colour	Physical state	Melting Point (°C)	Boiling Point (°C)	Solubility in organic solvents	Ring No.	Log K <sub>ow</sub>	Vapour pressure (mm Hg 25°C)
9,10-Anthraquinone		C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	208.21		Solid	287	377		3	/	7.0 10 <sup>-10</sup>
9,10-Phenanthrene-dione		C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	208.21		Solid	208	360		3	/	2.3 10 <sup>-9</sup>
1,9-Benz-10-Anthrone		C <sub>17</sub> H <sub>10</sub> O	230.26		Solid	/	/		3	/	/
Benzo(a)pyrene-1,6-dione	L0109	C <sub>20</sub> H <sub>10</sub> O <sub>2</sub>	282.3	Golden Orange	Needles	277	/	Soluble in Methylene Chloride and other common organic solvents	5	4.81	5.8 10 <sup>-12</sup>
Benzo(a)pyrene-3,6-dione	L0110	C <sub>20</sub> H <sub>10</sub> O <sub>2</sub>	282.3	Red	Solid	295	292	Soluble in Methylene Chloride, DMSO, and Chloroform	5	5.24	9.8 10 <sup>-13</sup>
Benzo(a)pyrene-6,12-dione	L0111	C <sub>20</sub> H <sub>10</sub> O <sub>2</sub>	282.3	Red Brown	Solid	312	/		5	3.05	2.2 10 <sup>-11</sup>
Benzo(a)anthracene-7,12-dione		C <sub>18</sub> H <sub>10</sub> O <sub>2</sub>	258.27		Solid	168	135		4	/	4.2 10 <sup>-13</sup>

In the following table (tab.7) the Oxy-PAHs' concentrations reported in literature are presented.

Benzo[a]pirene-1,6-dione; Benzo[a]pirene-3,6-dione; Benzo[a]pirene-6,12-dione	Munich Germany	0.05-0.334 ng/m <sup>3</sup> as single; 0,043-0,605 ng/m <sup>3</sup> as sum	February 1997	Environ. Sci. Technol. 1999, 33, 1552-1558 R.Koerber, JM. Bayona, R. Niessner
Benzo[a]pirene-1,6-dione; Benzo[a]pirene-3,6-dione; Benzo[a]pirene-6,12-dione	Munich Germany	sum bapd max equal to 353 pg/m <sup>3</sup>	July 1997	Environ. Sci. Technol. 1999, 33, 1552-1558 R.Koerber, JM. Bayona, R. Niessner
Benzo(a)pyrene-diones (1,6-3,6-4,5-6,12-7,8-7,10- 11,12-Bapd)	Munich Germany	0,008-0,070 ng/m <sup>3</sup>	October 2003	Anal. Bioanal. Chem (2005) 381: 508-519 J.Llintelmann, K. Fischer, E. Karg; A. Scroppe
Benzo(a)pyrene-diones (1,6-3,6-4,5-6,12-7,8-7,10- 11,12-Bapd)	Munich Germany	< LOD	June, July, August 2003	Anal. Bioanal. Chem (2005) 381: 508-519 J.Llintelmann, K. Fischer, E. Karg; A. Scroppe
9,10-Phenanthrenequinone	Boston Massachusetts	0,43-0,04 ng/m <sup>3</sup>	June 1994	Thesis of Massachusetts Institute of Technology 1997 JO. Allen, AF. Sarofim, KA. Smith
Benzo(a)pyrene -6,12- dione	Boston Massachusetts	0,096-0,009 ng/m <sup>3</sup>	June 1994	Thesis of Massachusetts Institute of Technology 1997 JO. Allen, AF. Sarofim, KA. Smith

Benzo(A)pyrene diones	Urban Area	0,008-0,605 ng/m <sup>3</sup>	Winter Sample
Benzo(A)pyrene diones	Urban Area	0,009-0,353 ng/m <sup>3</sup>	Summer Sample

Tab. 7 – Oxy-PAHs' concentrations reported from the indicated papers.

### 1.5.3 Nitrated Polycyclic Aromatic Hydrocarbons

Similarly to Oxy-PAHs, Nitro-PAHs are formed either directly during combustion, or by chemical reaction (photo-oxidation) initiated by oxygenated atmospheric oxidants (for example OH· and O<sub>3</sub>), [60].

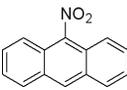
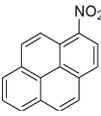
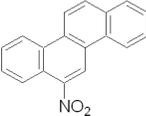
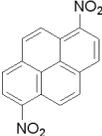
Atmospheric N-PAHs have two kinds of sources: direct (anthropogenic) emission and *in situ* formation involving parent PAHs and nitrating species (OH + NO<sub>2</sub>; NO<sub>3</sub><sup>-</sup>; HNO<sub>3</sub>) with isomerically different products. The 1-Nitro-Pyrene is one main nitro-PAH present in diesel exhaust and was therefore be found in every sample collected at the traffic influenced sampling site. Also the 3-Nitro-Fluoranthene is directly emitted.

While the 2-Nitro-Pyrene and 2-Nitro-Fluoranthene are mainly present on particles due to previous atmospheric formation in the gas-phase.

So, for example the concentrations between 2-Nitro-Fluoranthene/1-Nitro-Pyrene (2NFA/1NPY) weigh the relative impact of secondary vs. primary sources; 2-Nitro-Fluoranthene/2-Nitro-Pyrene (2NFA/2NPY) discriminate night time vs. daytime secondary formation [61].

In tab. 8 the registry numbers are represented and some structural information of Nitro-PAHs. There wasn't a match for information about solubility; boiling point, etceteras in the adopted bibliography.

Tab. 8 – Structure; MF, MW of Nitro-PAHs.

Name	1-Nitronaphtalene	9-Nitroanthracene	1-Nitropyrene	6-Nitrochrysene	1,6-Dinitropyrene
Structure					
Molecular Formula	C <sub>10</sub> H <sub>7</sub> NO <sub>2</sub>	C <sub>14</sub> H <sub>9</sub> NO <sub>2</sub>	C <sub>16</sub> H <sub>9</sub> NO <sub>2</sub>	C <sub>18</sub> H <sub>11</sub> NO <sub>2</sub>	C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>
Molecular Weight	173.17	223.23	247.25	273.29	292.25

The specific nitro-PAH isomers formed from the gas-phase OH radical-initiated reactions as well as their product yields, are given in Table 9. It should be noted that the nitrofluoranthenes and nitropyrenes formed from the gas-phase reactions of fluoranthene and pyrene have sufficiently low vapour pressures that they condense onto particles in the atmosphere, and at least for the 4-ring PAH, particle-phase nitro-PAH are formed from gas-phase PAH precursors.

Tab. 9 - Nitro-PAHs products formed from the gas – phase reactions of PAHs with hydroxyl radicals and nitrate radicals, in the presence of No<sub>x</sub>, and their yield.

PAH	Reaction with			
	OH		NO <sub>3</sub>	
	Product	Yield %	Product	Yield %
Naphthalene	1-Nitro-Naphtalene	0,3	1-Nitro-Naphtalene	17
	2-Nitro-Naphtalene	0,3	2-Nitro-Naphtalene	7
Acenaphtene	5-Nitro-Acenaphtene	0,2 (as sum)	4-Nitro-Acenaphtene	40
	3-Nitro-Acenaphtene		3-Nitro-Acenaphtene	2
	4-Nitro-Acenaphtene		5-Nitro-Acenaphtene	1,5
Acenaphthylene	4-Nitro-Acenaphthylene	2	No Reaction Products	
Fluorene	3-Nitro-Fluorene	1,4	No Reaction Products	
	1-Nitro-Fluorene	0,6	No Reaction Products	
	4-Nitro-Fluorene	0,3	No Reaction Products	
	2-Nitro-Fluorene	0,1	No Reaction Products	
Phenanthrene	Two Nitro-Isomers		Four Nitro-Isomers (including 9-Nitro-Phenanthrene)	
Anthracene	1-Nitro-Anthracene	low	1-Nitro-Anthracene	low
	2-Nitro-Anthracene	low	2-Nitro-Anthracene	low
Pyrene	2-Nitro-Pyrene	low	4-Nitro-Pyrene	0,06
	4-Nitro-Pyrene	low		
Fluoranthene	2-Nitro-Fluoranthene	3	2-Nitro-Fluoranthene	24
	7-Nitro-Fluoranthene	1		
	8-Nitro-Fluoranthene	0,3		
Acenaphtilene	two nitroarene isomers	0,1	No Reaction Products	

The nitro-PAHs' compounds present in the particulate matter could be formed from three processes: the direct gas-phase electrophilic nitration at high temperature (in the combustion process), the gas-phase nitration of PAHs in atmosphere on Sunday with OH radicals reactions and the nitration of PAHs in atmosphere in the night with NO<sub>3</sub> radicals reactions. These reactions are dramatically influenced by the substrate: the nitrations are promoted in a silica substrate; inhibited in a carbonaceous substrate – Jager and Hanus, 1980.

Even if the presence of HNO<sub>3</sub> on carbonaceous substrate (like in the smoke plume), favours the nitration [62]. In the figure 26 the daytime gas-phase photo-oxidation of naphthalene with OH radicals is presented, [63] and in figure 27 with an higher yield, with NO<sub>3</sub>.

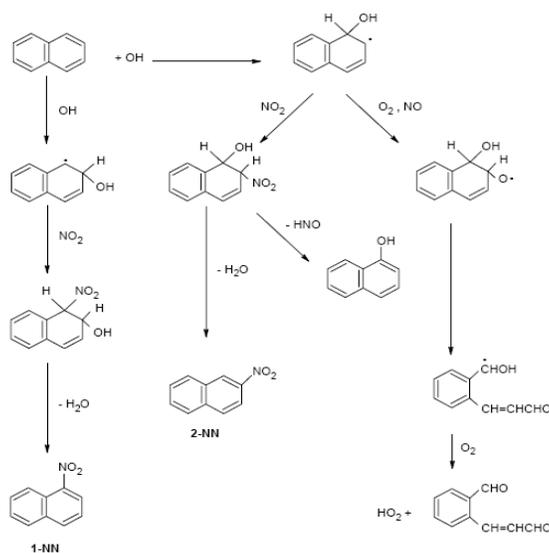


Fig.26 - Daytime gas-phase photo-oxidation of naphthalene with OH.

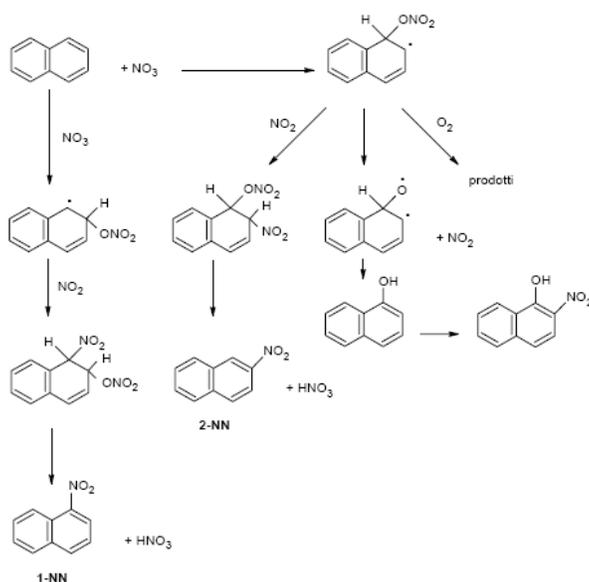


Fig.27 - Daytime gas-phase photo-oxidation of naphthalene with NO<sub>3</sub>.

While the pyrene reaction with OH radicals is represented in fig.28.

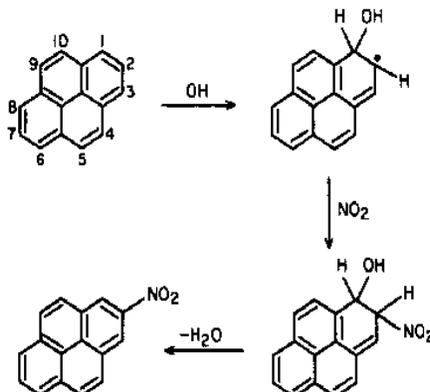
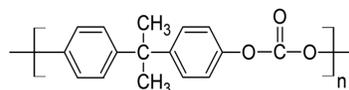


Fig.28 – Formation of Nitro-pyrene in atmosphere.

## 1.6 Bisphenol A

Bisphenol A (BPA), is an organic compound synthesized for the first time in 1891 from A.P. Dianin [15]. In 1936 the estrogenic behaviour of the molecule has been studied like a synthetic hormone. The research later has been abandoned in favour of the better response of Diethylstilbestrol, (DES) [16]. In 1938 P. Castan patented the epoxy resins, obtained from the reaction between BPA and epichlorohydrin [17], and the same year, in 1955, D. Fox (hired by General Electric) and H. Schnell (Bayer) patented the polycarbonate made from BPA [18].

This polymer is still obtained from the electrophilic aromatic substitution of phenol and acetone [17]. About 65% of BPA produced every year is used for the polycarbonate synthesis, the 25% for the epoxy resins and the remaining 10% for other products. The polycarbonates are thermoplastic polymers, used as commodities and plastics engineering, with a repeating chemical structure of:

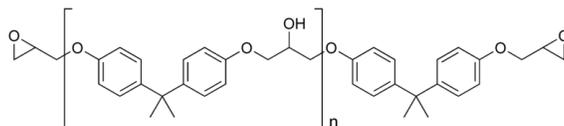


It is used for:

- compact discs, DVDs;
- baby's bottles;
- drinking bottles;
- drinking glasses;
- lab equipment, research animal enclosures;
- lighting lenses, sunglass/eyeglass lenses, safety glasses, automotive headlamp lenses;
- MP3/Digital audio player cases;
- Advertisement: signs, displays, poster protection;
- Building: domelights, flat or curved glazing, and sound walls;

- Computers;
- Industry: machined or formed, cases, machine glazing, riot shields, visors, instrument panels.

The epoxy resin has a repeating chemical structure:



and is used for:

- coatings;
- adhesives (polyurethane, acrylic, cyanoacrylate);
- composite materials such as those using carbon fibres and fibreglass reinforcements;
- master models, laminates, castings, fixtures;
- it is employed in motors, generators, transformers, integrated circuits, transistors and hybrid circuits, circuit boards printing, switchgear, bushings, and insulators in order to protect electrical components from short circuiting, dust and moisture;
- marine applications;
- aerospace industry as a structural matrix material which is then reinforced by fibre;
- mixed with pigment, it is used as a painting medium;
- manufacturing rotor blades of wind turbine.

Bisphenol A is used also as raw matter in the production of Tetrabromobisphenol A, a flame retardant and for Polyvinyl chloride (PVC). Bisphenol A Diglycidylether Methacrylated is employed for protective covering of tins for food and in the partial or seal denture.

Consequently, the annual production as raw material is of 2–3 million metric tonnes of BPA.

### 1.6.1 Human Exposure and Toxic Effect on Human Health

The human exposure has been proved to be continuative and chronic. Studies of “Center for Disease and Prevention” of the United States have highlighted a trace of BPA in 93% of human urine from 2003 and 2004 [64, 65]. It could come from different sources: the first is food ingestion for migration from commodities especially at high temperature [66]. The concentration of the monomer in urine is particularly alarming for babies, as shown in table 10, [65, 67-69]:

Age	Food and Drink eat	Exposition to BPA µg/Kg bw/day
3 month	Breast milk	0,2
3 month	Baby's bottle in PC or glass	2,3
3 month	Baby bottle in PC	11
6 month	Baby's bottle in PC and other commercial food	13
1-5 year	Commercial food	5,3
Adults	Commercial food	1,5

Tab.10 – Concentration the Bisphenol A in the human urine.

Other data reported the presence of BPA in urine, amniotic fluid, tissues and breast milk, all show human's broad exposure, [70, 71]. In fact from EFSA (2006), a range of concentrations are estimated for adults that equals to 0,02-59 µg/Kg bw/day, [72].

The Low observed Adverse Effect Level (LOAEL), from *in vivo* animal study is 50 mg/kg bw/day, [73]; the Oral Reference Dose (RfD) 0,05 mg/kg bw/day and the No Observed Adverse Effect Level (NOAEL) 0,016 mg/kg bw/day, [74].

The exposed data, in 2008, induced the Canadian Government to proscribe the feeding bottles made of polycarbonate and implemented restrictions for the release of the molecule in the environment from Industries and the 13th of March of 2009 the United States Government proscribed all food vessels containing Bisphenol A, [75, 76]

*In vitro* and animal studies have demonstrated that BPA effects are dose-linked, a high dose develops hyperinsulinemia, insulin-resistance and acts like “endocrine disruptor”, interfering with the growth of the central nervous system and the reproductive one. Exposure to low doses stimulates the insulin release and reduces the adiponectin secretion [77]. Moreover, the pollutant is tied to the adiponectin secretion and other biological mechanisms still unknown [78], cardiovascular diseases and progression of mammary and prostate carcinoma.

### 1.6.2 The Concentration of Bisphenol A in the Particulate Matter

The second most important exposure to Bisphenol A is by inhalation and was estimated at about 0,5% in comparison to the assumption by ingestion, [79]. But this data is important because of the continuous all day long exposure; an exposure that adds to the data of ingestion during meal; aside from culture and habits. In fact there are some studies about the urban indoor and outdoor concentration of the molecule, reported in table 11.

Reference	Year	Sample type	Site of Sampling	BPA measured concentration
Rudel et al. <sup>(80)(81)</sup>	2001	Indoor Air	Houses and Offices	2-3 ng/m <sup>3</sup>
			Plastic Factory	208 ng/m <sup>3</sup>
	2003	Indoor Dust	Houses and Offices	0,25 – 0,48 ng/mg
			Houses and Offices	0,2-17,6 ng/mg
Matsumoto et al. <sup>(82)</sup>	2005	Outdoor Particulate Matter	Urban City	0.02-1,92 ng/m <sup>3</sup>
Inoue et al.	2006	Indoor Particulate Matter	Urban City	<0,1-3,6 ng/m <sup>3</sup>

Tab.11 – Indoor and Outdoor BPA concentration.

The particulate matter analyzed fraction in the reported studies is not representative of the inhalable one, so the data could not be correlated with daily exposure and the biological health effect. We lack complete data about the presence of BPA in the fine fraction of indoor and outdoor of particulate matter differs by season.