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Carbon in Atmospheric Particulate Matter

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Preface

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Abstract

Carbon compounds account for a large fraction of airborne particulate matter (‘carbonaceous aerosols’). Their presence raises a number of scientific questions dealing with climate issues and possible effects on human health. This review describes the current state of knowledge with respect to the ambient concentrations levels (elemental carbon, organic carbon and organic matter) and the various emission sources, and summarizes the role of atmospheric carbon in the various environmental issues. The report finishes by identifying the actual gaps in knowledge and gives (related) suggestions for future research.

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1.1 Introduction

Carbon is a non-metallic element having the symbol C, an atomic number 6, an atomic weight of 12. There are four known allotropes[1] of carbon: amorphous, graphite, diamond and fullerene. Carbon is a critical element to all life. Since, by mass, carbon is the most abundant constituent of all the major molecules that organisms are formed from (e.g., nucleic acids, proteins, carbohydrates, and lipids). Carbon atoms continually move through living organisms, oceans, atmosphere, and the crust of the planet. Carbon dioxide is converted through different processes into many different carbon compounds, which are then converted to fossil fuels by decomposition, and, when burned, turns into carbon dioxide.

Carbon has 2 stable, naturally occurring, isotopes. Carbon-12 comprises about 99% of all carbon on Earth; Carbon-13 is the next most abundant, comprising slightly more than 1% of all carbon on Earth. Carbon-14 is the most abundant radioactive isotope of carbon at 1 part per trillion with a half life of 5730 years. It has been widely used to date such materials as wood, archaeological specimens etc. through radiocarbon dating. All other isotopes of carbon are highly unstable and therefore extremely rare.

For more than 200 years, chemists have divided carbon compounds into two categories. Those that were isolated from plants or animals were called organic, while those extracted from ores and minerals were inorganic. However, as Spencer Seager in the Chemistry for today (2004) wrote, the division between 'organic' and 'inorganic' carbon compounds while 'useful in organizing the vast subject of chemistry ... is somewhat arbitrary'. Organic compounds are those which contain carbon, although some carbon-containing compounds are traditionally considered inorganic. Over the past century, the precise classification of inorganic vs. organic compounds has become less important to scientists, primarily because the majority of known compounds are synthetic and not of natural origin.

1.2 Inorganic carbon compounds

There are two well known carbon oxides in the form of gases in the atmosphere: carbon monoxide (CO) and carbon dioxide (CO_2). Carbon monoxide, a gas, is odourless, colourless, tasteless and highly toxic. The major sources of carbon monoxide are technological processes (combustion and industrial processes), biomass burning and natural sources (e.g. volcanoes, bushfires). Carbon dioxide is a colourless, almost odourless gas that is formed by the combustion of fossil fuels, cement production and land use conversion.

The carbon compounds with metals involve carbonates and bicarbonates. An example is calcium carbonate ($CaCO_3$), a common substance found as rock in all parts of the world, and is the main component of shells of marine organisms, snails, and eggshells. The only known acid that is derived from the oxides of carbon is the carbonic acid (H_2CO_3). With the removal of protons from carbonic acid, carbonates and bicarbonates are formed.

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[1] Pure forms of the same element but differing in structure.

1.3 Organic carbon compounds

Organic compounds are defined by one of the following (chemical) criteria:

1. Two carbon atoms bonded to each other (e.g. C_2H_6 - ethane),
2. One carbon atom bonded to at least one hydrogen atom or halogen atom (e.g. CH_4-methane),
3. One carbon atom bonded to at least one nitrogen atom by a single or double bond[2] (e.g. CH_3NH_2- methylamine).

The state of matter (solid, fluid or gas) for organic compounds depends on how many carbon atoms are contained in it. When a compound has up to 4 carbons it is a gas, between 5 and 20 carbons it is in the liquid state, and in case of more than 20 carbons it is a solid. The simplest group of organic compounds is the hydrocarbons, where molecules are built up by carbon and hydrogen atoms only. As 'pure' hydrocarbons are denoted aromatics, alkanes, alkenes and alkyne-based compounds whereas other hydrocarbons with bonded compounds or impurities of sulphur or nitrogen, are referred to as 'impure', but remain somewhat erroneously referred to as hydrocarbons.

When a different functional group is attached to the carbon chains, other groups of organic compounds are produced (Fig.1.1). Examples are alcohol, phenols and ethers (e.g. ethanol, ethylene glycol, phenol, diethylether and tetrahydrofuran), aldehydes and ketones (e.g. formaldehyde, benzaldehyde, acetone and butanedione), carboxylic acids (e.g. acetic acid, lactic acid, citric acid), amines and thiols (e.g. amphetamine, methybutanethiol), halides (e.g. carbon tetrachloride, triclorofluormethane and benzene hexachloride), alkyne (e.g. acetylene, fungicide capillan), alkenes (e.g. etylene, isoprene), alkanes (e.g. hexane) and aromatics (e.g. benzene, naphthalene , benzopyrene, polyaromatic hydrocarbons (PAHs)).

Aalthough the properties of each of the several million organic molecules are unique in some way, all molecules that contain the same functional group have a similar pattern of reactivity at the functional group site. Thus, functional groups are a key organizing feature of organic chemistry. By focusing on the functional groups present in a molecule (most molecules have more than one functional group), several of the reactions that the molecule will undergo can be predicted and understood.

The majority of hydrocarbons are found in crude oil and natural gas, whereas decomposed organic matter provides an abundance of carbon. Hydrocarbons can when bonded form seemingly limitless chains. For example, polyethene (or polythene) is a very long hydrocarbon molecule and is one of the most common materials in our daily lives and accounts for 40% of the total volume of world production of plastic materials. An important fraction of organic compounds is still extracted from natural sources because they would be far too expensive to be produced artificially. Examples include, in general, those natural products with large or complicated molecules which are present in reasonable concentrations in living organisms. However, increasingly many polymers are synthetically produced.

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[2] With one exception: cyanide compounds are considered as inorganic compounds for classification purposes.

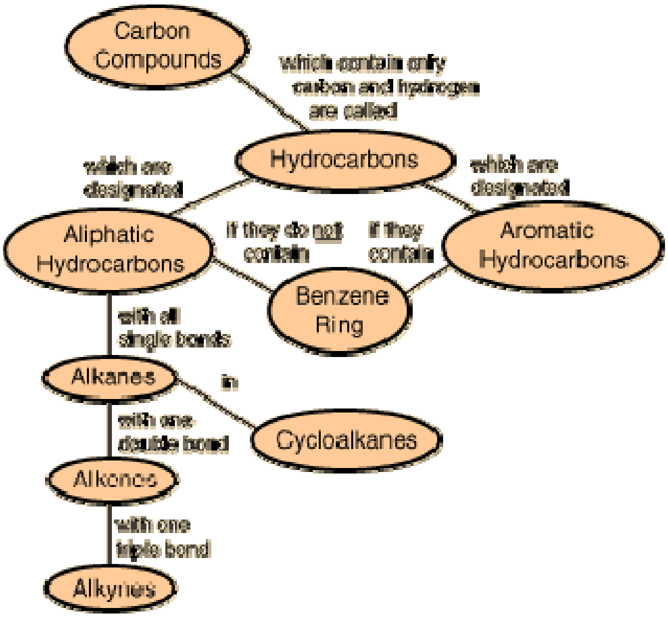

Figure 1.1 *Hydrocarbons are the simplest organic compounds. Containing only carbon and hydrogen, they can be straight-chain, branched chain, or cyclic molecules. Carbon tends to form four bonds in a tetrahedral geometry. Hydrocarbon derivatives are formed when there is a substitution of a functional group at one or more of these positions*

2. Carbon in particulate matter

2.1 EC, OC and OM

Particulate matter (PM) is composed of water soluble inorganic salts, insoluble mineral dust, and carbon material. Carbon compounds, sometimes called 'carbonaceous aerosol' account for a large fraction of PM. It includes the aerosol-constituents that are based on carbon, 1) organic carbon (OC), 2) elemental carbon (EC) and 3) carbonate minerals[3] (Seinfeld and Pankow, 2003).

The dominant fraction of carbonaceous aerosol is OC which includes all organic compounds present in the particle phase. EC constitutes a smaller fraction of the carbonaceous aerosol. EC is operationally defined as the material that does not volatilise and has been shown to be (partly) present as graphite. The fraction of carbonate minerals is insignificant in our region of the world.

The total carbon (TC) content of aerosol is defined as the sum of all carbon in the particulate matter (OC and EC). TC is easily determined by thermo chemical oxidation and evolved gas analysis. Discrimination of EC and OC is based on thermo-chemical techniques. EC is operationally defined as the material that does not volatilise in a first step of the analysis. OC is defined as the difference between TC and EC (TC=EC+OC). There are at present several approaches to discriminate EC and OC, providing values with a difference of up to a factor of three.

A next uncertainty is related with the quantification of organic matter (OM). The mass of OM is more than that of OC, because organic compounds contain other elements (O, H, N,) besides carbon. OM concentration is often approximated by OC concentrations multiplied by a constant factor. Mcostly the OM value is assumed as 1.2-1.4 times larger than the OC value. However, the factor relating OM and OC is not accurately known. According to Turpin and Lim (2001), ratios of 1.6 ± 0.2 for urban aerosol and 2.1 ± 0.2 for no urban aerosols appear to be more accurate. The value of the factor generally depends on the individual molecular composition of the respective aerosol. OM that consists only of hydrogen and carbon has a low ratio, e.g. alkanes or polycyclic aromatic compounds with non polar characteristics; however, highly oxygenated compounds have a higher ratio, e.g. dicarboxylic acids or sugars. They are generally water soluble. In urban aerosol, because of their nonpolar constituents from fossil fuel combustion sources, the OM/OC ratio are generally low (Hoffmann and Warnke, 2007).

There is another uncertainty concerning the OC values, which is the result of sampling artefacts (e.g. ten Brink et al., 2004; Novakov et al., 2005). OC concentrations are determined by analysis of particulate matter collected with quartz filters. Gaseous OC present in the sampled air also adsorbs on the filter. This is called a positive artefact because the measured OC concentrations will be enhanced. Additionally, some of the semi-volatile components of the particulate OC may evaporate from the filter during sampling. This process is known as a negative artefact as it results in an underestimation of OC concentrations (e.g. Bennett and Stockburger, 1994).

In order to correct for positive artefacts, the simplest approach is to use two quartz filters placed back-to-back. While the front filter removes all the particles, the OC on the back-filter can only come from adsorbed volatile organic compounds.

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[3] The carbonate minerals are almost exclusively found as in the soil dust in coarse size particles and will not further be discussed in this report.

NOTE: Black carbon (BC) is often used as a surrogate measure for EC. The reason is that BC is easily determined via the blackness of a filter sample. BC has been operationally defined as that equal to the amount of EC in reference samples with the same blackness.

2.1.1 Ambient concentrations

Two important points need the attention of the reader before going into the details of the existing data about concentrations of OM and EC in different sites around the world.

1. Atmospheric particulate matter can be divided into two groups according to particle size: the fine fraction, (PM2.5; diameter <2.5 µm) and the coarse fraction (PM_{10}-$PM_{2.5}$; diameter between 10 and >2.5 µm). These two groups have different sources, and therefore different shape, lifetime and most likely different health effects. It should be realized that PM_{10} measurements involve both the fine and coarse fraction of particulate matter.

   The size distribution of carbon aerosol in atmosphere shows generally two peaks: fine particles with a diameter of around 300 nm and are likely due to the combustion and secondary formations; and coarse particles, around at 2.5 µm which may be due to the primary biological particles or soil dust (Fig. 2.1).

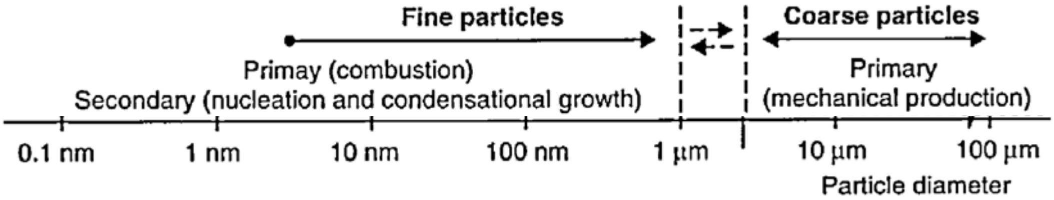


Figure 2.1 *Size modes of particles and important sources (from Hoffmann and Warnke, 2007)*

   More specifically, the mass distribution of EC emitted by automobiles is unimodal around 0.1 µm. However, the distribution of EC in polluted areas is bimodal with peaks in 0.05-0.12 µm and 0.5-1 µm. Generally the mode in the first range dominates, almost 75% of the total EC.

   Organic aerosol are also mainly found in the submicrometer size range. Their mass distribution is typically bimodal with the first peak around 0.2 µm diameter and the second around 1 µm (Seinfeld and Pandis, 1998).

   In the literature, more studies were found on the measurement of $PM_{2.5}$ components, since, although elevated levels of both PM_{10} and $PM_{2.5}$ were associated with the adverse health effects, it was shown that particles in the size range of $PM_{2.5}$ are most strongly and consistently associated with these adverse effects.

2. Most investigators report OC concentration as simply the concentration of carbon in µg (C)/m^3 and do not include the contribution to the aerosol mass of other elements, such as H, N and O being present in the organic aerosol compounds. If the results are not presented as OM values, the values in the following text should be considered as OC values.

   Studying literature the following recent references were found:

   - In an extensive study on chemical characteristics of particulate matter in 24 cities of Europe, OM appears to be the major component of PM_{10} and $PM_{2.5}$ at urban and kerbsides (16-29%), but not at natural and rural background sites. Black carbon contributed 5-10% to $PM_{2.5}$ and less to PM_{10} at all sites (Putaud et al., 2004).

- Series of 7 week sampling campaigns in urban background sites of 6 European cities (Duisburg, Prague, Amsterdam, Helsinki, Barcelona and Athens) showed that PM2.5 and PM2.5−10 were 8- 30 μg/m^3 and 5–29 μg/m^3, respectively. The contribution of OM to PM2.5 ranged from 21% in Barcelona to 54% in Prague, while that to PM2.5−10 ranged from 10% in Barcelona to 27% in Prague. The contribution of EC was higher to PM2.5 (5–9%) than to PM2.5−10 (1–6%) in all six cities (Sillanpaa et al., 2005)
- The measurements of carbonaceous compounds in $PM_{2.5}$ samples in three European cities (Amsterdam, Barcelona and Ghent) representing Southern and Western European urban environments, between 2004 and 2006, OC and EC concentrations were higher in the vicinity of roads and have higher averaged levels in Amsterdam (5.3 and 1.8 μg/m^3, respectively) and Barcelona (5.3 and 2.1 μg/m^3) than in Ghent (4.1 and 1.0 μg/m^3) (Viana et al., 2007).
- In another study between 2002 and 2004 in London and Birmingham EC accounted for an average of 26% and 10% of the total PM_{10} at kerbside and urban background sites, respectively, and that OM compounds were 23% and 21% of mass, respectively at two types of sites (Jones and Harrison, 2005).
- The campaign which was performed in urban background of 6 different European cities (Duisburg, Prague, Amsterdam, Helsinki, Barcelona and Athens) between 2002 and 2003 included the measurements with fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) size ranges. The campaign means of $PM_{2.5}$ and $PM_{2.5-10}$ were 8-30 μg/m3 and 5-29 μg/m3. The contribution of OM to $PM_{2.5}$ ranged from 21-54%, while that to $PM_{2.5-10}$ ranged from 10-27%. The contribution of EC was higher to $PM_{2.5}$ (5-9%) than to $PM_{2.5-10}$ (1-6%) in all 6 campaigns.
- Specifically in the Netherlands, the contribution in terms of mass of carbon components was 5 μg/m^3; of which 1 μg/m^3 was EC and 4 μg/m^3 comprises OM and 90% of the carbon-containing components were found in the $PM_{2.5}$ fraction (Visser et al. 2001; Buijsman et al., 2005).
- In a recent measurement which was performed along the highway A10 in Amsterdam, the contribution of carbonaceous aerosol was found 26 and 30% of total $PM_{2.5}$, with the average values of 5.4 and 9.3 μg/m^3 in summer 2005 and winter 2006, respectively (Weijers et al., in preparation). The averaged OC values in summer and winter were 3 and 5.5 μg/m^{3,} with 53 and 61% contribution to total carbon aerosol, respectively. Similar trends were observed in a study about the aerosol distribution over Europe (Langmann et al. 2008). During winter the highest concentrations of OC were determined over Eastern Europe due to domestic heating.

As a summary, typical mean concentration of OC in the atmosphere are in the range of 1 μg/m3 in clean areas to 10 μg/m3 in polluted areas, whereas peak concentrations might reach 50 μg/m3 during biomass burning episodes. EC concentrations in clean areas are typically 1 μg/m3, in polluted areas they might exceed 5 μg/m3 (Hoffmann and Warnke 2007).

2.2 Sources

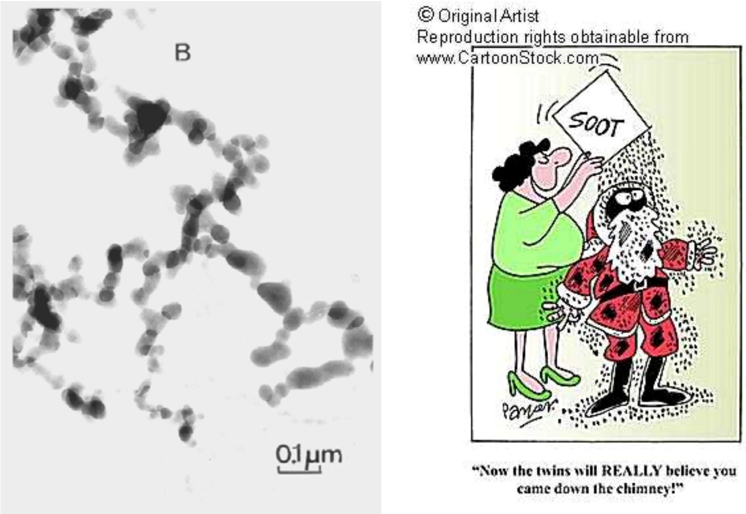
Although the source strength of OM and EC particles is very uncertain, Liousse et al. (1996) have estimated the global distribution of carbonaceous particles in fine particles (Table 2.1). Total OM emissions from different sources were always higher than EC emissions. They also reported the calculated average OM concentrations in fine particles for US as 0.5-2 μg/m3 and for several continents including the Central Europe as 10-12 μg/m3 (Liousse et al. 1996, Jacobson et al. 2000).

Table 2.1 *Yearly emission of submicrometer carbonaceous particles. Data has been compiled from the work of Liousse et al. (1996) by Jacobson et al. (2000). Biomass burning sources include burning of savannas, tropical forests, agricultural fires, and the burning of domestic fuels such as wood and charcoal.*

Source	**Organic Carbon (Tg/ yr)**	**Black Carbon (Tg/ yr)**
Biomass burning	44.6	5.6
Fossil fuel	28.5	6.6
Natural sources	7.8	0
Total	**81**	**12.3**

2.2.1 Elemental Carbon sources

The sources of EC are more easily identified than that of the more complex OC. EC is emitted as primary particles from incomplete combustion. In our region over 90% derives from diesel traffic. Generally such particles are agglomerates of small roughly spherical elementary particles (Fig.2.2). However, soot particles absorb organic vapours when the combustion products cool down. Therefore, soot should be considered as a mixture of EC and OC and small amounts of other elements such as, O, N and H incorporated in its structure (Seinfeld and Pandis, 1998). The emission is better known as ‘soot’.



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“Now the twins will REALLY believe you came down the chimney!”

Figure 2.2 *One diesel-soot particle made up of hundreds of smaller entities*

2.2.2 Organic Aerosol Sources

The sources determine both chemical composition and size distribution. Organic particles may be either directly emitted into the atmosphere (primary organic aerosol, POA), for example as products of fossil fuel combustion, biomass burning, disintegration of plant and microbes, or developed in situ by chemical reactions of gas phase compounds (e.g. benzene, xylene, terpene or isoprene) (secondary organic aerosol, SOA) (see Fig. 2.3 for an overview; note that, only the most dominant or best-known sources are shown).

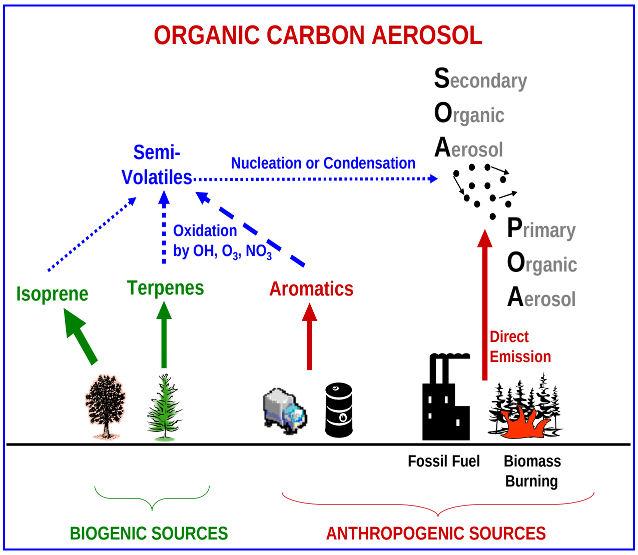

Figure 2.3 *Components of organic aerosol (http://www.vsp.ucar.edu/about/stories/ColetteHeald.html)*

It was reported that high abundance of POA in tropical air masses influenced by strong biomass burning, whereas SOA seem to dominate in mid-latitude air masses influenced by anthropogenic or biogenic emissions of precursor volatile organic compounds and high photo-chemical activity.

Both POA and SOA components can be internally or externally mixed with other aerosol components and efficiently transformed upon interaction with reactive trace gases. At present, however, the knowledge and understanding of OA composition, physicochemical properties, sources and transformation is very limited (Poeschl 2005).

Primary organic aerosol

Primary organic aerosols (POA) are directly emitted in the condensed phase (liquid or solid particles) or as semi-volatile vapours, which are condensable under atmospheric conditions (Poeschl 2005). They can enter into the atmosphere in many ways, including as particles from fossil fuel combustion, biomass burning, plant debris, bacteria-spores-virus etc. Generally known that most coarse organic compounds are of biological origin and most fine is anthropogenic. Most of the observed mass distribution is unimodal and 90% or more of the emitted mass is in the form of fine particles (Seinfeld and Pandis, 1998).

One form of natural POA results from the disintegration and dispersion of bulk plant material. Particles from this source are generally in the hypermicrometer size range and have a distinctive n-alkane signature with specific odd number carbons (e.g. Hildemann et al., 1996, Jacobson et al. 2000). Primary vegetation-derived aerosol were found as less than 3% of the total fine aerosol in an urban area, but other studies have indicated that in remote locations this source may be relatively more important (Mazurek et al., 1991).

Another form of POA involves the viable biological microbes such as bacteria, viruses, and fungal spores, which are ubiquitous in the atmosphere. They cover a very large size range from viruses (about 1 nm) to pollen (up to 300 µm) (Jacobson et al. 2000). These particles are mostly produced on the surface of plants and may be transported over very long distances. Fuzzi et al. (1997) showed with his measurements that fog droplets might be a very favourable growth media for bacteria and yeasts.

Biomass and fossil fuel burning are the two most important sources of POA globally. Combustion processes are, in general, the sole source of EC in the atmosphere (e.g. Liousse et al., 1996). The amount of OC compared with EC produced seems to depend on the type of material burned and the temperature of combustion.

Mainly studies about identifying compounds originating from biomass burning have concentrated on polycyclic aromatic hydrocarbons (PAHs), which are toxic. These compounds exist in both the gas and particle phase. The concentrations and sizes of PAH molecules emitted during burning episodes do not seem to be affected by the type of plant being burned, but depend highly on the efficiency of burning (Jacobson et al. 2000).

In urban areas, motor vehicle emissions account for a significant amount of POA and depend on generally the type, size, and age of the engine, as well as on the fuel and lubrication used. For example, the measurements of samples from automobile exhaust in the gas chromatography/mass spectrometry (GC/MS) performed by Rogge et al. (1993) indicated a great variety of chemical species, including n-alkanes, n-alkanoic acids, benzoic acids, and a host of other cyclic, polycyclic, and aromatic compounds.

Besides motor vehicles, other major sources of organic fine aerosol originate from meat cooking, fireplaces, road dust, tire debris, and brake dust.

Secondary organic aerosol

A secondary organic aerosol (SOA) is formed through the oxidation of volatile organic compounds (NMVOC-non-methane VOC’s) by the hydroxyl radical, ozone and the nitrate radical in the atmosphere that then condenses.

The formation of SOA is related with the temperature, relative humidity, and the concentrations of organic and inorganic nucleating and condensing vapours, which depend on atmospheric transport as well as local sources and sinks such as photochemistry and pre-existing aerosol or cloud particles (Poeschl 2005 and references within).

Generally, aerosol production would not occur if either the oxidation reaction is too slow or the vapour pressure of the product is higher than that of the reduced form (Jacobson et al. 2000).

In addition, the amount of aerosol formed by the oxidation of non –methane VOC (NMVOC) depends on the structure of the precursor. Cyclic structures generally have higher yields of SOA than acyclic compounds because most of carbon backbone of cyclic compounds stays intact when the double bonds are cleaved during oxidation.

SOA can form from both anthropogenic and biogenic NMVOC precursors. Important sources of NMVOCs include livestock, combustion of firewood and fossil fuels, trees, manufacturing petroleum (production and refining), natural gas (production and distribution), vehicular exhaust, and coal mining. Specifically xylene and toluene are anthropogenic precursors to SOA and present in the urban atmosphere. Terpenes are the best studied and possibly the most important biogenic precursors of SOA (Seinfeld and Pankow 2003).

On a global scale biogenic VOCs seem to be the predominant cause of SOA, however, in urban areas the dominant source can be the anthropogenic VOCs. V ery recently there are strong indications of even much stronger anthropogenic sources for SOA (Baltensperger, 2008). The total annual global biogenic organic emissions are estimated to be 1150 Tg/yr, while the estimate for total anthropogenic emissions is 142 Tg/yr (Seinfeld and Pandis, 1998).

Levels of Secondary Organic Aerosol vs. Primary Aerosol

The amount of primary versus secondary organic aerosol is not well studied and is very difficult to quantify. There are indirect methods, e.g. use of tracer compounds for POA or for SOA, use of models for the emission of POA and formation of SOA. For example, EC has often been used as a tracer of POA. It was assumed that EC and POA have the same sources so a representative ratio of OC/EC for POA was used. If the measured ratio is bigger than this expected value, the additional OC was considered as SOA. However, the weakness of this approach is that the ratio would vary by meteorology, seasonal fluctuations in emissions and local sources (Seinfeld and Pandis, 1998).

Most indications are that POA generally dominates, but the SOA contribution can exceed the POA during peak photochemical air pollution episodes (Seinfeld and Pandis, 1998) from 20% to about 80% of total OC. The SOA values are strongly dependent on the time of the year and on the origin of the air masses. For example, summer time and simultaneously low primary emissions (marine air) can lead to high SOA contributions to OC (Hoffmann and Warnke, 2007).

Products from oxidation of biogenic volatile organic compounds (e.g. terpenes) are thought to be the most important contributors to the secondary organic aerosol. Existing data show that the concentration of the terpene oxidation products in the particle phase vary strongly depending on location, weather conditions, daytime and season. The concentrations can range from 1 to 100 ng/m^3. However, the relative contribution is strongly dependent on the sampling site. In Finland, high concentration of careen products originates from the conifers in the boreal forest, however, in Germany, high sabinene was found in the atmosphere because of the broad leafed trees (summarized from Hoffmann and Warnke, 2007).

A good example of a detailed study of OC-compounds in aerosol and a first assessment of their origin in our region is that by Kubatova et al. (2002). The summary of their results is shown in Fig. 2.4. As it can be seen from the identified vs. unidentified fractions in the extractable part of OM, still the largest part of OM is not known. Mainly fatty acids dominate the identified fraction, but also alkanes contribute importantly. Generally the composition of aerosol particles is dependent by their sources as well as by the history of the investigated air mass (Hoffmann and Warnke, 2007).

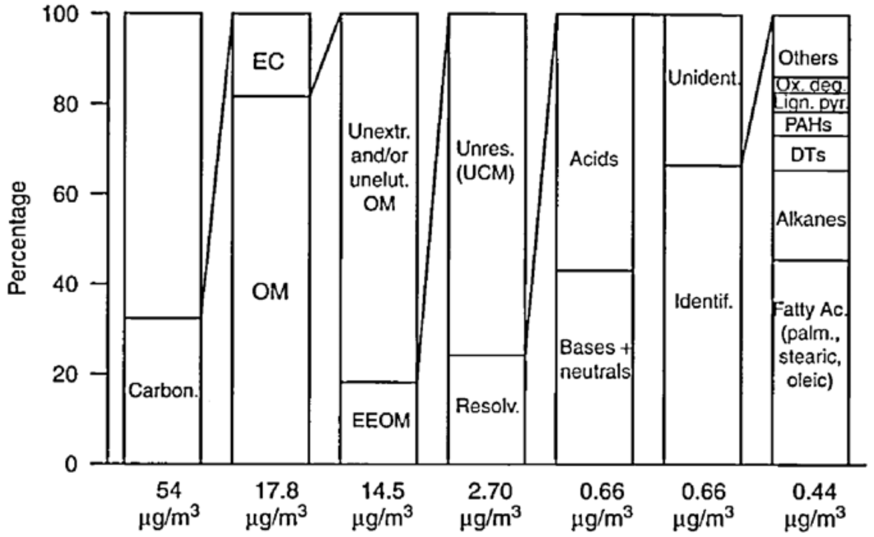

Figure 2.4 *Percentage contributions of different carbonaceous and organic compound classes in winter 1998 total filter samples from Gent, Belgium. The first column represents the contributions of Carbonaceous (OM+EC) aerosol to the particulate mass (PM). The atmospheric concentrations under the columns indicate the average concentrations for the sum of the species in the column EEOM=extractable and elutable organic matter, UCM=unresolved complex mixture, DTs=diterenoic acids, Lign. Pyr.=lignin pyrolysis products, ox. Deg.=oxidative degradation products (copied from Hoffmann and Warnke, 2007, originally based on Kubatova et al. 2002)*

Generally concentrations of alkanes are relatively high in urban areas because of the fossil fuel combustion, around 100ng/m^3. In more natural environments, they are very low, especially in remote marine areas, below 1ng/m^3.

Aldehydes with a concentration of 0.01 ng/m^3 in marine and 7 ng/m3 in urban areas and alcohols concentrations with 1 ng/m3 in marine and 100 ng/m^3 in urban areas show similar trends like alkanes.

Alkanoic acids shows concentrations of 10 ng/m^3 in remote marine areas, the usual concentration in urban areas is above 100 ng/ m^3. Peaks during biomass burning events could reach several thousand ng/m^3. PAHs are typical for the coal burning aerosol. Similarly, the concentration reaches to 100ng/m3 in urban and industrial areas.

Generally these compounds representing mainly the lipid constituents, levoglucosan, sugars and dicarboxylic acids are the water soluble organic compounds. Levoglucosan is a degradation product of cellulose and produced exclusively by the combustion of plant material. They are higher in urban areas due to the use of wood as fuel (100- 1000 ng/m^3) and can reach very high concentrations from massive biomass burning in tropical areas. Sugars, like glucose, sucrose and mycose, are lower than 100ng/m^3 and the source is believed to be mainly soil dust including suspended micro-organisms.

While levoglucosan, sugars and lipids represent the primary fraction of organic aerosol, short-chain dicarboxylic acids have primary and secondary sources. Oxocarboxylic acids derive mostly from secondary processes. The highest concentrations are observed in biomass burning aerosol. The degradation products of aromatic organic compounds have similarly lower values but their concentrations increase in urban areas.

2.2.3 Carbon isotopes and sources

A policy relevant question with respect to carbon sources is to what extent they are of an anthropogenic nature. Whether the carbon derives from fossil fuel combustion can be determined by isotope (^{14}C) analysis (Szidat et al., 2006). As mentioned in the introduction, this isotope has a decay half-life of a few thousand years and is thus absent in fossil fuel. Via measurement of the amount of ^{14}C, Szidat et al. showed that, surprisingly, most of the OC in Zürich was not of a fossil fuel origin and thus originated from wood-burning in winter. In the summer the carbon was due to biogenic activity and resulting secondary organic aerosol formation.

In addition to dating the carbon via ^{14}C-method, the origin can be assessed via measurement of the amount of the isotope ^{13}C present. The reason is that biological material is depleted in ^{13}C, since plants assimilate $^{12}CO_2$ more easily than $^{13}CO_2$ and this isotope is thus a marker for carbon that derives from the biosphere.

3. Environmental impacts of Organic Aerosol

3.1 Physiological response

Fine particulate matter in air is strongly correlated with (severe) health effects, including increased mortality, cardiovascular, respiratory and allergic diseases. Toxicological investigations have demonstrated the pulmonary toxicity of aerosol particles. However, the biochemical mechanisms and molecular processes causing the adverse effects have not been clarified with certainty.

Recently, epidemiological studies indicate strong associations between organic fractions of particulate matter and adverse respiratory and cardiovascular health outcomes (e.g. ARB (Air Resources Board, California) report, 2004; Mauderly and Chow, 2008). Organic compounds were especially mentioned as most hazardous. They are mainly the volatile organic compounds (VOCs; e.g. benzene, toluene, xylene), polycyclic aromatic hydrocarbons (PAHs like benzo(a)pyrene) and persistent organic pollutants (PCBs, dioxines and pesticides). While the acute exposure to PAH result in skin problems, chronic exposure may lead to cancer, lung irritation, damages in some organs (lungs, liver, skin, and kidneys), respiratory problems and behavioral effects. Some PAHs are classified as potent carcinogens. The benzo(a)pyrene is referred to as ‘one of the most potent carcinogens known’(e.g. Gelboin, 1980; Straif et al., 2005; http://www.cpcb.nic.in/air/new/other_air3.pdf).

Generally the major sources of air toxics are point sources. However, toxic air pollutants also come from area sources. For example, especially man-made PCBs and organochlorine which are generally used as pesticides, found in a wide range of environments throughout the world, including Arctic ecosystem where only very few species in the food chain exist. The accumulation of toxic substances in the arctic terrestrial, aquatic, and marine ecosystems represents a potentially serious threat to the regional environment. Toxic compounds, particularly organochlorines and some heavy metals, have been found in potentially worrying amounts in snow, waters, and organisms in arctic North America, Greenland, and Svalbard. The organochlorines (e.g., dioxins, furans, PCBs) accumulate in fatty tissue or bone marrow. Arctic animals have large amount of lipids in their tissues in order to conserve heat, and depend on reserves of marrow during periods of inactivity or hibernation. Therefore, some remarkably high concentrations of toxins can result through short and simple food chains (http://www.carc.org/pubs/v18no3/1.htm).

3.2 Radiative climate forcing by carbon aerosol

Particulate matter has a significant influence on climate (IPCC, 2007). Carbon in aerosol either increases or reduces the effects of global warming (Fig. 3.1). All carbon aerosol scatters sunlight back to space, which reduces the warming caused by greenhouse gases. Only Black Carbon (BC) has a dual effect: it also absorbs sunlight, thereby heating the atmosphere, which has a warming effect. There is, in addition, the indirect effect of aerosol: the increase in reflectivity of clouds resulting in more of the sun's radiation being reflected back into space, which reduces the warming of the earth surface. The role of carbon in the indirect aerosol effect (now known as Aerosol Cloud Interaction effect) is not quantified yet.

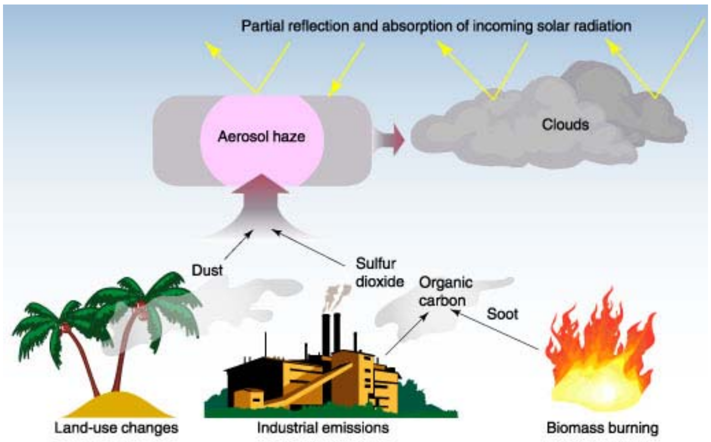

Figure 3.1 *Overview of climate effects by particles (https://www.llnl.gov/str/April03/Chuang.html)*

3.3 Tropospheric ozone (O_3)

The amount of organic compounds generally plays a role in the production of O_3 which is produced through the photolysis of NO_2, which produces atomic O, leading to O_3 after reaction with molecular O_2. The organic peroxy radicals (RO_2) react with NO, converting it to NO_2. Peroxy radicals are intermediate products resulting from initial reaction of organic compounds with OH radical. Thus, O_3 production is sensitive to the amount of organic material with respect to the amount of NO_x. Although discussion and research into this organic component have traditionally been linked to (VOCs), there is speculation that organic particulate matter is also involved in O_3 production (negatively or positively) (see Jacobson et al., 2000).

3.4 Biogeochemical cycling

It is known that organic aerosol is produced in significant quantities from the large amount of VOCs emitted naturally by vegetation (Jacobson et al., 2000 and references within). The cycling of natural organic compounds plays a large role in balancing the global carbon cycle and also in the formation of oxidants. For example, the measurements of terpenes in the gas phase at many forested sites around the world, including Scandinavia (Janson, 1993) and the rest of Europe (Simpson et al 1995) and modeling study for a Swedish forest (Johansson and Janson, 1993) showed that terpenes are a significant sink for O_3 during nighttime hours and during periods of high organic emission. The products of these reactions are highly oxidized organic compounds that are likely to have low vapor pressures and therefore appear as aerosol (Jacobson et al., 2000).

In addition to health, climate effects, the increase in the acidification of rainwater and urban visibility degradation are also associated with the presence of organic compounds in the atmosphere. However, studies in these areas need further investigations.

4. Knowledge gaps and suggestions for further research

There were hardly any data in Europe a decade ago on the contribution of carbon to PM. The first preliminary data for the Netherlands date back to the period 1998-1999. Since then the situation has changed with respect to data. However, there are still (large) uncertainties regarding many aspects associated with the carbon in PM. The most important gaps in knowledge are:

1. The unknown spatial gradient of OC deriving from traffic.
2 Discrimination of carbon in OC and EC and assessment with respect to the health impact of the two fractions.
3 Contribution of secondary organic aerosol to the total OC fraction and its role in health effects.
4. The proportion of anthropogenic versus (natural) biogenic sources of secondary organic aerosol.
5 The solubility of OC in water / lung-liquid and the role of the solubility in the health effects of the carbon in PM.
6. The amount of water-soluble OC that is in the proper size class to be active in the formation of clouds and thus active in the important Indirect Aerosol Effect.

Suggestions for national efforts to improve knowledge in the gaps identified above, which would be also in-line with the national expertise:

- Implementation of instrumentation with high time-resolution to quantitatively assess local gradients in OC. ('1.')
- Relating optically measured ‘BC’ (as measured with the ECN black carbon monitor) with chemically determined EC, making use of the reference material that has recently become available, to be followed by assessments of the relationship with health effects. ('2.')
- Discrimination of the sources of OC into that deriving from fossil fuels versus that from the biomass. For biomass a further distinction should and can be made between OC deriving from the combustion of biomass and the OC present as secondary organic aerosol from biogenic sources other than combustion. This can be done via measurements of 14C is addition to measuring specific tracers for biomass combustion, like levoglucosan and possibly potassium. Measurement of 13C can be sude to further identify the specific sources of the biogenic carbon. ('3.', '4.')
- Collection of the Water Soluble fraction of OC directly in the water-phase, with the MARGA-approach. Coupling of this collection with existing analysis methods that discriminate the components in group/functionality classes. With this analysis a search can be made for the group of components that is most associated with health stress factors. Also toxicity tests can be coupled with the group-analysis. (‘5’).
- Size-resolved measurements of OC and of the OC that is water-soluble fraction to assess the potential of organic carbon aerosol in the climate effects of aerosols, specifically the indirect aerosol effect, as well as the possible role in health effects. ('5.', '6.')

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