Universidade de Aveiro Departamento de Ambiente e Ordenamento
2008

ALEXANDRE FILIPE FERNANDES CASEIRO

COMPOSIÇÃO QUÍMICA DO AEROSSOL EUROPEU

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requesitos necessários à obtenção do grau de doutor em Ciências do Ambiente, realizada sob a orientação científica do doutor Casimiro Adrião Pio, Professor do Departamento de Ambiente e Ordenamento da Universidade de Aveiro e do doutor Hans Puxbaum, Full Professor do Institut für Chemische Technologien und Analytik da Technische Universität Wien.

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Palavras-chave

Aerossol orgânico, levoglucosan, celulose, queima de biomassa, partículas biogénicas, Áustria, Europa

Resumo

Nos últimos anos, o aerossol tem vindo a ser alvo de crescente interesse por parte da comunidade científica internacional. Tal interesse deve-se aos vários efeitos que o aerossol atmosférico ambiente provoca: efeitos na saúde, efeitos no clima, efeitos no património edificado e nos ecossistemas. A queima de madeira tem sido identificada como uma importante fonte de aerossol. Mais recentemente, foram identificadas as partículas biogénicas como uma fonte potencialmente importante de aerossol ambiente.

Para regular de forma eficiente as actividades humanas que afectam os níveis de partculas finas presentes na atmosfera, é primordial conhecer quais as fontes que contribuem para os níveis actuais de partículas assim como as suas contribuições relativas. Uma estratégia usada para esse efeito tem sido o uso de marcadores moleculares que agem como assinaturas para uma única fonte ou tipo de fontes. Neste trabalho, o levoglucosan, um conhecido traçador molecular para a queima de biomassa, foi usado para quantificar a contribuição dessa fonte em vários locais austríacos e europeus. Também no âmbito deste trabalho, foi desenvolvido um método inovador para a determinação deste composto. A celulose foi usada como traçador para os detritos vegetais e a possibilidade do uso de açúcares como marcadores de partículas biogénicas foi investigado.

Keywords Organic aerosol, levoglucosan, cellulose, biomass burning, bioparticles, Austria, Europe

Abstract

Through the last years, aerosol has been the object of growing interest from the international scientific community. Such interest is due to the effects of the ambient atmospheric aerosol: effects on public health, effects on the climate, effects on the built environment and on ecosystems. Wood burning has been since very early identified as a main source of ambient atmospheric aerosol. Though more recently, bioparticles have also been positively identified as a potentially sizeable fraction of the aerosol.

In order to efficiently regulate human activities that have an impact on the atmospheric aerosol, it is of first importance to identify and quantify the different sources that contribute to the ambient aerosol. One way to do this has been with the use of molecular organic tracers that act as a signature for a single source or type of sources. In this work, levoglucosan, a known tracer for biomass burning has been used to quantify the emissions from that source in a series of Austrian and European sites. Also in the scope of this Ph. D., a novel method has been developed for the determination of this compound. Cellulose has been used as a tracer to quantify the contribution of plant debris and the possible use of sugars as traces for biogenic particles has been investigated.

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Introduction

Chapter 1

Background and goals

Air pollution results in poor air quality that can affect the entire population. Epidemiological studies and tragical episodes have shown that, though the scientific basis is somehow still unclear, a raise in ambient atmospheric particulate matter (PM) concentrations leads to an increase in morbidity and mortality [1]. Also, particulate matter has effects on the climate, through both direct and indirect effects. At the present time, aerosols are a major uncertainty in the modelling of the future global climate. [2]

These public health concerns have lead policy makers towards the adoption of more stringent standards. However, these limits have recently been violated in many European cities [3, 4]. In order to reduce PM concentrations, knowledge about the magnitude of individual source contributions is required. Emission inventories may help to understand the relative contribution of primary emissions, but large contributions from fugitive sources as well as from secondary formed aerosol are generally not accounted for in emission inventories. Therefore, methods based on the analysis of ambient PM combined with the analysis of PM from different sources have emerged (e.g. [5]) These techniques are called receptor models. To apply them, one needs not to measure the PM emission of each source and know the subsequent dispersion in order to estimate the exposure at a given location, as it would be using the emission inventory approach. Instead, the chemical composition of the aerosol collected at the exposure location is partially determined, and from that point the contribution of a set of sources is estimated.

The goal of this work was to study the european aerosol saccharidic composition and, relating it to the source emission levels, assess the importance of the contribution of their sources to the PM ambient levels.

Chapter 2

The atmosphere

2.1 Evolution and composition of the atmosphere

After the solar system formation some 4.6 billion years ago, the earth's very earliest atmosphere probably was swept into space by a strong stream of particles emitted by the sun, the solar wind. As the planet slowly cooled down, the molten surface solidified into a crust and volatile compounds were released in a process called outgassing. [6, 7]

The primordial earth's atmosphere, thought to have resulted of the release of trapped volatile compounds from the planet itself, was most probably a mixture of gases as the ones that volcanoes release today: carbon dioxide (CO_2), nitrogen (N_2) and water vapour (H_2O), with small amounts of hydrogen (H_2). [7] As the planet continued to cool, the water vapour condensed and formed clouds, wich generated rains, accelerating the cooling of the planet and slowly forming oceans, thus reducing the presence of water vapour in the air, as well as CO_2, dissolved into the oceans and which formed sedimentary rock at their bottom. [6, 7] Being inert and insoluble in water, nitrogen accumulated to become today's most abundant gas on earth. [7]

The first life-forms on earth, probably bacteria, appeared in a mildly reducing atmosphere. Through photosynthesis, in which sugars are synthesised from the atmosphere's CO_2 with the input energy of solar radiation, oxygen is realeased into the air as a by-product. This way, bacteria and their successors, plants, released the first oxygen into the air. This early oxygen first oxidised other substances dissolved in water, such as iron. Once these substances were almost fully oxidised, oxygen started to accumulate in the atmosphere and today's level is maintained by a balance between photosynthesis (production) and decay of organic carbon (removal). [6, 7]

Today's atmosphere is strongly oxidising. It is composed of the main gases: nitrogen (78%), oxygen (20%) and argon (1%); water vapour (highly variable content, up to 3%), and trace gases such as ozone, carbon dioxide, neon, helium, methane, krypton, hydrogen and many more. [6, 7] The atmosphere also comprises aerosols (particles) [7].

Table 2.1: The composition of the atmosphere includes major and minor (trace) gases [6]

main gases	N_2	abundance controled over geologic time scales
	O_2	biosphere, crustal material
	Ar	degassing of planet's interior
vapour	H_2O	highly variable
trace gases	CO_2	important for radiative balance
	Ne	
	CH_4	mole fraction $<10^6$, important for radiative balance
	Kr	$< 1\%$ of the atmosphere
	H_2	originate from geological, biological,
	He	chemical and anthropogenic processes

2.2 Height and structure of the atmosphere

2.2.1 Altitudinal variations in temperature

Regarding to temperature, the atmosphere can be divided into four major altitudinal zones. Within those zones, temperature increases or decreases with altitude depending on the existence of heat sources.

The bottom layer stretches from the sea level up to an altitude of 9 to 16 km and is called the troposphere. The height of the tropopause depends on the latitude, with the polar tropopause lying at the lower end of the range and the tropical one at its maximum. Surface temperatures (the heat source) and the consequent thermal mixing are responsible for this difference. [6] The troposphere is characterised by a good transfer of atmospheric properties by large-scale turbulence and mixing.

Above the tropopause lies the stratosphere. Between the tropopause and a height of about 20 km, the temperature remains almost constant. From that height up to the tropopause (about 50 km above the earth's surface), temperature increases with altitude. Ozone absorbing solar ultraviolet radiation is the heat source at the stratopopause. [6] Characteristic of the stratosphere is a poor vertical mixing. [7]

The third thermal layer of the atmosphere is the mesosphere, stretching from the stratopause to the mesopause (about 80 km of altitude), where temperature again decreases. This layer is characterised by good vertical mixing. [7]

The thermosphere, the fourth and last thermal layer, contains only a very small fraction of the atmospheric mass. Within that layer, the temperature increases, with the absorption of very short wave, high energy, solar radiation by ozone and azote atoms. The gas atoms and molecules of the thermosphere move very quickly, having a high temperature. However, being the thermosphere so depleted, the collective quantity of heat of the gases is very low. [6]

2.2.2 Altitudinal variations in composition

The atmosphere can be divided into two vertical layers in view of its composition: the homosphere and the heterosphere. The lower layer, the homosphere, streches up to 80 km in altitude and is characterised by an uniform makeup of its component gases. The upper layer is instead heterogenous in its vertical composition: the heterosphere. It can be subdivided into four layers, from bottom up, these are dominated by azote, atomic oxygen, atomic helium and atomic hydrogen. This layering has to do with the different strength of gravity upon the different molecules or atoms. [6]

Between roughly 80 and 400 km, azote molecules and oxygen atoms are readily ionised due to the absorbtion of short wave, high energy, solar radiation. This electrically charged portion of the atmosphere is known as the ionosphere. [6]

2.3 The radiative balance of the earth-atmosphere system

The driving force of the earth's climate is absorption of solar radiation at the surface and, to a lesser extent, by the atmosphere. Absorption of solar radiation of course results in heating of the system. As the temperature of the system increases, it emits increasing amounts of thermal infrared radiation. The absorption of solar (shortwave) radiation by the earth-atmosphere system is approximately balanced by emission of thermal infrared (longwave) radiation, so that the earth may be considered to be in radiative equilibrium – more accurately, steady state – at least in global and annual average. [8]

Radiative forcings (RF) are changes in the energy fluxes of solar radiation (maximum intensity in the spectral range of visible light) and terrestrial radiation (maximum intensity in the infrared spectral range) in the atmosphere induced by anthropogenic or natural changes in atmospheric composition, earth surface properties, or solar activity. [2] Anthropogenic contributions to the chemical composition of the atmosphere affect the balance of both visible and infrared radiation of the earth-atmosphere system [9]. The first examinations of climate change addresses heat-trapping or "greenhouse" gases such as CO_2. This greenhouse effect is the best known and most targeted for mitigation. The opposite effect of "atmospheric cooling" is provided by increases in scattering or reflective aerosols, primary sulphates. While particles of any composition reflect light back to space, only a few can absorb light. These include black carbon or "soot", desert dust and some organic carbon species.

Also, particulate matter has the ability to alter the hydrological cycle and thus indirectly introduce a RF.

Chapter 3

The atmospheric aerosol

The many microscopic particles (aerodynamic diameter (a.d.) between 0.001 and 100 μm) that remain suspended for considerable periods of time are called aerosols. They originate from many sources, both natural and anthropogenic, and include sea salts from breaking waves, fine soil blown into the air, smoke and soot from fires, pollens and microorganisms lifted by the wind, ash and dust from volcanic eruptions and many more. [6] Some of these particles are solids, by-products of combustion, or incombustible matter; whereas others are secondary aerosols such as sulphate and nitrate species or semi-volatile organic compounds (SVOCs) [10]. Aerosols are most numerous in the lower atmosphere near their source, the earth's surface. Particles present in the upper atmosphere are either carried from the lower atmosphere by rising currents or originate in desintegrated meteroids. [6]

These particles can act as surfaces on which water vapour may condense, contributing to the formation of clouds and fogs. They alter the radiative balance of the earth by absorbing or scattering solar light. They affect the oceans, soils and plants, human health and the build environment.

The aerosol of the lower atmosphere, the troposphere, is the focus of this work.

3.1 Physical characteristics of the tropospheric aerosol

3.1.1 The aerodynamic diameter

Aerosol particles have all kinds of shapes. Usually, these shapes are normalised to the diameter of a sphere with the same aerodynamical properties. The particles can then be characterised by their aerodynamical diameter, a.d. PM_x means particulate matter with a.d. below $x\mu$m. [7] However, the particles' unregular shapes and sampling limitations makes it impossible to have a well-defined a.d. below which particles are collected and above wich they are not. Therefore, a PM_x sampler is defined as a sampler that has 50 % collection efficiency for particles with a.d. $< x\mu$m.

3.1.2 Particle formation pathways

Friction and abrasion Mechanical processes (friction and abrasion) are preponderant in the formation of larger particles. These processes may occur between two solid surfaces (e.g. tyre wear abrasion) or between a solid/liquid surface and the wind driven atmosphere as a fluid (e.g. sea salt: interface between the sea and the atmosphere; soil dust: interface between the soil surface and the atmosphere). These particles may also grow secondarily through condensation and coagulation processes.

Nucleation Nucleation plays a fundamental role whenever a phase transition (condensation, precipitation, boiling, ...) occurs. Four types of nucleation processes can be distinguished:

Homogeneous-homomolecular: self-nucleation of a single species. No foreign nuclei or surfaces involveed.

Homogeneous-heteromolecular: self-nucleation of two or more species, without the participation of foreign nuclei or surfaces.

Heterogeneous-homomolecular: nucleation of a single species on a foreign nuclei or surface.

Heterogeneous-heteromolecular: nucleation of a more than one species on foreign substance.

[7, 11]

The formation of water droplets in the atmosphere is the most evident example of nucleation. This reaction occurs much more readily when it is heterogeneous, and the nuclei are called cloud condensation nuclei (CCN). Also, foreign nuclei are needed for the water to freeze at 0°C. Without these nuclei (ions or particles), which act as ice cristals nuclei, the freezing point would be lower. Besides the ice cristals and water droplets, nucleation of trace substances from the vapour phase to the solid (droplet) phase is of interest in atmospheric science. This step is fundamental in the formation of secondary aerosol, defined as the gas-to-particle conversion of vapours: trace gases emitted at high temperature readily condense when cooled in the atmosphere. Organic vapours may undergo such processes. Also, the reaction products of inorganic gases (SO_2, NH_3, NO_x) and other pollutants (e.g. OH, O_3) may suffer homogeneous nucleation. Once the inicial nucleation step occurs, the nuclei of the new phase grows rapidly through condensation of gases onto its surface. Coagulation of more than one of these particles also leads to their growth. [7, 11]

3.1.3 The size distribution function

The atmosphere over all kind of areas contains significant amounts of aerosols, up to 10^7–10^8 cm^{-3}. Their size (a.d.) spans over four orders of magnitude, from a few nanometers to around 100 μm. The particle size affects both atmospheric lifetime and chemical and physical properties. The division of the particle size range into discrete intervals and the accounting of the number of particles in each size bin leads to a size distribution. It is common to normalise the distribution by dividing the concentration by the respective size range (the concentration is then expressed in μm^{-1} cm^{-1}). When the size bin is shortened to the limit (0), one reaches a continuous distribution. This can be done not only with particle number (as illustrated till here) – the number distribution – but also with particle surface area, volume and mass – the surface area, volume and mass distributions, respectively. For convenience, the aerosol a.d. is often log or lognormal transformed. [7]

The most used size distribution function is the mass distribution function. It evidences that the aerosol usually has 2 or 3 modes: one or two smaller modes, with maxima below

1 and around 1 μm, the nucleation and accumulation modes; and one coarse mode, with a maximum above 1 μm. The nucleation and accumulation modes are denoted as fine particles, a.d. below 1 μm (2.5 μm for some authors, mainly in a health effects perspective). The nucleation mode particles are formed by nucleation processes, while the accumulation mode ones are formed by condensation and/or coagulation processes involving nucleation mode particles or accumulation mode particles. [12, 7, 11, 13] Coarse particles are formed mainly by friction and abrasion processes. Though, some secondary particles may be found in this mode, mainly from the condensation of vapours into existing particles. [7]

3.2 Sources and production mechanisms of the tropospheric aerosol

There are plentiful sources of atmospheric aerosols, which cover a very broad range of size distributions and other physical properties as well as chemical characteristics. In the following sections, the principal aerosol sources are reviewed and their fluxes, effects and main physical and chemical characteristics are briefly described. In regard to their origin, aerosols may be:

Primary: directly emitted to the atmosphere. Formed by mechanical processes, mainly coarse. These particles retain much of the chemical properties of their sources.

Secondary: formed by gas-to-particle conversions through chemical reactions (by nucleation and further coagulation and condensation processes). These particles may undergo great chemical changes.

Anthropogenic: formed by human activities.

Biogenic: formed as a result of ecological activity.

Two kind of mixings can be distinguished:

external mixing: different sorts of particles (origin, composition, ...) are mixed inside a plume.

internal mixing: the individual particles of a plume contain different kind of origins and compositions.

In the following subsections, the main sources of PM are described, their origin mechanisms, their physical properties, their fluxes, their effects and briefly their chemical characteristics. For the purpose of this work, greater emphasis is given to primary aerosol, namely primary biological aerosol and biomass burning aerosol.

3.2.1 Soil and road dust

Dust are primary particles resulting from the friction of a fluid (the wind) with a solid (the earth's crust). Its sources may be natural and anthropogenic [14]. The atmospheric lifetime of dust depends on the particle size: the larger the particle, the shorter its atmospheric residence time (submicron particles may have atmospheric lifetimes up to several weeks). Dust is characteristically $< 100\mu$m a. d., most of it is coarse aerosol [7, 15, 16] and is mainly composed of mineral material, such as Si, Ca, Mg, Al and Fe [7]. However, processes leading to its emission, involving wind, may also resuspend some primary biological material. [17]

Natural dust sources are mainly deserts, dry lake beds and semi-arid desert fringes [15, 16]. The Saharan sources are considered the most active (more specifically, the Bodélé depression in Chad), other major global sources are deserts in the Arabian Peninsula, Iran, Turkmenistan, Afghanistan, Pakistan and Northern India, the Tarim basin in China, the Namid and the Kalahari deserts in Southern Africa [14]. Dust deflation occurs in a source region when the wind speed at the surface exceeds the threshold velocity to lift deflatable material. [15, 14] This velocity is a function of surface roughness elements, grain size and soil moisture. It is thus dependent on the climatic conditions and varies in the range 5 –12.5 m s^{-1}. [15, 14].

The wind speed at which deflation occurs is determinant for the aerosol number and mass distributions, which evolves with altitude and the time after the deflation [15], as observed by Xin *et al.* (2005) [18]. Typical volume median diameters of dust particles are of the order of 2 to 4 μm [15]. Chun *et al.* (2001) [19] observed shift towards larger size ranges in the aerosol number distribution in comparison to non-dust events. Levin *et al.* (2005) as cited by Kelly *et al.* [20] observed dust distributions with three modes at an elevation of about 500 m and high fine-dust number concentrations from the surface to altitudes up to and above 2000 m. Also, dust may get internally mixed with other types of aerosol (sea salt, sulphate, . . .) [15, 18], thus affecting is size distribution and lifetime, as well as the characteristics relevant to its climate effect. [21, 22]

Human activities also contribute to the atmospheric dust budget and such impact may contribute significantly to regional dust emissions [14]. The ways in which humans can influence dust emissions are:

- by land use which changes soil surface conditions that modify the potential for dust emission (e.g. by agriculture, mining, livestock, vehicles or water management)
- by modifying climate, which in turn modifies dust emissions, for example, by changes in surface winds or vegetation growth
- road dust and building activities are an anthropogenic input to the global dust budget

[14]

Annual global dust emissions are estimated between 1000 and 3000 Tg. Of these, the Saharan contribution is estimated to 130 – 760 Tg yr^{-1} or even up to 1600 Tg yr^{-1} [14]. The highly uncertain estimation of the anthropogenic contribution to dust is evaluated to 0 – 50 % [14]. Satellite imagery and dust concentration measurements confirm that dust emitted from desert sources can be transported over large distances in the atmosphere affecting life, ecosystems and climate far from its origin (see 3.6.4) [14, 23]. However, only the smaller particles travel large distances, sometimes up to 5000 km [7].

Virtually any anthropogenic and biogenic source emissions to the urban atmosphere can, via atmospheric removal processes (e.g., dry deposition), contribute to the road dust composite. This road dust can be resuspended into the atmosphere by the passing traffic or wind, followed by redeposition of some of that material back onto the streets. The main identified organic components of road dust, in the urban area of Los Angeles, were the same as for tyre wear: n-alkanes and n-alkanoic acids. [24]

3.2.2 Sea salt

Sea spray is generated by the process of breaking waves with direct sea spray emission or by a process which forms small sea water air bubbles. To become airborne, these bubbles might be small enough, or a considerable part of their water content may evaporate. [7]

They cover a wide size range (approximately from 0.5 to 10μm), and have a correspondingly wide atmospheric lifetime. Their size distribution depends on numerous factors (among them is, given their hygroscopic nature, relative humidity) [15, 25] and is usually characterized by three modes: the nuclei (a.d. $< 0.1\mu$m), the accumulation (a.d. between 0.1 and 0.6 μm) and the coarse (a.d. $> 0.6\mu$m) modes. The coarse mode typically comprises 95 % of the total mass but only 5 – 10 % of the total number. [7]

The total sea salt flux from the ocean to the atmosphere is estimated to be 3300Tg yr^{-1}. [25] Estimates of relative contributions of dry and wet removal processes to total sea-salt removal vary largely, from roughly 70–33 % for wet and dry deposition, respectively, over open ocean to 30–70 % in the coastal zone and further down to 15–85 % on the continent. [26]

On a global scale, sea salt is important for aerosol effects on climate. [15, 27, 28] They are very efficient cloud condensation nuclei (CCN) and can directly supply more than 80 % of the cloud condensation nuclei in the marine boundary layer (MBL) when wind speeds are moderate and high (above 12 m s^{-1}), especially for winter seasons over middle and high latitude regions. The secondary aerosol formation in the MBL due to oxidation of sulphur and nitrogen oxides also depends on sea spray. [29] On a regional scale, in places not far from the sea, they are important contributors to the aerosol loading, thus impacting human health, the natural and build environments, . . . [30, 31, 29, 26]

The chemical composition of aerosols originated in the sea is dominated by NaCl and sulphates (Na_2SO_4, $MgSO_4$ and K_2SO_4).

3.2.3 Volcanic primary and secondary aerosols

Two components of volcanic emissions are of most significance for aerosols: primary dust and gaseous sulphur [15]. Also, other volcanic gases can be removed from the atmosphere by chemical reactions, wet and dry deposition and by adsorption onto volcanic ash [32].

Volcanic sources are important to the sulphate aerosol burden in the upper troposphere, where they might contribute to the formation of ice particles and lead to a change in the radiative balance of the earth-atmosphere system (see 3.4.4 and 2.3). Emissions from volcanoes that are strong enough to penetrate the stratosphere are rare. But due to their long lifetime they have a sensible effect on the climate. [15]

Volcanic dust fluxes into the atmosphere were quantified for the 1980s as ranging from 4 to 10000 Tg yr^{-1}. The lower limit is representative of continuous eruptive emission while the upper limit represents large explosive eruptions. [15] Jaenicke [33] present a source strength of approximately 15–90 Tg yr^{-1} for volcanoes. Sulphur emissions occur mainly in the form of SO_2, with minor amounts of SO_4^{2-} aerosols and H_2S. This sulphur is very important in the formation of secondary aerosol. Historical records have shown that 100 Tg of SO_2 can be emitted in a single event (Tambora volcano eruption in 1815). Such large eruptions have lead to a strong transient cooling effect but there is no indication of any significant trend in the frequency of highly explosive volcanoes. Thus, while variations in volcanic activity may have influenced climate at decadal and shorter scales, it seems unlikely that trends in volcanic emissions could have played any role in establishing a longer-term temperature trend [34, 15], except maybe in catastrophical events that occur in hundreds or thousands of years.

Volcanic gases, such as acids and metal salts that adsorb onto volcanic aerosol during the eruption, dissolve within the hour when they come into contact with water, releasing acids and metals in the environment. They cause the acidification and contamination of soils and surface waters, impacting seriously the vegetation, animals and people (e.g. half of the icelandic livestock perished due to fluorosis after the Laki eruption of 1783-84). [32] Volcanic ashes also have a fertilizing action on soils, and by increasing oceans primary productivity they enhance the sequestration of atmospheric carbon dioxide by the oceans [32].

Quiescent (non-explosive) degassing of volcanoes worldwide also inputs trace metals as aerosols to the atmosphere [35].

3.2.4 Primary and secondary biogenic aerosols

Primary biological aerosol particles (PBAPs) comprise material that originally derives from biological processes which was released into the atmosphere without change in its chemical composition. These particles may maintain their physical characteristics (pollen, spores, bacteria, viruses, algae, fungi, etc...), specifically their cellular structure, or be the result of an abrasive process (fractionated material: plant or animal debris such as epithelial cells). [36] They are mainly in the aerosol coarse mode [7].

Some PBAPs are the cause of allergy-related diseases such as asthma, rhinitis, and atopic eczema [37]. They may be of importance for both direct and indirect climatic effects. The presence of humic-like substances makes this aerosol light-absorbing, especially in the UV-B region [15], and they are also able to act both as cloud droplet and ice nuclei [15, 36] and may play an important role for the long-range transport of trace elements into and away from specific biomes and in the spread of biological organisms and reproductive materials [38, 39]. Atmospheric PBAPs have been detected in various size ranges (e.g. $PM_{0.2-2}$, $PM_{>2}$, $PM_{2.5}$ [40, 41, 42, 43, 44, 45, 38]).

Biological particles may, like aerosol particles of other origin (e.g. mineral dust, sea salt, biomass smoke, pollution particles, particles nucleated from gas phase emissions of many types), influence cloud formation and precipitation processes via the following paths:

- the phase change from vapour to liquid
- the acceleration of coalescence by large particles
- the phase change from vapour or liquid to ice

In the second path listed above only the size, shape, and density of the particles are important. The other two processes depend on more specific properties, such as chemical composition. It may be pointed out that from what is presently known, ice nucleation by biological aerosol particles is expected to have the greatest potential of influence on cloud evolution by this class of particles. [46, 36]

In a study conducted in Germany, Després and co-workers [38] found that most of the extracted DNA sequences in $PM_{2.5}$ were from bacteria (mainly *Proteobacteria*). The authors also found sequences from *ascomycota* and *basidiomycota* fungi, whose presence in the atmosphere had been reported by Elbert *et al.* (2007) [47], green plants and moss spores as well as one protist.

Very little is known about their contribution to aerosol mass, specifically PM_{10} mass [15]. Among structural units, the largest PBAP particles are pollen. In the atmosphere, pollen are typically of a size of 30 μm and above, with a few exceptions (birch pollen) as small as 10 μm. Even as pollen can be carried over large distances, they generally tend to deposit due to their large size, thus high concentrations will be limited close to their emission sources. [37]

Allergenic material derived from pollen is known to also occur at smaller particle sizes, but only as a consequence of a fractionation process. [39]

Fungal spores, bacteria and viruses are clearly differentiated by their mass. The mass of spores is in the range of 33 pg (13 pgC/spore) [48]. Spores can be assumed to remain suspended in air for an extended period of time. Elbert and co-workers [47] estimated a global emission rate of total fungal spores of 50 Tg yr^{-1}.

Bacteria have a mass about three orders of magnitude smaller (17 fg C [48]) than spores. Due to this vastly diminished mass, their contribution to total aerosol mass becomes negligible. The same is the case for viruses, to which far smaller mass has been attributed. They are not considered to occur as individual particles but instead to form clusters or droplets. [39]

Quantification of fractionated material is more difficult, as neither structure nor size are well defined. Matthias-Maser and co-workers [45] used protein as a tracer compound for a general quantification of PBAP, while Kunit and Puxbaum [49] developed a method to determine cellulose, a compound contained in fractionated plant tissue or plant debris, also occurring in fractionated pollen. Rogge and co-workers [50] indicated n-alkanes, n-alkanals, n-alkanols and aliphatic acids as the main organic groups present in green and dead leaf abrasion products.

Vegetation emits large amounts of reactive carbon to the atmosphere [51]. Secondary biogenic aerosols are formed in the atmosphere by the mass transfer (condensation processes) to the aerosol phase of low vapor pressure products of the oxidation of volatile organic compounds (BVOCs). [7, 52, 51] These biogenic organic gases are dimethylsulfide (DMS) produced by phytoplankton, monoterpenes produced by forests or other BVOCs, though less important. [7, 52] Recently, photo-oxidation products of isoprene have also been reported as sources of secondary biogenic aerosol. [53, 54, 55, 56]

The total global biogenic (primary and secondary) organic emissions are estimated to range from 491 to 1150 Tg yr^{-1}, exceeding the estimated anthropogenic emissions by as much as an order of magnitude [57].

Subsection 3.4.3 deals with the chemical precursors and the origins of biogenic secondary organic aerosol (SOA_b), while subsection 3.5.3 refers to the end compounds observed in ambient aerosol.

3.2.5 Primary and secondary anthropogenic aerosols

Transportation, coal and biomass combustion, cement manufacturing, metallurgy and waste incineration are among the industrial and technical activities that produce primary aerosols [15]. These have been widely monitored and regulated in recent years in developed countries, where, as a result, air quality has improved. However, fast-growing industrialisation in developing countries may lead to increases of these sources to values above 300Tg yr^{-1} by 2040 [15].

These aerosols cover a very wide range of size distributions and are mainly found in urban and suburban areas, where the anthropogenic activities have greater expression. However, they can be transported to remote sites. The differentiation of the quantification of various sources can be done with chemical analysis of source specific tracer species.

This subsection describes the main anthropogenic aerosol sources. Due to the scope of this work, greater emphasis is given to biomass burning, more particularly wood burning.

Industry, metallurgy, extraction industry and cement and ceramics manufacturing

Industry is a significant source of particulate matter in the atmosphere. The industry type and the used technology, the raw materials, the localisation and the abatement strategies used are factors that make the aerosol from those source highly variable in chemical composition, physical properties and fluxes. For example, the main components for a steel sintering plant, a cement plant and a foundry plant are:

steel sintering plant: Fe_2O_3 and K_2O

cement plant: CaO and SiO_2

foundry plant: SiO_2, with minor amounts of Fe_2O_3 and Al_2O_3

[58]

Construction, demolition, quarries, mining, . . . are a source of generally coarse aerosols. The generation of aerosol by those activities, their chemical and physical characteristics depend on the mechanical activity, the raw material composition and wind speed.

Cement and ceramics manufacturing also produce mainly coarse aerosol.

It is difficult to asses the properties of such particulates due to their resemblance to soil dust.

Traffic sources

Traffic aerosol may arise from fossil fuel (mainly gasoline and diesel) combustion, tyre or break wear. Traffic is also responsible for the resuspension of road dust (see 3.2.1). Also, the gases produced by the evaporation of fossil fuels or their combustion taking place in the internal combustion engine can produce secondary aerosol (see 3.4.3, 3.4.4). Generally, diesel engines produce a greater number and mass of aerosols than gasoline engines.

Passenger cars, light- and heavy-duty vehicles, mopeds and motorcycles all contribute to the atmospheric aerosol burden. Particulate emissions in the vehicle exhaust mainly fall in the $PM_{2.5}$ size range. The aerosol produced by the combustion engine are dominated by fine aerosols and trace species such as Zn, Mo, Ni, Cu, Ag, Cd, Sb, Br, Se, dioxins, furans, PAHs and carbonaceous aerosols are emitted. [59, 60, 61, 62, 63, 64] Also, the nitrogen, sulphur and volatile organic species associated with this source are very active in the formation of the secondary aerosol. The emission factor and particle physical and chemical characteristics of exhaust particulate matter are highly dependent on the vehicles velocity, the engine condition (cold or hot), its maintainance, the driver's behaviour and altitude. However, emission factors per mass of fuel are very similar among vehicle classes. [9, 62]

Tyre material is a complex rubber blend, although the exact composition of the tyres on the market is not usually published for commercial reasons. Tyre tread wear is a complex physicho-chemical process which is driven by the frictional energy developed at the interface between the tread and the pavement aggregate particles. Tyre wear particles and road surface wear particles are therefore inextricably linked. The actual tyre wear abbrasion rate depends on a large number of factors, including driving style, tyre position, vehicle traction configuration, bulk surface material properties, tyre and road condition, tyre age, road surface age, and the weather. [62]. The abbrasion of tyre wear produces more coarse aerosol, but an appreciable part (around 20% of the total particles emitted) are below 1 μm a.d. Estimates of emissions range from 16 to 120 mg per vehicle-km, most of it being carbonaceous material [62]. n-Alkanes and n-alkanoic acids were the major identified organic classes in Los Angeles road dust and tyre wear. [24]

In breaks, linings generally consist of four main components – binders, fibres, fillers, and friction modifiers – which are stable at high temperatures. Various modified phenol-formaldehyde resins are used as the binders. Fibres can be classified as metallic, mineral, ceramic or aramide, and include steel, copper, brass, potassium titanate, glass, asbestos, organic material, and Kevlar. Fillers tend to be low-cost materials such as barium and antimony sulphate, kaolinite clays, magnesium and chromium oxides, and metal powders. Friction modifiers can be of inorganic, organic, or metallic composition. Graphite is a major modifier used to influence friction, but other modifiers include cashew dust, ground rubber, and carbon black. Break pads including asbestos fibres have now been totally removed from the European fleet. Estimates of emissions range from 8.8 to 84 mg per vehicle-km. The lower end of the range is typical for small passenger cars, while the upper end is representative for heavy vehicles. [62] The main identified organics in break lining wear by Rogge and co-workers [24] were n-alkanoic acids and polyglycol ethers.

For the EU15, the total exhaust and non-exhaust particles emissions, including roadwear abbrasion, of the road transport source is estimated to 338.1 and 298.4 kt of PM_{10} and $PM_{2.5}$, respectively. The non-exhaust sources account for 63.1 and 23.9 kt of PM_{10} and $PM_{2.5}$, respectively, including roadwear abrasion. [62]

Other traffic sources are off-road vehicles and aviation, shipping has also, recently, been pointed as a source of aerosol. [9, 65, 66]

Fossil fuel combustion – coal, fuel oil and gas

Particulate emissions, their physical and chemical characteristics, from solid fuel burning facilities vary geatly with the size of the facility because different combustion and abatement techniques are applied. In general, smaller facilities will emit more material (per unit of energy input) than larger ones. [10, 62]

The use of coal has diminished in the developed countries, and, in Europe, this source is significant only in some northern areas.

The chemical and physical nature of particulate emissions from coal-fired powerplants are considered to change considerably after emission into the atmosphere, varying with factors such as location, temperature, humidity and the presence of other pollutants [10].

When burning betuminous coal, the initial burning phase is dominated by the combustion of devolatilised organic matter. It is possible that uppon adding coal chunks to the fire, the chunks become hot enough for the devolatilisation to occur but not for their combustion (lukewarm ignition). [67]

Pulverised coal fly-ash aerosol leaving an electrostatic precipitator size distributions appear to possess three distinct modes. These include a coarse fragmentation mode with particle diameters greater than 5 μm, a fine fragmentation mode with diameters between 0.5 and 5 μm, and a ultrafine vaporisation mode: particles with diameters less than 0.5 μm. Fine and coarse fractions are formed by fragmentation, wheras ultrafine coal fly-ash particles (a.d. $< 0.5\mu$m) are formed primarily through ash vaporisation nucleation and coagulation/condensation mechanisms. [68, 69]

The composition of the coal combustion aerosol is dependent on the appliance used. Modern energy producing units will emit mainly mineral material that is not burnable. Units without abatement technologies and not as efficient as thermo-electrical power plants emit also carbonaceous material (both BC and OC). Submicron and ultrafine coal fly-ash particles typically contain a large number of alkali and alkaline earth metals (Na, K, Mg, Ca) and transition metals (Ti, Mn, Fe, Co, Ni, Zn, V, Cr, Cu), and can be enriched in a number of metalloids and other trace elements including Sb, As, Se, S, and Cl. Non-volatile species such as Si are also found in the ultrafine fraction; carbon, probably soot originating from coal tar volatiles, has also been reported to be enriched in submicron particles. The amount of C depends on coal type and combustion device. [68, 69]

The other two modes, fine and coarse, originating from fragmentation, have a composition more similar to the original material, and soot, SiO_2 and Al_2O_3 are the main components.

The SO_2 emissions resulting from coal combustion are very important in the inorganic secondary aerosol formation (see 3.4.4). Secondary sulphates are, in terms of mass, the proeminant aerosol emitted from coal-fired power plants. [10]

Fuel oil, and principally natural gas, are considered much cleaner fuels for power plants than coal. Their growing implementation as energy source worldwide is an important contributor to the improvement of air quality. Fuel oil combustion is considered the major source of atmospheric V and Ni. [70] Of the identified organic classes, n-alkanoic acids were the most abundants, followed by n-alkanes and chloro-organics with smaller amounts of aromatic acids, PAH and oxy-PAH.

PAH and oxy-PAH were the major organic classes identified by Rogge *et al.* [71] for gas combustion, with minor amounts of n-alkanes and n-alkanoic acids.

Biomass combustion

Biomass burning has been used since pre-historic times for many purposes: clearing of forests and brushlands for agricultural use, control of pests and weeds, prevention of litter accumulation to preserve pastures, production of charcoal, cooking and room heating, aesthetic reasons, waste disposal, cooking animal feed, celebration and rituals, among others. [72, 9, 67]. Biomass burning also occurs for natural reasons (e.g. wildfires). [72]

Biofuels may be agricultural waste, animal waste or charcoal, but the main biomass burned is wood. [9, 67] There is a large uncertainty in quantifying biofuel use (and hence its emissions) inherent in the nature of the system. Wood and other biofuels are usually part of a complex system that meets a multiplicity of needs (animal fodder, building material, energy requirements). [9] Wood typically consists of various lignins (20–30% dry weight), holocellulose (cellulose and hemicellulose, 40–50% and 20–30% dry weight, respectively) and extraneous compounds [73]. Cellulose provides a supporting mesh reinforced by lignin polymers. [67] On a regional scale, types of fuel used vary seasonally according to availability; within a household, constraints such as land tenure, animal ownership and storage space are of interest. [9] Softwood (pines, spruces, larches and firs) are prolific resin producers and comprise longitudinal wood fibers (or tracheids) and transversal ray cells. Softwoods lack vessel elements for water transport that hardwoods have; these vessels manifest in hardwoods as pores. In softwood water transport within the tree is via the tracheids only. Besides these major components, wood tissues undergo photochemical degradation during wood weathering and yield organic acids, vanillin, syringaldehyde and other water-soluble high-molecular weight compounds. [67]

As a result of the processes during burning, biomass smoke contains a host of unaltered and thermally altered biomarker compounds from major vegetation taxa in the carbon number range C_8–C_{31} [67]. The major compounds giving rise to tracers upon burning are:

Lignin is present only in woody plants and is the main biopolymer in wood. It is a complex biopolymer with both aliphatic and aromatic constituents. Its main monomers are cinnamyl alcohols, either sinapyl alcohol (angiosperms – hardwood), coniferyl alcohol (gymnosperms – softwood) or p-coumaryl alcohol (gramineae – grasses).

Lignans are dimers of sinapyl , coniferyl or p-coumaryl alcohol contained in many wood tissues. They serve as toxins, supportive fillers or for other purposes.

Diterpenoids are resin acids such as abietic or pimaric acids synthesised mainly by conifers (gymnosperms – softwood) in temperate regions.

Cellulose is present in all plants. Cellulose molecules are linear polymers of 7000–12000 D-glucose units, forming bundles organised into parallel fibrous structures that support the wood tissue.

Hemicellulose is a mixture of polysaccharides formed by 100–200 units of glucose, mannose, galactose, xylose, arabinose, 4-o-methylglucoronic acid and galacturonic acid. There is a wide variation among wood species.

Sterols are produced by the biota in the carbon number range C_{25}–C_{30}. In higher plants, β-sitosterol is the main sterol.

PAHs originally present in wood can also produce markers upon burning.

[74, 75, 76, 67, 17].

There are several types of biomass burning:

Fireplaces and heating stoves are the only wood-burning appliances, used for space heating and aesthetic reasons, when other energy sources (electricity, natural gas) are available for cooking. Typically wood is burned in large pieces and the fire is untended. Type of wood, fuel loading, heat release and sap, ash and moisture content affect the total emission.

Boilers burn wood for building heat. They are common in Europe but not so in the U.S. Wood and vegetal waste are also burned for heat and power in industry, mainly in developing countries. In developed countries, industrial combustion of biomass (district heating, electrical production . . .) is expected to have a small impact in the aerosol budget due to the use of abatement technologies.

Cooking: wood and other fuels are burned, mainly in developing countries for cooking and heating as well as a range of other applications. Efficiency, including exhaust design, is a key factor in PM emission. A fire optimised for heat transfer (usually where wood is scarce and its acquisition is ressources consuming) may remain in the flaming- and glowing-combustion mode longer than fireplaces or open burning. Total PM (expressed as g of PM per kg of fuel) emitted from cooking fire has been reported as low as those from fireplaces or stoves. Besides wood, agricultural waste (vegetal residues or animal dung, depending on availability, production and suitability for other purposes) may be used as fuel.

Table 3.1: Estimates for the global burned biomass.

Source	*Emission*
tropical FC	500–1000 TgC yr^{-1} [67]
tropical SBC	300–1600 TgC yr^{-1} [67]
RB and cooking (including dung and crop residues)	600–1200 TgC yr^{-1} [67]
AF – firewood	300–600 TgC yr^{-1} [67]
AF – agricultural waste	300–600 TgC yr^{-1} [67]
WF – firewood	150–300 TgC yr^{-1} [67]
savanna	3752 Tg yr^{-1} [9]
forest	1939 Tg yr^{-1} [9]
Agricultural residue	475 Tg yr^{-1} [9]

Bond *et al.* [9] gave data in Tg dry biomass, Gelencsér *et al.* [67] gave data in TgC dry biomass.

Charcoal is often used in urban areas for being a cleaner fuel. The charcoal fuel cycle emits particulates at two stages: manufacture and use.

Open burning emissions depends on many factors that are specific to location and season, such as fuel moisture content. Open burning (OB) englobes wildfires (WF) (savanna fires, tropical or temperate forest fires, . . .), forest (FC) and savanna/brushlands clearing (SBC) as well as the burning of large agricultural residues (agricultural fires – AF). Forest and savanna fires occur for many reasons and in very distinct places, where the vegetation cover (the fuel), varies a lot. Agricultural fires are an inexpensive means to advance crop rotation and control insects, diseases and invasive species.

[72, 77, 9, 67, 78, 79], refer to Table 3.1.

Though not yet fully resolved, there are studies showing that the molecular signatures of these different fires are distinct. The small combustion sources, mainly residential burning (RB) but also smaller AF, are so numerous that they have a significan impact. [77, 67]

Table 3.2: Contribution (as %) of Biomass Smoke to PM compiled from recent studies.

		contribution to OM / to OC ^{a} (%)	contribution to PM (%)	method used	reference
alpine valley	daytime	77		^{14}C as tracer and	[80]
winter	nighttime	90		multi-λ absoprtion technique	[81]
South California, US	average 1982 PM_2	7–26	1.4–10.5	CMB (organic compounds)	[5]
S. Joaquin valley, US	residential/industrial	17–49		CMB (organic compounds)	[82]
winter 1995, fine particles	remote	0.6			
Southeastern US	$PM_{2.5}$	25–66	56–80, winter	CMB (organic compounds)	[83]

CMB: chemical mass balance

The process of biomass burning The first step in biomass burning, drying/distillation, releases water (capillary water first and then the bound water stored in cell walls) and volatile species. The next step, pyrolysis, forms char (portion of carbon that never leaves the original fuel particle – charring removes hydrogen and oxygen, so that char is composed primarily of carbon) of high carbon content, tar of intermediate molecular weight and volatile compounds in the form of a flammable white smoke. Above 450K the process is exothermic and at about 800K glowing combustion releases tar and gaseous products. These substances (tar and volatiles) are dilluted in an oxydising atmosphere (usually air) and ignite, forming a flaming combustion. Smouldering takes over when the supply of volatile speces in the near-surface of the fuel lessen. At this stage, usually under 850K, a vast amount of partially oxydised pyrolysis products are emitted. Open vegetation fires are typically dynamic fires where all the stages of combustion are expected to happen simultaneous and sequentially. [67]

Formation of smoke particles Particle formation in the flaming fire phase begins with the creation of condensation nuclei (such as PAH) from ejected fuel gases (volatile compounds) as well as from a variety of "soot-like" species. These original particles grow through chemical and coagulative processes and become condensation nuclei for other pyrolised species (volatile compounds), and may experience considerable growth. Further oxidation in the flame zone, with high enough temperatures (above 1100K), may subsequently reduce those particles in size. If insufficient oxygen is transported into the flame or if the temperature is not enough to complete oxidation, the particles may undergo a secondary condensation growth phase and be emitted in the form of smoke. In general, particles production increases with increasing flame size, lower amount of oxygen in the fuel and increased flame intensity (reduced oxygen transport to the fire). [79]

smouldering combustion begins when most of the volatiles have been expelled from the cellulose fuel. It is a surface process where oxygen diffuses to the surface and reacts exothermically with carbon ($T > 710K$). Because PAHs tend to form at higher temperatures, the mass fraction of soot in smoke particles produced during the smouldering phase is extremely low, and particle formation may occur around other nuclei (condensation of volatilised organics on any available particles or surfaces). [79]

Biomass burning is one of the largest sources of accumulation mode particles globally, with approximately 90% of the emitted particles in the accumulation mode (a.d. $< 1\mu m$). [79] Coarse particles are not built during the combustion process; the residence times involved are insufficient for either building these particles or coagulating them from smaller ones. Rather, these particles are left over from large particles present at the start of combustion, although these initial particles may divide during the combustion process. Coarse particles may include both mineral matter or char. [9]

Several macroscopic variables affect the emissions from wood combustion: burning rate, type of wood, moisture content and fuel size are the main ones. [9]

Physical properties of fresh smoke particles Accumulation mode smoke particles exhibit a wide variety of shapes and morphologies: chain aggregates, solid irregulars and liquid/spherical shapes. This feature depends on various parameters: combustion efficiency (oxygen availability) and combustion phase, among others. Coarse mode particles (about 10% of smoke particles, in mass) have a typical diameter of 2–15μm. Giant ash particles may also be emitted, with a.d. up to 1 mm. They are usually generated by very intense fires and consist not only of combustion-derived particles but also of small non-combustible matter on or around foliage in the fire zone entrained into the fire plume (e.g. soil particles). Because this coarse mode consists of ash, carbon aggregates, partially combusted foliage and soil particles, their shapes are very varied. The count median diameter (CMD) for fresh smoke particles is in the range 0.10–0.16 μm (centered at 0.13), while the volume median diameter (VMD) lays between 0.25 and 0.3 μm. Also, on account of their highly water soluble composition, fresh smoke particles can be very effective cloud condensation nuclei. The secondary production of soluble material during the aging process further enhances the particle hygroscopicity and CCN efficiency (see 3.2.5). [84, 78, 79]

Chemical properties of fresh smoke particles Smoke accumulation mode particles have three principal components: organic matter (OM), black carbon and trace inorganic materials (mostly Na, Mg, Si, S, Cl, K and Ca). In average, fresh smoke particles from WF are composed of 80% organic matter, 5–9% black carbon and 12–15% trace inorganic species. Though there are wide variations, some conclusions about the composition of WF smoke particles may be drawn:

- smouldering combustion, occurring after most of the fuel solids were expelled and at lower temperatures without flame pyrolysis where the combustion of OM could take place, has higher organic carbon (OC) contents.
- The black carbon content of the flaming phase smoke particles is lower and not as variable as for the smouldering phase.
- The ratio OM/OC is variable and uncertain, in general between 1.4 and 1.8 and higher.
- water extraction efficiency for carbon is in the order of 40–80%, being mainly organic acids, alcohols and sugars. Other compound classes observed are PAHs, esters and alkanols.
- Trace inorganic species (about <10%) are dominated by alkali earths and halides. Potassium and chloride each account for 2–5%. Sulphur is present in the form of sulphate (about 1%). They can form from vaporisation of minerals and subsequent condensation or from bursting of mineral inclusions of the fuel. Unlike carbonaceous aerosols, mineral material cannot be eliminated from the flue gas by oxidation.

[85, 9, 79].

For AF, Hays *et al.* [78] found 42 and 84% of C in $PM_{2.5}$ from wheat and rice straw burns, respectively. K and Cl were much more present in wheat than in rice straw burns. The composision of particles emitted by RB depends in a very large scale on the fuel used, also on the appliance and the type of fire. Pine, eucalyptus and oak wood burning emit mainly lignin derived compounds, syringols, resin and n-alkanoic acids, but the amounts of each of these classes varies, indicating a difference in the composition of smoke particles between softwood and hardwood. [86, 87, 88] Of the carbonaceous species resolved, levoglucosan is by far the major compound identified.

Aging of smoke particles Various studies have shown that smoke aerosol can be transported for long distances and impact distant and even remote regions. (e.g. [89, 90, 91, 92, 93]) During that transport, smoke particles undergo physical change and/or chemical evolution, the plume evolves from fresh emitted smoke to regional smoke. It is thought that most changes occur in short time scales, with great changes taking place in the first 30 to 90 minutes after emission and more modest changes in the subsequent days. [94, 79] The first factor in the aging of smoke plumes is the fact that smoky hazes are a result of numerous fires, each with their own characteristics. Typically, smoke particles increase in size with age. Typical values for CMD and VMD (WF) are in the ranges of 0.12–0.23 μm (centered at 0.18) and 0.26–0.35 μm (centered at 0.30), these values can be larger in the case of highly concentrated plumes. Aged particles are also more spherical than freshly emitted ones. [79] Optical properties are also changed during the aging process. [94] Pósfai *et al.* [95, 96] studied individual atmospheric particles in smoke plumes from biomass fires. The authors identified three distinct types of carbonaceous particles: organic particles with inorganic inclusions, tar ball particles, and soot. The relative number concentrations of organic particles were largest in young smoke, whereas tar balls were dominant in a slightly aged (about one hour) smoke from a smouldering fire. Flaming fires emitted relatively more soot particles than smouldering fires, but soot was a minor constituent of all studied plumes. Further aging caused the accumulation of sulphate on organic and soot particles, as indicated by the large number of internally mixed organic/sulphate and soot/sulphate particles in the regional haze. They also hypothesised that organic and soot particles are the cloud-nucleating constituents of biomass smoke aerosols. Aging affects the chemistry of smoke particles. [97, 98] Like in fresh smoke, there is a considerable variability in the quantity of BC and trace elements present. Potassium and BC form generally a smaller mass fraction for aged smoke aerosols (in part due to the mixing of other pollutants). However, aged particles exhibit a significant enrichment of species associated with secondary aerosol formation (e.g. sulphate, ammonium, nitrates, organic acids). Organic species can increase the aerosol mass by up to 40% due to condensation near the fire source and other processes in the long term aging. The effects of aging on smoke particles are, in part, due to the mixing of other pollutants, and it is not clear to what extent this factor influences the aerosol evolution. [79] The processes by which these changes occur are:

Brownian coagulation depends heavily on environmental factors – average smoke particle size, concentration, ambient temperature and pressure

Gas-to-particle conversion envolves at least three components: (1) near source condensation of primary low vapour pressure organics, (2) production of inorganic particulate matter, (3) gas-to-particle conversion of organics

[79]

Biomass burning emission factors As for the coal combustion, the emission rate of a source burning biomass is very dependent on the facilities characteristics, such as oxygenation and the temperature of the fire as well as the abatement technology used. [78] The type and length of fire phase (flaming, glowing or smouldering) is influenced by many factors, both intrinsic and extrinsic of the fuel. Humidity and temperature are two environmental variables affecting it, as the water and oxygen amount of the fuel, fuel bed density and structure (mainly for residual and agricultural fires). [78, 79]

Particle emission factors (EF) logically increase with decreasing combustion efficiency (increasing relative amount of smouldering combustion). Other factors affecting the highly variable EF are: fuel type and characteristics, fire size and intensity and sampling bias. For

Table 3.3: Biomass burning emission factors for fine particles, compiled from Reid *et al* [79] for wildfires (WF), Hays *et al* [78] for agricultural fires (AF) and Fine *et al* [87, 88] for residential burning (RB).

fuel type	*EF*	
all WF – flaming	18±15	
all WF – smouldering	68±60	
grass/shrub	6–15	Small and dry fuel, low loadings, dominated by the flaming phase, higher efficiencies
forest	27±14	Larger fuel, higher loadings. Fuel is wetter, contains more organic compounds and oils
north temperate forest/ flaming	> 30	Higher smouldering contribution
tropical forest/ flaming	10–15	Lower smouldering contribution
wheat residuals	9.42±0.08	
rice residuals	25.90±0.60	
RB – Northeastern US	6.8–17.6	softwood
	4.8–10	hardwood
RB – Southern US	2.8–6.6	softwood
	6-12.2	hardwood

Average±standard deviation, units: g kgC$_{burned}$ $^{-1}$.
Hays *et al* [78] gave EF in g PM$_{2.5}$ kg^{-1} dry biomass, a factor of two was used to get it per kg of C.
Fine *et al* [87, 88] gave EF in g PM$_{2.5}$ kg^{-1} biomass, moisture was extracted using the data provided and a factor of two was used to get it per kg of C$_{burned}$.

RB, the type of burning appliances (open, partly closed or closed fireplaces, type of stove, manually or automatically fuelled, . . .) is also an important variable. [62]

Nevertheless, fuel characteristics only explain little of the total variation of EFs. Combustion efficiency and fire intensity are also very important in explaining the variation.

Besides the difficulty in determining the EF of the fuel, computing global emissions is further made difficult because

- biofuels, including wood, are usually not only needed for energy requirements. Other functions to be fullfilled are animal fodder and building materials. Also, types of fuels used within a community vary seasonally according to availability, and within a household according to land tenure, animal ownership or storage space.
- There is a large interannual variability and uncertainty for OB

[9]

Waste combustion

When waste collection is unavailable, inconvenient or expensive, garbage may be burned in open piles or makeshift combustors such as metal cans. Common practices include combustion of waste at streetside and burning at landfills, either because of spontaneous combustion or deliberately to reduce waste volume [9]. Emission factors for waste combustion are quite uncertain, as waste-burning practice could be highly localised depending on the available alternatives [9]. In developing countries, waste generation is low because goods are inherently recycled. Availability of packaged goods is usually limited, but that packages, including plastic, are burned when available, often for energy use [9]. In developed countries, waste combustion, apart from agricultural waste (see 3.2.5) is more commonly conducted in plants (e.g. for district heating), and abatement technologies assure low emissions. However, the combustion of industrial quantities can affect local and regional air quality (e.g. used tyres and electronic components). [99, 9] Bond *et al* [9] estimated the open waste combution to 33 Tg yr^{-1} of dry matter, with an uncertainty of 200%.

3.2.6 Other aerosol sources

Agriculture is an important source of NH_3 for the atmosphere, which can evolve into secondary inorganic aerosol. [100, 99, 101] Church candle burning, kerosene and oil lamps, meat cooking and natural gas home appliances have been reported as small sources. [50, 102, 72, 77] Broiling and cooking operations have been reported as potentially important. About 20% of the organic fine aerosol in the Los Angeles basin are from meat cooking operations. [103, 104, 72] Outdoor tobacco smoke may also contribute to the aerosol burden [102, 72], as well as roofing tar emissions [105] and steam boilers [106]. Cryospheric (polar) aerosol is formed by the same process as soil aerosol, but by the wind action over ice or snow surfaces. Fugitive sources usually emit very large particles that settle relatively quickly. [7]

3.3 Sinks and removal mechanisms of the tropospheric aerosol

Wet and dry deposition are the ultimate paths by which trace gases and particles are removed from the atmosphere [7].

3.3.1 Wet deposition

Wet deposition is the process by which material is scavenged by atmospheric hydrometeors – cloud and fog drops, rain and snow – and delivered to the earth's surface. [7]

Below cloud scavenging removal of species by a raining cloud, depends on the sizes of the particle and the drop and their relative positions. As the raindrop falls down through the air, it collides with aerosol particles and collects them.

In-cloud scavenging aerosols are incorporated into cloud droplets (interstitial aerosol collection) or serve as cloud condensation nuclei (CCN) or as ice nuclei (IN), originating the cloud (nucleation scavenging). Of the two processes present, nucleation scavenging is fast and efficient, often incorporating most of the aerosol mass into the cloud, while interstitial aerosol collection is rather slow.

Cloud interception impaction of cloud droplets on the surface

Fog deposition removal of material by settling fog droplets

Snow deposition removal of material during a snow storm

[7]

Many of these processes are reversible. For example, a particle may act as CCN and grow into a cloud droplet. If the water evaporates, the aerosol may remain in the solid phase. For all these processes, the particle must first be brought to the presence of condensed water, it must then be scavenged by the hydrometeors and finally be delivered to the earth's surface. In each of them chemical transformations may occur within the particle. [7]

3.3.2 Dry deposition

Broadly speaking, dry deposition is the transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation. The relevant factors are the level of atmospheric turbulence, the properties of the depositing particle (size, density and shape) and the nature of the surface itself (smooth surfaces decrease turbulence hence leading to a less efficient dry deposition). [7]

The dry deposition is assumed to consist of three sequential steps which, together, represent the delivery of particles to the surface:

1. Aerodynamic transport by turbulent diffusion (eddy transport) down through the atmospheric surface layer to a very thin layer of stagnant air just adjacent to the surface (the quasilaminar sublayer). Sedimentation may also contribute to the downward flux of larger particles.

2. Brownian transport through the quasilaminar sublayer to the surface. Interception or impaction may also occur at this stage for larger particles.

3. Uptake at the surface is the final step. Solid particles may bounce off a smooth surface while liquid particles are more likely to adhere.

[7]

To each of these steps there is a resistance associated (the aerodynamic resistance, r_a, the quasi-laminar resistance, r_b, and the surface (or canopy) resistance, r_c). These three resistances may be visualised as operating in series. Generally, perfect removal for particles is assumed so that the surface resistance may be left out.

The particle's vertical dry deposition flux F to the surface (material depositing to a unit surface area per unit time) at a certain height is directly proportional to the concentration C at that height. The proportionality constant being the deposition velocity ν_d, defined as the inverse of the total resistance.

$$F = \nu_d \times C \tag{3.1}$$

If C_3 is the particles' concentration at a certain height and C_2 the concentration at the border between the atmospheric surface layer and the quasi-laminar layer and C_1 that at its bottom, then:

$$F = \frac{C_3 - C_2}{r_a} + \nu_s C_3 = \frac{C_2 - C_1}{r_b} + \nu_s C_2 = \frac{C_3 - C_1}{r_t} \tag{3.2}$$

where $\nu_s \times C$ is the sedimentation flux (particle settling operates in parallell to the three steps process). Because of the perfect removal assumed, $C_1 = 0$, thus

$$\frac{C_3}{r_t} = \frac{C_3 - C_2}{r_a} + \nu_s C_3 = \frac{C_2}{r_b} + \nu_s C_2 \tag{3.3}$$

thus, the deposition velocity is

$$\nu_d = \frac{1}{r_t} = \frac{1}{r_a + r_b + r_a r_b \nu_s} + \nu_s \tag{3.4}$$

.

3.4 Chemical characteristics of the tropospheric aerosol - Carbonaceous and inorganic aerosol

Tropospheric particulate matter is a complex mixture resulting from multiple sources, processes and atmospheric conditions. They contain sulphates, nitrates, ammonium, organic material, crustal species, sea salt, hydrogen ions and water. From these, the predominant species are sulphate, ammonium, organic and elemental carbon and certain transition metals [7]. The many source and removal mechanisms contribute to form various kinds of ambient atmospheric aerosols. The main categories characterised are: polar, background, maritime, remote, continental, desert dust storm, rural and urban. Each of these classes are characterised by a three modal log-normal size distribution function. [33, 12]

The chemical characterisation of the aerosol is useful to the aerosol source identification and quantification. Particles of different chemistry have separate generation mechanisms. [9]

This section deals with the general chemical characteristics of the aerosol. Coumpounds found in the aerosol are divided into carbonaceous and non-carbonaceous. The carbonaceous fraction is further divided into soot, primary organic and secondary inorganic. The next section (3.5) looks into the organic fraction of the aerosol more in detail. In the scope of this work, the carbonaceous fraction, namely the saccharidic component of the primary organic aerosol of wood burning and biogenic origin, receives more attention.

Carbon, one of the largest (if not the largest) elemental fraction in aerosols, present in many chemical and physical forms, consist of two major components:

graphitic or black carbon can only be produced in combustion processes, solely primary

organic material can be primary or secondary, both anthropogenic and biogenic

[7, 67]

Besides these two categories, carbonate carbon from calcite ($CaCO_3$) is another possible form of carbon. Carbonate carbon can be a sizable constituent of some types of aerosol, namely desert dust. [107]

Black carbon (BC) and some organic species are known to absorb visible radiation, thus having a warming effect on the radiative balance of the earth-atmosphere system. BC is emitted together with organic carbon (OC), which has a net negative climate forcing. Hence, their net climatic effect is ambiguous [9, 52]. Fine aerosols have sizes close to wavelengths in the visible and are thus expected to have a stronger direct climatic impact than larger particles [52]. Besides their global climatic direct effects, carbonaceous particles have a host of other effects ranging from the mesoscale to the personal:

- large changes in the regional radiative budgets may affect the hydrological cycle
- an increase in the number of particles may reduce cloud droplet size, thus altering cloud brightness and cloud precipitation efficiency

- organic species affect the formation of cloud droplets (most organic aerosol components cool the Earth's atmosphere, in a magnitude depending on their chemical composition, since hydrophilic aerosols can act as cloud condensation nuclei)
- heating of the atmosphere by BC may reduce cloudiness
- addition of light-absorbing particles to the aerosol mix may cause circulation and rainfall shifts
- BC may play a role in the atmospheric chemistry of NO_y and sulphates
- particles pose a health risk

[9, 52]

Organic material is an important contributor to PM, making about 20–50 % of it in mid-latitudes. In tropical forests, this percentage rises to about 90. [52]

Sources of carbonaceous material include biomass burning [52, 86]; traffic: end-of-pipe (fossil fuel combustion) [52, 59], and non-end-of-pipe (tyre and break wear abrasion) [24]; cooking [103, 108]; industrial boilers with various types of fuels [71, 106]; asphalt vapourisation [105]; organic material [52, 50, 49]; environmental cigarette smoke [102] and dust resuspension [24]. There has been a very large number of studies published about the characterisation of the aerosol carbonaceous fraction both at sources [87, 88, 109] and in the ambient air, including various kinds of sites: urban, suburban, rural, background, maritime, ... [110].

The following subsections describe the origins and characteristics of the carbonaceous fraction of the aerosol, dividing it into inorganic and organic (primary and secondary) aerosol, as well as the main classes of inorganics compounds and elements.

3.4.1 Soot – black, elemental and graphitic carbon

There are numerous definitions for this category of carbonaceous matter, which is method dependent since no method can unambiguously separate it from organic carbon. Those several definitions overlap by a great extent, but do not mean the same.

The definition of soot encompasses all the others. Soot is defined as a black, blackish or brown substance formed by combustion, present in the atmosphere as fine particles. Soot is associated with combustion-generated primary carbonaceous material. It is an array of individual organic compounds, soluble in organic solvents, and a refractory and insoluble carbonaceous matter called elemental carbon (EC), graphitic carbon or black carbon (BC). [7, 67]

Elemental carbon is in conjunction with methods suitable for the selective measurement of the refractory component. It consists entirely of C, though no method is capable of measuring it as an element. In most cases referring to the fraction of carbon that is oxidized in combustion analysis above a certain temperature threshold, and only in the presence of an oxygen-containing atmosphere (may be corrected for charring, depending on the technique used).

Graphitic carbon is a synonim for EC which infers the presence of graphite-like microcrystalline structure. Uneasy to quantify since even graphitic black carbon particles have a wide variety of oxygen-bearing functional groups on their surface.

Black carbon is responsible for the absorption of visible light. This term is linked to the use of optical methods.

[7, 67, 111]

EC is conventionally the preferred term in conjunction with thermal and wet chemical determinations, which are deemed suitable for the selective measurement of the refractory component. The term BC implies that this component is responsible for the absorption of visible light, and is generally used when optical methods are applied for its determination. [111]

If atmospheric soot particles were pure graphite and all the methods were calibrated against graphite, BC and EC readings would give exactly the mass concentration of soot carbon as intended. But since graphite is only a trace component of atmospheric particles, BC and EC measurements usually give different results, which may have little in common with the true mass concentrations of atmospheric soot particles. In the literature, however, these discrepancies are usually disregarded and the terms BC and EC are used interchangeably as synonyms for C_{soot}.

Morphologically, soot particles cluster together to form aggregates of spherules made of graphene layers, consisting almost purely of carbon, with minor amounts of bound heteroelements, especially hydrogen and oxygen. This definition does not include the organic substances (oils, . . .) frequently present in or on combustion particles. [67, 111] These clusters may have an open (more related to flaming conditions, more susceptible to aging transformations) or a closed (more related to smouldering conditions, less affected by aging) configuration. The particles themselves (around 20–30 nm in diameter) may be internally mixed (a shell consisting of organics, sulphates, etc. surrounding a BC core) or externally mixed (individual BC particles combined with non-absorbing particles). [67, 111] Their chemical composition depends strongly on the source. Soot particles may be regarded as a complex, three-dimensional organic polymer with the capability of transferring electrons rather than merely an amorphous form of elemental carbon. It is chemically dominated by carbon, but not necessarily in its zero oxidation state [67]. The main elements other than C present at the soot surface are: O, N and H. The presence of organic groups on the soot surface makes it active in atmospheric processes. [67]

The main sources for soot/EC/BC are:

Biomass burning: of the major biopolymers of woody tissue, soot formation is preferred from lignin, whereas holocellulose (cellulose and hemicellulose) primarily promotes volatilisation of organic species during combustion. Soot is chiefly produced in intense flaming fires where the oxygen supply is deficient (fuel-rich). The smouldering phase commonly produces little soot. Coarse BC particles may originate in the suspension of charred material.

Fossil fuel combustion: Emissions from diesel internal combustion engines are a major source for soot particles. This is a source for which the vehicle's engine maintenance is of utmost concern, besides road condition and the driving cycles used. Emission of soot by commercial air traffic, though small, is relevant for the climatic effect of aerosols.

[9, 67]

The formation of BC is therefore governed by the time-temperature history of the fuel and combustion products [9].

Only a small fraction of the carbon in a fuel is transformed to black carbon, with the remainder being emitted as CO_2 or a variety of other products of incomplete combustion. The emission rate of BC depends in a significant extent on the combustion process. Black carbon remains in the atmosphere for about a week. [9]

Recently, the evidence of the occurrence of atmospheric carbon which absorbs light but clearly is not black and that there is a continuum of carbonaceous substances in atmospheric aerosols have brought the community to refine these definitions. [111, 112] Andreae end Gelencsér (2006) have proposed to expand the scope of the term light-absorbing carbon (LAC), previously used as a synonim of soot and measured through the proxy BC (optical methods) [113], to a larger general term covering all light-absorbing carbonaceous substances in atmospheric aerosol, including C_{soot} and C_{brown}. Brown carbon is light-absorbing organic matter (other than C_{soot}) in atmospheric aerosols of various origins (e.g., soil humics, humic-like substances (HULIS), tarry materials from combustion, bioaerosols, . . .). [111] These authors have also reviewed the possible interferences introduced by the presence of C_{brown} in samples of atmospheric aerosols on the BC measurements.

3.4.2 Primary organic aerosols

Particulate organic matter is a complex mixture of many classes of compounds [7]. Organic compounds that are emitted directly in particulate form are referred to as Primary Organic Aerosol (POA) [52]. They are released directly from various sources. A part of them is released as individual particles (e.g. bioaerosols or vegetation waxes). Another fraction is released on primary particles that are not carbonaceous in themselves (e.g. surface active organic matter on sea salt aerosol). Internally mixed particles of predominantly primary origin can be released by nucleation of inorganic species on carbonaceous cores. Semi-volatile organic compounds (SVOCs) can condense onto inorganic or soot particles to produce internally mixed primary particles (e.g. smoke plumes). In case the concentration is high enough, organic vapours may directly (i.e. without intermediate oxydation products) form particles by nucleation (e.g. biomass burning). In the case of combustion, the vapours may be products of incomplete combustion, or they may not have passed through a combustion zone at all (pyrolysis of wood releases organic material that condenses rapidly after it is emitted). This last case shows that the distinction between primary and secondary aerosol is not always clear. There is in fact a gradual transition (see 3.2.5). [9, 67, 52]

Main biogenic sources of primary organic aerosol are

Vegetation A possible process is the emission of small epicuticular wax removed under stress conditions. They are very small particles and have therefore long atmospheric lifetimes.

Bioaerosol and soil Bioaerosols are particles that are living, contain living organisms or were released by biological activity (see 3.2.4). They are present in all kind of environments. Organic matter (OM) in the soil might be resuspended by the action of the wind on soils, and even enriched in relationship to the soil's OM content.

Ocean As they rise towards the water surface before bursting bubbles can scavenge or adsorb OM, producing submicrometre particles enriched in insoluble and high molecular mass organic matter (e.g. during phytoplankton blooms). OM can also accumulate at the air-water interface.

The principal anthropogenic sources are:

Table 3.4: Worldwide estimates (Tg yr^{-1}) for the aerosol emissions from biomass burning [9, 67, 78].

Source	$PM_{2.5}$	*TC*	*OC*	*BC*	
Savanna and grassland		11.7	10.6	1.5	
Tropical forest		8.7	7.0	0.88	
Extratropical forest		5.3	5.6	0.36	
Biofuel burning		14.0	10.7	1.6	
Charcoal burning		0.24	0.18	0.06	
Agricultural residues		2.2	1.8	0.37	
Total		**42.2**	**36.1**	**4.8**	[67]
rice residues	12.6				[78]
wheat residues	4.5				[78]
Open burning					
Forest			11	1.2	
Savanna			12	1.7	
Agricultural residues			1.6	0.3	
Waste			0.058	0.044	
Total			**25 (12.7-57.1)**	**3.3 (1.6-9.8)**	
Contained combustion					
Total			**8.9 (5.1-17)**	**4.6 (3.1-10.1)**	[9]

Biomass burning: The combustion process was explained in 3.2.5. Table 3.1 lists the main sources of C burned, while Table 3.4 lists the emissions by biomass combustion processes.

Fossil fuel combustion: Globally, coal burning is one of the major sources of primary OM. Other fossil fuels also contribute significantly. The total flux from fossil fuels was estimated to 10.1 Tg OC yr^{-1}

[114, 115, 9, 67, 52]

Global emissions of POA were estimated by Kanakidou *et al.* [52] to 9.1, 34.6, and 3.2 Tg POA yr^{-1} for biofuel, vegetation fires, and fossil fuel burning, respectively.

3.4.3 Secondary carbonaceous aerosols

This subsection deals with the chemical precursors and the origins of anthropogenic and biogenic secondary organic aerosol.

VOCs: Volatile components of atmospheric aerosols are not condensable under actual atmospheric conditions and reside in or on the condensed phase only to the extent to which they can be absorbed (dissolved) in the particle bulk or adsorbed on the particle surface.

SVOCs: Semi-volatile components are condensable and can reside largely in the condensed phase or in the gas phase, depending on atmospheric conditions.

LVOCs and NVOCs Low-volatility and non-volatile components reside almost exclusively in the condensed phase.

[116] Volatile organic compounds (VOCs) are emitted into the atmosphere from natural sources in marine and terrestrial environments, as well as from anthropogenic sources [52]. Many gas-phase organic compounds undergo oxidation in the gas phase to yield products, generally oxygenated, that have sufficiently low vapour pressures that they will partition themselves between the gas and aerosol phases. Such products are often referred to as semi- or non- volatile, and when residing in the aerosol phase, as Secondary Organic Aerosol (SOA) [52].

Secondary organic aerosol, both anthropogenic (SOA_a) and biogenic (SOA_b), are radiatively active constituents of the atmosphere: scattering radiation and acting as cloud condensation nuclei (see 3.6.2 and 3.6.3). [52]

The formation of SOA is a major sink for many anthropogenic hydrocarbons and biogenic volatile organic compounds (BVOCs). Yet, it is presently poorly understood and quantified, though Tsigaridis and Kanakidou [51] modelled a global SOA (SOA_a and SOA_b) production of 18.6 Tg yr^{-1}. This process of aerosol formation from volatile organic precursors occurs mainly where photochemical ozone formation is significant. Gas-phase chemical reactions leading to condensable species starts with the addition of oxidant (OH, O_3 or NO_3, during daytime for the first two, the reaction is slower and at nighttime for the latter) to the double-bond of the hydrocarbon. H-atoms abstraction, for the OH reaction, is also possible, but is thought to be of lesser importance. This step is further followed by the gas-to-particle partitioning of reaction products. Its yield depends mainly on the temperature and the relative humidity. [67]

This picture is rather simplistic, since the processes leading to secondary organic aerosol formation are far more complex and dynamic. As proposed by Fuzzi *et al.* (2006) [116]:

- primary particles of atmospheric aerosols are formed within a source and directly emitted to the atmosphere
- secondary particles are formed in the atmosphere by condensation (nucleation and growth) of gaseous precursors
- aged particles have undergone physical or chemical transformation in the atmosphere (coagulation; structural rearrangement; phase transition; growth/shrinkage by condensation/evaporation of semi-volatile components; adsorption/absorption of volatile components; chemical transformation)

Obviously, both primary and secondary particles can undergo atmospheric aging. Also:

- primary chemical components of atmospheric aerosols are substances formed within a source and directly emitted into the atmosphere
- secondary chemical components are substances formed by chemical reactions in the atmosphere, these can be formed in the gas phase and condense onto pre-existing particles or lead to the formation of new particles, but they can also be formed by chemical transformation of primary components in the condensed phase

Aged primary aerosol particles can contain secondary chemical components (e.g., transformation of primary non-volatile components or uptake of secondary semi-volatile components) and secondary aerosol particles can contain primary chemical components (e.g., contribution of primary semivolatile components to the nucleation and growth of secondary particles) [116]. Aging processes may include cloud processing. [117, 116]

The dynamics of the aerosol chemistry and composition is well illustrated by recent smog-chamber studies conducted with diesel exhaust and wood burning plumes, which investigated the influence of the dilution ratio on emission factors. [97] Following these studies, Robinson *et al.* (2007) [98] proposed that most POA emissions from such sources are semi-volatile that partially evaporate with atmospheric dilution. These low-volatility vapours, after photo-oxidation, would then form SOA (mainly through condensation). On the other hand, Pósfai *et al.* [95, 96] identified tar balls (amorphous, carbonaceous spherules with diameters typically between 30 and 500 nm) as a gas-to-particle, homogenous, conversion product within smoke plumes. The authors proposed the following pathway for their formation: first, low-volatility organic gases are emitted that convert into aerosol particles and form water-soluble compounds; these then polymerise in hydrated smoke particles and, by becoming less soluble, they likely lose water.

Thousands of VOCs are emitted into the atmosphere from various biogenic and anthropogenic processes, most are involved in tropospheric photochemistry. Only a small suite of those are relevant to the SOA global budget. Biogenic sources of VOCs (BVOCs) include oceans and fresh water, soil and sediments, microbial decomposition of organic litter, geological hydrocarbons reservoirs, plant foliage and woody material. Woods, crops and shrubs contribute by 55%, 15%, and 14%, respectively, to the non-isoprene biogenic emissions, whereas oceans emit <1% [52]. Excluding isoprene and methane, VOCs from biogenic sources are often divided into the categories:

The terpenic compounds emitted by plants have a $C = C$ bond wich can react with molecular oxygen, ozone or OH radicals (products of the photochemistry of nitrogen oxides) forming new organic compounds. These new products have the ability to polymerise and further participate in gas-to-particle formation processes (homogenous or heterogenous nucleation, as well as condensation on existing particles). It is estimated that 15 % of the terpenes emissions react in a very short timescale to form SOA. The main oxidant for the terpenes molecules in the atmosphere is ozone, followed by OH and NO_3 radicals.

Other reactive VOC (ORVOC) have lifetimes <1 day, such as terpenoid alcohols, n-carbonyls, aromatics, sesquiterpenes ($C_{15}H_{24}$), terpenoid ketones and higher olefins.

Other VOCs (OVOCs) are the less reactive VOCs, with lifetimes >1 day; typically methanol, various aldehydes and ketones. These are belived to have little SOA formation potential (though $C_{>7}$ carbonyls may be important contributors to SOA).

[52, 51]

Only about 30% of the ORVOC and OVOCs have the potential to form SOA. In contrast, the monoterpenes, and especially the sesquiterpenes, have large potential for SOA formation [52]. The 14 compounds which dominate biogenic SOA formation are the monoterpenes:

Bicyclic olefins: α-pinene, β-pinene, δ^3-carene, sabinene

Cyclic diolefins: limonene, α-terpinene, γ-terpinene, terpinolene

Acyclic triolefins: myrcene, ocimene

Sesquiterpenes: β-caryophyllene, α-humulene

Oxygenated terpenes: linalool, terpinene-4-ol

[67, 57]

The monoterpenes represent a significant fraction of the BVOCs emitted from vegetation to the atmosphere with contributions ranging from 10 to 50% [52].

Claeys *et al.* [53, 54] have shown that also isoprene oxidation products are important sources of SOA. Isoprene, a hemiterpene, accounts for about half of all natural VOC emissions and is, on a mass basis, the dominant emitted biogenic VOC component [52, 51]. The hydroxyl radical is the dominant oxidant for ispoprene degradation. [51]

The large suite of oxidation products of VOCs span throughout a large range of volatilities and smog-chamber studies, due to limitations in producing quantifiable SOA at atmospheric relevant concentrations. [52] Therefore, the identification of the products which indeed partition into the particle or condensed phase as well as the extent to which this partitioning takes place under variable ambient conditions and, thus, the yields of SOA formation from VOCs oxidation products are still, to a large extent, open questions.

Kanakidou *et al.* [52] estimated that global SOA formation could be attributed as follows: 19.1 Tg yr^{-1} from terpenes, 15 Tg yr^{-1} from ORVOCs and 2 Tg yr^{-1} from isoprene oxydation products and that the contribution of SOA to the organic aerosol (OA) was 10–70%. Tsigaridis and Kanakidou [51] modelled somewhat different estimates: 12.2 Tg yr^{-1} from terpenes and 4.6 Tg yr^{-1} from isoprene oxydation products.

Among the numerous anthropogenic VOCs, only the aromatic (e.g. toluene, xylene, trimethylbenzene) and the large aliphatic species were found to originate significant SOA. Estimates of the anthropogenic VOCs potential SOA precursors emissions are 6.7 Tg yr^{-1} of toluene, 4.5 Tg yr^{-1} of xylene, 0.8 Tg yr^{-1} of trimethylbenzene and 3.8 Tg yr^{-1} of other aromatics. These emissions add up to about 10–15 % of all anthropogenic non-methane VOCs (NMVOCs). The OH radical is considered the almost exclusive oxidant for aromatics. [51] Compared to biogenic VOCs, Gelencsér [67] and Kanakidou *et al.* [52] estimated they were a minute source for SOA globally, though on a regional scale, principally where anthropogenic emissions are important, they do contribute significantly to the PM load. Tsigaridis and Kanakidou [51] modelled a global SOA$_a$ production of 1.8 Tg yr^{-1}.

3.4.4 Non carbonaceous aerosol

Sulphate and nitrate

The origin of sulphate and nitrate is mainly associated with anthropogenic activities; the combustion of fossil fuels for transportation, domestic heating, power plants and industrial activities emit elevated quantities of sulfur dioxide and nitrogen oxides, which in the atmosphere are oxidized into sulfuric and nitric acids, respectively. [118] The formation of sulphate and nitrate particles from the corresponding acids can occur by reacting with gaseous ammonia (e.g. from agricultural activities) or with salts (e.g. NaCl from sea spray, $CaCO_3$ present in soil dust). [118] Sulphate, associated with ammonium, is primarily present in the fine fraction of the atmospheric aerosol. Nitrate is also present in the coarse fraction, as a consequence of the reaction of HNO_3 with sea-salt particles or with soil particles containing calcium or magnesium carbonates. [118]

Sulphate aerosols are produced by chemical reactions in the atmosphere from gaseous precursors (with the exception of sea salt sulphate and gypsum dust particles) [15]. The main precursors of sulphate in the atmosphere are SO_2 emissions from fossil fuel burning (about 72%), with a small contribution from biomass burning (about 2%), while natural sources are from dimethyl sulphide emissions by marine phytoplankton (about 19%) and by SO_2 emissions from volcanoes (about 7%). [15, 2] Estimates of global SO_2 emissions range from 66.8 to 92.4 TgS yr^{-1} for anthropogenic emissions in the 1990s and from 91.7 to 125.5 TgS yr^{-1} for total emissions [2]. Sulphate is formed by aqueous phase reactions within cloud droplets, oxidation of SO_2 via gaseous phase reactions with OH, and by condensational growth onto pre-existing particles (e.g. sea salt particles with the formation of $MgSO_4$) [15, 2].

Nitrate aerosols derive from the oxidation and neutralisation of NO_x and NH_3, which may have a biogenic or anthropogenic origin. Nitrogen oxides are oxidised to nitric acid, which condenses onto pre-existing particles. These acidic aerosols may be neutralised by biogenic gasous NH_3, producing ammonium nitrate. Aerosol nitrate is closely tied to the relative abundances of ammonium and sulphate. NH_3 is important in the neutralisation of H_2SO_4. If ammonia is available in excess of the amount required to neutralise sulphuric acid, nitrate can form small ammonium nitrate aerosols. In the presence of accumulation-mode sulphuric acid containing aerosols, however, nitric acid deposits on larger, alkaline mineral or salt particles.

Heavy metals

Major focus has been put on the elements As, Cd, Cr, Ni, Pb and Hg. [119, 120, 121] The knowledge on sources and fluxes of atmospheric heavy metals is still somehow limited [122]. The main anthropogenic sources for the havy metals As, Cd, Cr, Ni and Pb in the atmosphere are:

- Combustion of coal and oil in utility (power plants), industrial, residential, and commercial boilers; of gasoline (only a source of Pb)
- Iron, steel and cement production
- Non-ferrous metal manufacturing
- Waste incineration

[119]

Considering those sources, Pacyna and co-workers [119] estimated an annual European production (year 2000) of 763, 590, 2711, 4797 and 13156 tonnes of As, Cd, Cr, Ni and Pb, respectively. The major source regions were southern UK, Benelux and southern Poland. For Cd, Cr and Pb those estimates are considerably larger than those from the EMEP 2006 inventory. [123, 119] The authors also refer a continuous reduction of those heavy metal emissions in Europe during the last 40 years and consider a appreciable potential for further reduction [119].

Mercury is one of the most important contaminants emitted to the atmosphere due to its toxic effects on the environment and human health, persistence in the environment, and global atmospheric transport with air masses. The largest emissions of Hg to the global atmosphere occur from combustion of fossil fuels, mainly coal in utility, industrial, and residential boilers. Global emissions estimate (2000) of Hg to the atmosphere was 2190 tonnes, two-third of which coming from the combustion of fossil fuels. Various industrial processes (major contribution from gold production using Hg technology) account for additional 30% of Hg emissions from anthropogenic sources worldwide. [121] For Europe, the 2000 production was 239 tonnes, half of which from the combustion of coal in power plants and residential heat furnaces. The second and third strongest source of anthropogenic Hg are the production of caustic soda with the use of the Hg cell process (17%) and cement production (13%). Minor sources are iron and steel production, waste incineration, non-ferrous metal manufacturing and oil combustion. [120]

3.5 Chemical characteristics of the tropospheric aerosol - Organic compounds

This section and the following subsections briefly describe the principal classes of organic carbonaceous aerosol. In the scope of this work, saccharidic compounds, PBAPs and wood burning are particularly stressed.

OC concentrations may range up to some tens of μg m^{-3}, and its distribution is globally unbalanced, with higher concentrations occurring over continental areas. However, both concentrations (and therefore its share in PM) and distribution varies throughout the year. Little is known about the OC size distribution, but studies so far point towards a unimodal distribution with a peak in the accumulation mode. Over the ocean, another peak may appear, corresponding to the marine aerosol mode. Generally, OM is internally mixed with the main aerosol constituents. The various OM constituents are very different and therefore have different polarities and solubilities, which makes it difficult to extensively recover and speciate. Water soluble OC (WSOC) usually accounts for $\frac{1}{5}$ to $\frac{2}{3}$ of the total OC. [67]

Atmospheric particles contain organic tracers which are characteristic of their source, the mode of formation and subsequent alteration during downwind transport [72]. Organic matter (OM) of atmospheric aerosols derives from two major sources and is admixed depending on environmental conditions and global location.

Recent research has revealed that, in addition to numerous organic compounds of low polarity, compounds belonging to various types of saccharides are important constituents of the atmospheric aerosol [124, 125, 126, 17, 127]. Simoneit *et al.* [17] have linked the composition of the saccharide mixtures in ambient PM to the soil biota and proposed resuspension of soil and unpaved road dust as a major component of aerosol particles (the input being either by wind erosion or resuspension from anthropogenic activities) and saccharides could be used as specific tracers. Anhydrosugars have been related to the biomass burning process. [124]

Primary monosaccharides (monosaccharides that are not the result from oligosaccharides hydrolysis) are the major carbon source for living organisms, the most widely occurring of them being glucose. Primary monosaccharides arise from photosynthetically assimilated carbon in vascular plants, and are an important source of carbon for other living organisms. Some organisms combine two primary monosaccharides into a primary dissacharide for purposes of transport (e.g. sucrose in plants), reserve carbohydrate or stress protectant (mycose in bacteria, yeast – a unicellular fungi –, a few higher plants as well as insects). Other organisms such as fungi (including lichens, a nutritionally specialised symbiotic association of a fungus with a photosynthetic partner) and bacteria reduce (hydrolyse) them to alditols (sugar alcohols) for storage, transport or intracellular osmoregulation. Alditols may also be photosynthetically produced. Plants polymerise primary monosaccharides into polysaccharides (e.g. cellulose, a polymer of glucose, and hemicellulose, a polymer of various primary monosaccharides) for growth purposes. When these are burned, anhydrosaccharides are formed as the thermal degradation products of holocelluloses. [128, 129, 130, 131, 124, 132]

It has already been shown that primary biological aerosol particles, PBAPs, comprising pollen, spores, bacteria, fungi, algae, protozoa, viruses and fragments such as vegetative debris, human or animal epithelial cells and parts of insects, are significant for the aerosol budget on a global scale, and this in all size ranges [40, 43, 44]. Fungal spores contribute significantly to the atmospheric aerosol (bacteria do to a very limited extend) [48, 115, 133, 134, 47] as well as plant detritus [49, 135]. Wood burning has also been since long identified as a major global source for the atmospheric aerosol [136, 137, 89, 138].

Due to this relevance, the presence of compounds from all the described classes in the airborne particulate matter is expected to be significant. Atmospheric saccharides originate from different source types: microorganisms, plants and animals release primary saccharides (mono- and disaccharides) to the atmosphere; fungi, lichens and bacteria emit saccharide polyols, while anhydrosaccharides are the primary thermal degradation products of polysaccharides present in biomass. [124, 17, 127]

Molecular tracers in aerosol are indicator compounds that can be traced down to individual sources. [67] The apportionment and mass quantitation of smoke in urban and rural areas is of importance to evaluate health hazards to the population, and on a global scale smoke contributes to the particle burden wich changes the reflective albedo of the atmosphere, thus affecting climate [72].

The major compound groups identified in smoke particles from biomass burning consist of natural (unaltered) and combustion alteration products (e.g. oxygenated, aromatised, dehydrated, decarboxylated, etc… compounds). The compound classes include the following: homologous series of n-alkanes, n-alkanoic acids, n-alkanols, methoxyphenolics from lignin, monosaccharides derivatives from cellulose, steroid and terpenoid biomarkers and PAHs. The distributions and abundances of these constituents depend on combustion temperature (smoldering versus flaming conditions), aeration and burn duration, besides the original fuel composition. [139, 72]

The various wood constituents (see 3.2.5) generate different volatile products and char upon burning. The main ones identified in the ambien aerosol are:

Lignin combustion yields phenols, aldehydes, ketones, acids and alcohols, generally with the retention of the original substituents on the phenyl ring. Lignin derivatives, as described in Figure 3.1 are not unique to a taxa, but their relative proportions may carry useful information on potential sources.

Lignans are basically dimers of p-coumaryl, coniferyl and sinapyl alcohols and serve as toxins, supportive fillers and other purposes. They are released unaltered in the smoke of softwood and, to a lesser extent, in the smoke of hardwood. They have not been detected in grass smoke. Lignin pyrolysis products may as well undergo radical recombination and yield secondary dimers.

Diterpenoids are released unaltered in the smoke of pine wood. All resin acids are, in the atmosphere, oxidised to dehydroabietic acid, the major marker for conifers.

Cellulose decomposes, above 300°C, by transglycosylation, fission and disproportionation reactions, yielding tarry anhydrosugars and volatile products (see Figure 3.3).

Hemicelluloses yield anhydrosugars from its sugars units – levoglucosan, mannosan, galactosan, …

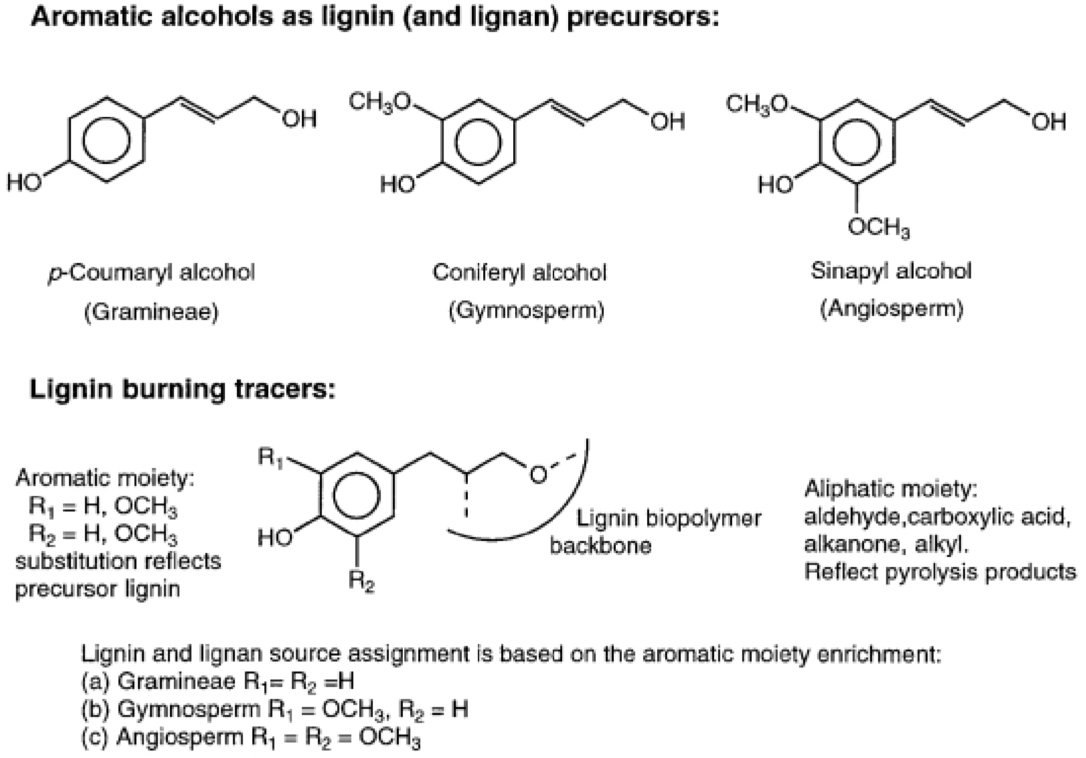


Figure 3.1: The lignin combustion products, from [72]

Sterols thermal dehydration compounds were not detected in woodsmoke, unlike β-sitosterol, found unaltered in pine and oak wood smoke. A product of its mild thermal degradation, stigma-4-en-3-one was detected as well.

PAH derivatives found in wood smoke are oxy-PAHs, namely polycyclic aromatic ketones (PAKs) that are probably the oxidation products of parent PAHs. Some could also be decomposition products of lignin.

[74, 72, 67]

Wood is the major biomass burned, but other types of biomass burned may also contribute to the aerosol:

- Emissions from immature coal burning (peat and lignite) emit organics which are specific of their maturity, very similar to contemporary biomass.
- Cooking operations such as griling, frying, deep frying, charring
- Fugitive emissions (urban): building fires, dung chip burning, domestic garbage fire, rubber tyre burning,
- Fugitive emissions (rural): agricultural burning and wildfire of vegetation and vegetation detritus from the countless species present in agricultural and ecosystem environments, as welll as dung burning.

- Burning of parafin and beeswax candles.
- Tobacco smoke

3.5.1 Lipid fraction of organic aerosol

Alkanes are minor, primary components. Their sources are diverse: direct emission by vegetation, part of soil detritus, volatilisation by burning, sea surface microlayer by bubble bursting, ... They are typically manifested in the form of a distinctive homologue series from about n-C_{15} to n-C_{30}. Wax-derived n-alkanes are dominated by odd carbon number homologues. Petroleum-derived odd and even carbon number n-alkanes homologues are emitted roughly in the same proportion.

N-alka(e)noic acids (n-fatty acids) typically range from $<C_{10}$ to C_{32}. Their origins are bioaerols, the marine aerosol, biomass burning, vegetation waxes, food preparation, vehicle exhaust and tyre wear debris. Some may be of partly secondary origin.

N-alkanols (n-fatty alcohols) cover a range from C_{10} to C_{34}, with a strong even carbon number predominance and have been observed in urban, marine and forest aerosols. The source of the lower homologues series is the marine aerosol. The higher ones derive from the waxes of higher terrestrial plants. Since they are easily thermally degraded to olefins, they present highly variable concentrations in biomass smoke.

N-alkanals extend from C_9 to C_{23}. They are thought to be primarirly of biogenic origin, though it is not clear whether they are primary or secondary.

N-alkan-2-ones distribute themselves between C_8 to C_{38}, with an odd number preference over rural areas. Shorter compounds are assumed to derive from anthropogenic activities or microbial degradation, while longer ones are mainly from plant waxes.

Long-chain wax esters are important in continental aerosols, with a strong even carbon number predominance.

[140, 141, 142, 143, 72, 67]

3.5.2 Other high molecular weight organic compounds of primary origin

Cellulose is a wettable, but unsoluble substance related to plant debris (about 50% of its dry weight) and, to a lesser extent, to pollen. Some (about 72%) of it is free, i.e. not encapsulated by lignin and readily available for enzymatic saccharification.

Humic acids and carbonaceous residue originate in soils and lacustrine mud, but are also potentially secondary organic compounds.

[49, 135, 67, 144]

Cellulose, the structural material of the higher plants is a polymer of D-glucose with a characteristic X-ray diagram. The purest state in which cellulose is found in nature is cotton, which seldomly contains more than 5% of other compounds (excluding water). More commonly, in woods, plants, ... cellulose is associated with lignin and hemicelluloses. [75] More precisely, cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units (aften abbreviated to anhydroglucose or even to glucose for convenience) joined together by β-1,4-glycosidic bonds. It is capable of forming inter- and intramolecular hydrogen bonds, thus being partly crystalline. The surface of the ribbon consists mainly of H atmos linked directly to C atoms and the molecule. Therefore cellulose is hydrophobic and insoluble in water. However, water vapour can be adsorbed strongly on fibrillar surfaces and in the less ordered regions of the molecule. [75]

The hemicelluloses comprise a group of polysaccharides (excluding pectin) that remain associated with cellulose after lignin has been removed. Unlike cellulose, the constitutions of hemicelluloses differ from plant to plant: they contain different sugar units (whereas cellulose only contains 1,4-β-D-glucopyranose units), they exhibit a considerable degree of chain branching (cellulose being strictly linear) and have a degree of polymerisation about one hundred times smaller. Hemicelluloses have linear polysaccharide backbones, often but not always homopolymers, composed of β-1,4-linked xylose, glucose or mannose units. The short side chains of the hemicelluloses may include xylose, glucose, arabinose, fucose, rhamnose and glucuronic acid. [76] The most abundant of the wood hemicelluloses are the xylans (polymers of 1,4-linked β-D-xylopyranose, with some 1,3-linked α-L-arabinofuranose units or 1,2-linked α-D-glucuronic acid units). Particularly important in softwoods are the 1,4-β-D-glucomannans, with randomly distributed glucose and mannose units with the most common side chains being of 1,6-linked α-D-galactopyranose units. This delignified wood (consisting of cellulose and hemicelluloses) is refered to as holocellulose. [75]

Fulvic and humic acids are common in soils, where they are thought to be the microbial degradation products of various organic tissues. It was hypothesised that their presence in atmospheric aerosols could be due to soil resuspension [67]. Recently, however, Reemtsma *et al.* [144] have identified fulvic acids, as well as sulphted, nitrated and mixed sulphted and nitrated molecules, in the $PM_{2.5}$ ambient aerosol, some of which had never been identified in soil samples. Furthermore, the authors point that in that size fraction, little material is expected to originate from soil resuspension and thus propose that those substances most likely originate from secondary formation, by two possible ways: the oxidative transformation of primary biological material, leading to degradation of the larger molecules into fulvic acids or the free radical oligomerisation of the oxidation products of primary volatile organic compounds. In both cases, sulphte and nitrate could be introduced after SOA is formed or be incorporated upon (acid-catalysed) SOA formation.

3.5.3 Compounds of predominantly secondary origin

The still poorly understood formation mechanism of SOA can be viewed as a sequential process: Emission of gases $\longrightarrow$ Gas-phase chemistry $\longleftrightarrow$ Nucleation / gas-particle partitioning $\longleftrightarrow$ Aerosol phase / aqueous phase chemistry / cloud processing. The reactions of VOCs with OH, NO_3 or ozone lead to a large suite of oxygenated reaction products which include aldehydes, oxy-aldehydes, carboxylic acids, oxy-carboxylic acids, hydroxy-carboxylic acids, dicarboxylic-acids, organic nitrates, etc ... Also, other oxidants and secondary reactions may be involved in oxidised SOA formation. [52].

These new, oxygenated, products must be particularly non-volatile in order to homomolecular nucleation to take place. The inclusion of polar functional groups (hydroxy, keto and, particularly, the carboxyl group) maintaing the carbon number, reduce the product volatility. Besides the volatility, another key property in the formation of new particles is the surface energy of the compounds because of the importance of the Kelvin effect for nucleation.

Nucleation may not be the only pathway of compounds from the gas to the aerosol phase. Heterogenous reactions (acid-catalysed) may also take place, namely following oligomer and/or polymer formation from VOCs. Also, the nucleating products, or those that change phase to pre-existing particles, may not be the end-products observed in the aerosol since the oxydation might go on in the particle phase. [52]

Oxygenated compounds

These are compounds which are mainly the end products or the intermediates of the oxidation of a suite of gaseous and primary particulate species. Many of them are found both in the gaseous and in the aerosol phase, with the oxidation taking place in both phases. The gas-particle partitioning may be homo- or heterogenous.

Monocarboxylic acids are the end products or the intermediates of the oxidation of olefins by ozone, of non-methane hydrocarbons by various oxidants and may as well be emitted directly to the atmosphere. These compounds are volatile and are mainly present in the gaseous phase. The main monocarboxylic acids found in the ambient aerosol are formic (C_1) acid, acetic (C_2) acid and propionic (C_3) acid. [145] Biomass combustion is a primary source of both formic and acetic acids, while motor exhaust also produces propionic acid. In forested environments, soil and plants may also be an important source of those three monoacids. Formicine ants have also been reported as a biogenic primary source of formic acid, though not important at the global scale. [145]

Dicarboxylic acids are ubiquitous and generally thought to be of secondary origin, though primary traffic emissions have been proposed as a source. [67, 146, 147] These compounds are likely to dominate in the aerosol phase since their vapour pressure is lower by a factor of 10^2–10^4 than that of corresponding MCAs. [145] These important contributors to WSOC have received much attention due to their strong hydrophilic and hygroscopic properties and thus potential ability to act as CCN altering cloud formation. In atmospheric aerosols, one of the major sources of DCAs is the photooxidation of unsaturated hydrocarbons and fatty acids, both biogenic and anthropogenic (cycloolefins and aliphatic diolefins). [145, 67, 148, 149] Alternatively they may be the particle phase aging products of other organics, namely other DCAs (longer-chain seem to be precursor of shorter-chain DCAs – e.g. succinic acid can be oxidised to oxalic acid with malonic and malic acids as intermediates – and oxidation of ambient DCAs can contribute to oxo-, hydroxy-DCAs and other substituted DCAs). Probably for this reason, within this class, low molecular weight compounds are predominant, the prevailing one being oxalic (C_2) acid. [67, 149, 150] Main DCAs are malonic (C_3), succinic, tartaric, malic, maleic, fumaric and methylmalonic acids (C_4), glutaric, methylmaleic and methylsuccinic (C_5) acids, phthalic, isophthalic, adipic and 2-methylglutaric (C_6) acids, pimeric (C_7) acid, suberic acid (C_8) and azelaic acid (C_9). [147, 149, 151, 150] Another example is pinic acid (end product of the ozonolysis of α- and β-pinene [52]). Due to their partially secondary nature, it is difficult to apportion their origin to anthropogenic or biogenic sources. However, some insights have been made stating that urban oxalic and succinic acids have a traffic origin, succinic and maleic acids are predominantly from anthropogenic sources while malic acid has biogenic ones. Also, as azelaic acid has been proposed as one of the reaction products by ozonolysis of biogenic unsaturated fatty acids and adipic acid has been proposed as one of the products by oxidation of anthropogenic cyclohexene, the $\frac{C_6}{C_9}$ ratio can be used as a potential indicator to show the relative strength of biogenic and anthropogenic sources. [145, 146, 147, 149] Altieri *et al.* (2008) [152] showed that carboxylic acids from methylglyoxal (a product of the ozonolysis of a large number of VOCs, both anthropogenic and biogenic) could undergo oligomerisation through cloud processing.

Functionalised carboxylic acids are mono- or dicarboxylic acids with additional functional groups, such as keto-(oxo-), hydroxy- or nitro-groups. They have been found in lower concentrations that dicarboxylic acids and thus are possibliy less important contributors to the aerosol. However, it is possible that multi-functional oxygenated organic compounds are preponderant contributors to OM. [67, 153] Functionalised carboxylic acids are likely to be produced in oxidation reactions in the atmosphere. Potential sources could be radical reactions in the liquid phase, leading to hydroxylated or oxygenated acids. [154] Also, it was proposed that the oxoacids are likely intermediates in the production of dicarboxylic acids. [146] Common keto-acids identified in the aerosol samples are glyoxylic (oxoacetic) (C_2) acid, pyruvic, ketomalonic (mesoxalic, oxomalonic), 3-oxopropanoic (C_3) acids, 4-oxobutanoic (C_4) acid, 4-ketopimelic (C_7) acid and 9-oxononaoic (C_9) acid. [147] The most common hydroxy-carboxylic acid is lactic (C_3) acid. [155]

Dicarbonyls Common dicarbonlys are glyoxal (C_2) and methylglyoxal (C_3). [147]

Methyltetrols (2-methylthreitol and 2-methylthritol) were found to be the oxidation products of isoprene in the particulate phase. [53, 54]

Other oxygenated compounds have also been identified in the aerosol, e.g. methanesulfonic acid diacyl peroxides have been proposed as the products of cyclic alkenes ozonolysis [156], some tricarboxylic acids observed are possibly degradation products of α-pinene [157].

HULIS

The presence of water-soluble macromolecular compounds in aerosols was first reported in the 80s [158]. Later, studies showed that not the totality of that fraction is water-soluble [159],and that they are rather medium to high molecular weight (MW) compounds (the average MW is in the range 215–345 Da [160], another study referred 556 Da [161]). They show many similarities to naturally occurring humic acids, but are chemically not related, and were thus termed HUmic-LIke Substances (HULIS) [67, 162]. The differences between atmospheric HULIS and humic substances in other media may be due to the possibility that HULIS consist of supramolecular associations rather than macromolecular polymers, or that they represent some non-equilibrium phase resulting from a quasi-steady state between formation and destruction (by UV radiation, ozone or hydroxyl radicals) of larger species. Also, the possibility that HULIS are a complex, unresolved mixture of relatively small molecules has not been ruled out. Other reasons might be the different modes of formation and the duration of formation, as well as the fact that extraction methods could alter the compounds. [158].

The origins of HULIS are still somewhat unclear and primary and secondary sources have been proposed, of which biomass burning is the main one. [163, 158] HULIS are produced in an atmospheric polymerisation process from low molecular weighted organics of different origin. Cloud drops may act as reactor in this HULIS formation process but more likely are gas-phase or gas-to-particle interactions. [164] A primary pathway could result from the incomplete breakdown of polymeric carbohydrates with lignin as the primary component, which can be further modified in the process of combustion. [67, 165]The atmospheric oxidation of soot was reported [166] as a secondary route. Another secondary formation mechanism of humic matter in the atmosphere via the evaporation, condensation and aerosol-phase polymerisation of low molecular weighted polar degradation products of organic debris in soil was proposed by Gelencsér *et al.* [167]. Dienes, like isoprene (in the gaseous phase) were shown to be possible precursors of HULIS with [67],or without [67, 57],carbonyl intermediates in the presence of sulphuric acid. Polymerisation of carbonyls and their hydrates, formed after photo-oxidation of aromatic compounds was shown to be a possible pathway. [67]Another proposed secondary route could be the condensation of lignin pyrolysis products reactions with other molecules. [125, 67, 165]A single phenolic (aromatic hydroxyacids) precursor in OH-induced free radical polymerisation can form products similar to HULIS [168]. This possibility was verified in the field in conditions with biogenic semi-volatile phenolic precursors and a high photochemical activity [165], but the aromatic hydroxyacids may also originate from biomass burning and lead to HULIS formation [169]. Holmes and Petrucci (2006 and 2007) proposed the oligomerisation of levoglucosan, either through acid-calaysed cationic ring opening [170] or through reaction with the OH radical from Fenton chemistry [171]. Surrat *et al.* (2007) [172] proposed that sulphate esters from isoprene, α-pinene and other terpenes (through particle-phase reactions) could be a significant contributor to HULIS. Altieri and co-workers [152] proposed that the organic acid monomers formed through in-cloud hydroxyl radical reactions of methylglyoxal oligomerise through esterification.

The precise chemical structure of HULIS is still unknown. It has been found that HULIS consist of condensed and partially oxydised phenolic structures cross linked with short-chain aliphatic bridges which form by the oxidative cleavage of the phenolic ring [173, 67]. It is assumed that they are a composite material, and thus many subsets are expected regarding to different properties. HULIS have a water-soluble, a base-soluble and an insoluble fraction [158, 161]. Organosulphates could be a chemical subset [174, 172, 161], as well as nitrogen-rich organic compounds [175]

In the ambient aerosol, HULIS are more typical to continental (both urban and rural) than marine aerosol [176, 125, 159] and are a major contributor to OC and, principally, WSOC [163, 176, 177, 178, 161] (in the hydrophobic fraction [179]) which make them a compound of interest in terms of interactions between the aerosol and the hydrological cycle [180, 181]. The presence of such substances in the aerosol, because of their colour, may enhance absorption of solar radiation [158]. They are considered as a preponderant component of brown carbon.

3.5.4 Polycyclic aromatic hydrocarbons

Polycyclic (Polynuclear) aromatic hydrocarbon (PAHs) compounds are a class of complex organic chemicals, which include carbon and hydrogen with a fused ring structure containing at least 2 benzene rings. PAHs may also contain additional fused rings that are not six-sided. [63] Because of their low vapour pressure, some PAHs are present at ambient temperature in air, both as gas and associated with particles. The lighter PAHs, such as phenanthrene, are found almost exclusively in gas phase whereas the heavier PAHs, such as benzo[a]pyrene (B[a]P), are almost totally adsorbed onto particles [63]. PAHs are the most stable form of hydrocarbons having low hydrogen-to-carbon ratio and usually occur in complex mixtures rather than single compounds [63].

PAHs are formed primarily during incomplete combustion processes but are also found in wood and crude oil, among others [67, 63, 182]. PAHs in the atmosphere can be derived (pyrosynthesis and pyrolysis) from natural combustion sources (forest fires, volcanic eruptions) or be formed by anthropogenic processes as products of uncomplete combustion of fossil (petroleum, natural gas and coal) or non-fossil fuels [72, 67, 63], the ultimate product of combustion being graphite itself. The majority of the PAHs present in ambient air is due to anthropogenic emissions [63]. Although the levels of low molecular weight PAHs are high in vapour phase, most of the probable human carcinogenic PAHs are found to be associated with particulate matter, especially in fine mode particles in ambient air [63]. The concentrations and sizes of PAHs depends most strongly on the burning efficiency, and less strongly on the type of biomass burned. Fossil fuels have variable contents of PAHs before combustion (petroleums and their products have the least, coals have the highest concentrations), biomass generally does not contain PAHs. The commonly analysed compounds range from naphthalene (molecular mass –MW– 128) and phenanthrene (MW 178) to coronene (MW 300). Combustion-related PAHs (9 major nonalkylated compounds: fluoranthene, pyrene, benz[a]anthracene, chrysene, benzofluoranthenes, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene) are predominantly smaller particles. Petrogenic PAHs (phenanthrene, methyl- and dimethylphenanthrene) are predominanlty larger particles. [72, 67]

Because the major PAHs in wood smoke are generally the same as from other anthropogenic combustion emissions, other biomarkers are prefered as indicators of the organic materials being burned [72]. However, some PAHs have been reported as source-specific. But it is the use of ratios that allows a more precise source apportionment. The binary ratio method for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions: PAHs resulting from the use of coal, oil, and wood are low in coronene relative to B[a]P, while mobile source combustion emissions from diesel and petroleum use are high in benzo[ghi]perylene and coronene relative to B[a]P. Some authors have also used the ratio of groups of PAHs instead of individual compounds. [63]

3.5.5 Carbohydrates - Mono and polysaccharides

Carbohydrates are the single most abundant class of organic molecules found in nature. Monosaccharides (also called simple sugars) are the simplest carbohydrates. Monosaccharides consist typically of three to seven carbon atoms and are described either as aldoses or ketoses, depending on whether the molecule contains an aldehyde function or a ketone group. With very few exceptions, the chemical formula of mosaccharides is $H(CHOH)_nC = O(CHOH)_m$. If n or m are 0, then it is an aldose, otherwise it is a ketose. Aldoses and ketoses have three, four, five or six carbon atoms in their structure. Hexoses are the most abundant sugars in nature, though all are important in metabolism.

Of the daily 1.5×10^{22}kJ the earth receives from the sun, about 1% is used by photosynthesis. Cells capable of photosynthesis combine carbon dioxide from the air, water and solar radiation to produce hexoses in an aqueous form and gaseous oxygen. A variety of chemical and enzymatic reactions produce derivatives of the simple sugars. These modifications produce a diverse array of saccharide derivatives: sugar acids, sugar alcohols (discussed in the next section), deoxy sugars, sugar esters, amino sugars, acetals, ketals, and glycosides. The simplest oligosaccharides are the disaccharides, which consist of two monosaccharide (the hexoses glucose, fructose, mannose, and galactose and the pentoses ribose and xylose) units linked by a glycosidic bond. Sucrose, maltose and lactose are the most common disaccharides, others are trehalose, cellobiose and isomaltose. By far the majority of carbohydrate material in nature occurs in the form of polysaccharides. Polysaccharides, also called glycans, are formed by monosaccharides and their derivatives. [183]

The main primary monosaccharides found in the biosphere are:

Aldotriose: glyceraldehyde

Aldotetroses: erythrose, threose

Aldopentoses: ribose, arabinose, xylose, lyxose

Aldohexoses: allose, altrose, glucose, mannose, gulose, idose, galactose, talose

Ketotriose: dihydroxyacetone

Ketotetrose: erythrulose

Ketopentoses: ribulose, xylulose

Ketohexoses: psicose, fructose, sorbose, tagatose

[184, 183]

Energy from the sun captured by green plants, algae, and some bacteria during photosynthesis is stored in the form of carbohydrates. In turn, carbohydrates are the metabolic precursors of virtually all other biomolecules and thus fulfill most of the needs of the plant organism: structure and growth, stress protectant, etc... For animals, the breakdown of carbohydrates, that can be stored either as such or transformed, provide the energy that, through the food chain sustains, life.

Functions of polysaccharides are:

Storage: organisms store carbohydrates in the form of polysaccharides rather than as monosaccharides to lower the osmotic pressure of the sugar reserves. Storage polysaccharides are: starch, glycogen and dextran.

Structure: The structural polysaccharides (holocelluloses – cellulose and hemicelluloses – , chitin, alginates, agarose and glycosaminoglycans) have properties that are dramatically different from those of the storage polysaccharides, even though the compositions of these two classes are similar.

The primary saccharides commonly found in PM are α- and β- glucose, α- and β- fructose, sucrose, mycose (trehalose) and other minor compounds such as arabinose, galactose, mannose, maltose, etc..., cellulose has also been reported. [17] The saccharides are emitted directly from sources, although they may also be emitted significantly by thermal stripping during burning (e.g. in wildfires) [17]. Direct emission processes include mainly friction operations (wind action on the leaves of a tree, etc...) Emission may also arise from soils. Organic matter that reached the soil (e.g. deciduous or dead biomass) may be resuspended by friction processes such as wind action, traffic, etc....

Table 3.5: Concentrations of primary sugars reported in the bibliography, in ng m^{-3}.

Compound	*Sources*	*Reported concentrations*
Glucose	Fungi [129] Lichens [132] Large fungal spores, fern spores, pollen grains, plant fragments [185] Soil biota [17] Biomass burning (increase during episodes) [85, 127]	8.4–93/4.3–12 ($PM_{10}/PM_{2.5}$; Oslo, urban background, fall [134]) 13-54/2.1-5.2 ($PM_{10}/PM_{2.5}$ Oslo, curbside, fall [134]) 5.4-32/15-29 ($PM_{10}/PM_{2.5}$ Elverum, suburban, winter [134]) 10-34/3.6-6.9 ($PM_{10}/PM_{2.5}$ Elverum, suburban, summer [134]) 0.93-7.2/0.36-4.4 ($PM_{10}/PM_{2.5}$ Birkenes, rural [134]) 3.1-50.1 ($PM_{>1}$, Howland experimental forest [127]) 3.2-84.4 ($PM_{2.5}$, Hong-Kong [186]) 8-28 (PM_{10}, Tel-Aviv, winter [187]) 1.1-8.5 ($PM_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 11-111 (TSP, Gosan, Korea, April-May 2001 [189]) 1.2 -33.5 (TSP, Sapporo, Japan, April-May 2001 [17, 189]) 2.3-7.9 (TSP, Chichi-jima, China, April-May 2001 [189]) 2.6-27 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 28-180 (PM_{10}, Melpitz, Germany [190]) 1.3-4.1 (PM_{10}, Hyytiälä, Finland [190]) 590-3830/<220 (TSP, savannah fire/background [85]) 30-153/110-610 (PM_{10}, Gent, winter/summer [126]) 1.88-16.32/1.65-124.49 ($PM_{2.5}/PM_{>2.5}$, Amazonia, July 2001 [185]) 13.9-62.1/4.6-40.9 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125]) 5.4/10/15 ($PM_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138])
Fructose	Lichens [132] Large fungal spores, fern spores, pollen grains, plant fragment [185] Soil biota [17]	4.6-90/<5.1 ($PM_{10}/PM_{2.5}$ Oslo, urban background, fall [134]) 8.8-37/0.79-2.1 ($PM_{10}/PM_{2.5}$ Oslo, curbside, fall [134]) 3.4-21/7.9-22 ($PM_{10}/PM_{2.5}$ Elverum, suburban, winter [134]) 3.3-25/2-4.5 ($PM_{10}/PM_{2.5}$ Elverum, suburban, summer [134]) 0.3-3.9/<3.3 ($PM_{10}/PM_{2.5}$ Birkenes, rural [134]) 11.2-44.3/1.9-9.1/2.5-5.9($PM_{2.5}$, Amazonia – dry, transition and wet periods [177])

Compound	*Sources*	*Reported concentrations*
		<5.3 (PM_1, Howland experimental forest [127]) 12 (TSP, Sapporo, Japan [17, 189]) 49-95 (TSP, Gosan, Korea, April-May 2001 [189]) 4.9 (TSP Chichi-jima, China, April-May 2001 [189]) 4 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 10-126/39-440 (PM_{10}, Gent, winter/summer [126]) 1.71-9.66/1.86-75.09 ($PM_{2.5}/PM_{>2.5}$, Amazonia, July 2001 [185]) 2.8-19.9/2.3-22.8 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Arabinose	Lichens [132]	0.4-3.7 (PM_1, Howland experimental forest [127])
Mannose	Soil biota [17]	0.8-14.1 (PM_1, Howland experimental forest [127]) 48-6800 (TSP, Kuala Lumpur, Malaysia [17]) 0.6-4.1/0.5-3.1 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125]) 4.5/9.3/13 ($PM_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138])
Xylose	Soil biota [17] yeasts [191]	0.7-474.8 (Xylose used as calibration standard for the group of isomers of identical MW, $PM_{2.5}$, Hong-Kong [186]) 1.33-33.2 (PM_{10}, Amazonia, burning and dry-to-wet season [125]) 0.7/9.1/17 ($PM_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138])
Galactose	Soil biota [17]	1.4-22.2 (PM_1 [127]) 0.4-2.4 (Rondonia, Brasil, $PM_{2.5}$ and PM_{10} [125, 17]) 0.2-2.4/0.1-1.3 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Maltose	Soil biota [17]	<4.1 (PM_1 [127]) 6-2390 (TSP, Santiago, Chile [17]) 2-550 (TSP, Kuala Lumpur, Malaysia [17]) 3.2-4.0 ($PM_{2.5}$, urban, winter, San Joaquin Valley, US [138])
Sucrose	Large fungal spores, [185] fern spores, pollen grains, plant fragment Soil biota [17] Plants [127]	17-320/5.1-3.2 ($PM_{10}/PM_{2.5}$ Oslo, urban background, fall [134]) 25-130/2-5.1 ($PM_{10}/PM_{2.5}$ Oslo, curbside, fall [134]) 6-160/- ($PM_{10}/PM_{2.5}$ Elverum, suburban, winter [134]) 22-270/4.8-55 ($PM_{10}/PM_{2.5}$ Elverum, suburban, summer [134]) 0.11-3.5/0.16-6.4 ($PM_{10}/PM_{2.5}$ Birkenes, rural [134]) 1.3-11/0.8-4.6/0.4-2.4 ($PM_{2.5}$, Amazonia dry/transition/wet period [177])

Compound	*Sources*	*Reported concentrations*
		<5.6 (PM$_1$, Howland experimental forest [127]) <202.5 (PM$_{2.5}$, Hong-Kong [186]) 15-3060 (TSP, Santiago, Chile [17]) 0.4-9.2 (TSP, Sapporo, Japan, April-May 2001 [17, 189]) 0.3-1.2 (PM$_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 6-444 (TSP, Gosan, Korea, April-May 2001 [189]) 0.2-2.7 (TSP, Chichi-jima, China, April-May 2001 [189]) 0.6-422 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 8-60 (PM$_{10}$, Tel-Aviv, winter [187]) <0.06-1.90/<0.06-77.10 (PM$_{2.5}$/PM$_{>2.5}$, Amazonia, July 2001 [185]) 16-213 (PM$_{10}$, Melpitz, Germany [190]) <0.3-10 (PM$_{10}$, Hyytiälä, Finland [190]) 7.2-98/7.7-200 (PM$_{10}$, Gent, winter/summer [126]) 0.8-25.7/1.4-39.4 (PM$_{10}$, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125]) 0.9/4/3.2 (PM$_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138])
Mycose (Trehalose)	Yeast [130] Bacteria, funghi [130, 129] Yeasts and other small fungal spores [185] Soil biota [17]	<65/<11 (PM$_{10}$/PM$_{2.5}$ Oslo, urban background, fall [134]) 11-45/0.77-3.5 (PM$_{10}$/PM$_{2.5}$ Oslo, curbside, fall [134]) 2.3-18/4.8-16 (PM$_{10}$/PM$_{2.5}$ Elverum, suburban, winter [134]) 15-51/2.6-5.8 (PM$_{10}$/PM$_{2.5}$ Elverum, suburban, summer [134]) 0.76-10/0.14-3.9 (PM$_{10}$/PM$_{2.5}$ Birkenes, rural [134]) 1.5-18.3 (PM$_1$, Howland experimental forest [127]) 8-1660 (TSP, Santiago, Chile [17]) 0.2-12 (TSP, Sapporo, Japan [17]) 0.1-2.5 (PM$_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 2.5-30 (TSP, Gosan, Korea, April-May 2001 [189]) 0.1-15.5 (TSP, Sapporo, Japan, April-May 2001 [189]) 0.1-9.2 (TSP, Chichi-jima, China, April-May 2001 [189]) 0.2-16 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 8-20 (PM$_{10}$, Tel-Aviv, winter [187])

Compound	*Sources*	*Reported concentrations*
		4.89-11.77/21.16-89.71 ($PM_{2.5}/PM_{>2.5}$, Amazonia, July 2001 [185])
		5.1-17.8/2.3-20.1 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])

3.5.6 Carbohydrates - Polyols

Sugar alcohols (polyols) are obtained when the aldo or keto group of a sugar is reduced to the corresponding hydroxy group. The carbon chain of polyols can be either linear (acyclic polyols or alditols) or arranged in a ring (cyclic polyols or cyclitols). They have three or more carbons, each of them bearing an OH group. In the plant they are almost always closely related, in their biogenesis and metabolism, to the companion sugar (usualy the ketose). In many organisms, particularly fungi, they replace the sugar in many of their functions (e.g. translocation of carbon skeletons and energy between source and sink organs). Polyols have been found to be of particular importance in the "lower" plant groups such as bacteria, the brown algae, the Ascomycetes and Basidiomycetes, and the Marchantiophyta. [128, 192, 193]

Among the most common alditols, mannitol is derived from mannose, sorbitol (glucitol) from glucose, galactitol (dulcitol) from galactose, arabitol (or arabinitol) from either arabinose or lyxose, ribitol (or adonitol) from ribose.

Mannitol is by far the most abundant polyol in nature. It was first found to be characteristic of the oleaceae. Two groups of algae are characterised by the presence of mannitol: the Phaeophyceae (brown algae) and the Crysophyceae (golden algae). More important to the atmospheric aerosol are the two major fungi groups Ascomycetes and Basidiomycetes, to the extent that very few, if any, species lack it. In the organisms of those two groups, mannitol is often associated with arabitol (another polyol) and trehalose (a disaccharide) and take the place of glucose, fructose and sucrose in the metabolism. The three act as the main storage and respirable carbohydrates, with carbohydrate utilisation being a direct process from stored mannitol. Lichens, a commensal association between an ascomycete (occasionally a basidiomycete) fungus and an alga from the Chlorophyta or Cyanophyta, always contain mannitol and usually another polyol as well. Some Bryophyta, Monocotyledonae and higher plants (e.g. Oleaceae and Rubiaceae) may also contain mannitol.

Sorbitol occurs generally in higher plants of the woody Rosaceae. In other higher plant families, the distribution of sorbitol is much more scattered. Unlike mannitol, sorbitol is not commonly found in the lower plants. It is characteristic of one group of Marchantiophyta, the Marsupellaceae. It has been reported in a few of the unicellular green algae, the filamentous fungi and yeasts and a red alga but in none of the brown algae.

Other hexitols such as L-iditol and allitol are also found in the plant world, though very scarcely. Galactitol, is more widespread. It is very seldom in red algae, filamentous fungi and yeasts. The main groups containing galactitol are in the three dicotyledenous families.

Unlike the major hexitols, mannitol, sorbitol, and galactitol, which are normally present in their organisms independently of external factors, tetritols and pentitols quite often vary in their occurrence.

Tetritols: L-threitol does not appear to occur naturally, D-threitol has been reported from only a few fungi while erythritol is frequent in fungi, mainly the Ustilaginales and Agaricales, where it often seems to function in parallel with mannitol as another carbohydrate storage product. A number of unicellular and filamentous green algae contain erythritol. In the higher plants, erythritol is found in a small number of mono and dicotyledonae.

All four pentitols occur naturally, most notably in the fungi, though data are scattered.

Ribitol is the major pentitol in plants. Several of the Chlorophyceae produce it as their main photosynthetic product. Yeasts and some other fungi produce it in culture. It has not been reported for the Bryophytes and the Pteridophytes, but occurs in some dicotyledon species.

Arabitol is a comon companion of mannitol in the various basidiomycetes, ascomycetes and yeasts. Both D- and L- anomers are thought to be present. It hasn't been recorded for any algae.

Xylitol is the less abundant of the pentitols. It is an intermediate in the general pathway for metabolism of myo-inisitol in animals, but not in plants. It has not been reported from the algae. Some yeasts can utilize D-xylose, apparently by way of xylitol.

[128, 192]

The only octitol and three of the six heptitols known to occur naturally have been each reported from only a single source. The remaining three heptitols are related to one another and may tend to occur together. Of these, volemitol has been found in basidiomycetes and yeasts, one brown alga, several families of Marchantiophyta and higher plants. Other polyols found in plants are simple derivatives of the straight-chain polyols: styracitol (1,5-anhydro-D-mannitol), polygalitol (1,5-anhydro-D-glucitol), 2-C-methyl-erythritol and siphulitol. All are very restricted in distribution. [128]

The metabolism of polyols is closely tied in with sugar metabolism. In general, where a particular polyol occur, its related ketose will occur as well. Polyols may be produced both photosythetically or by metabolisation of primary sugars as substrates (phloem translocated carbohydrate). [128, 192]

Photosynthetic production: In the photosynthesis of polyols, the polyol frequently behaves as if it layed in the mainstream of carbohydrate synthesis and not like a slowly cycling secondary metabolite. The photosynthetic production of hexitol is a variant of conventional C_3 photosynthesis where the pathway up to at least fructose-6-phosphate and glucose-6-phosphate is unmodified. The hexitol being formed either by reduction of hexose phosphate or the hexose itself.

Metabolisation of primary sugars: When free glucose, fructose and sucrose are supplied as substrate to polyol containing tissues (e.g. leaves), fungi or lichens, they are rapidly metabolised to polyols. There is no evidence whether this occurs via the hexose phosphates or by direct reduction of the sugars. When, instead of sugar, the polyol itself is supplied, it tends to be accumulated in that form rather than metabolised, suggesting that the transformation of polyols into sugars does not occur readily.

Several roles for polyols have been proposed:

Sugar interconversion: sorbitol is important for the glucose-fructose interconversion in mamals. Because the three sugars often coexist in plants, a similar role is possible.

Redox agents: either acting as ”stored reducing power” in the tissue, or arising as end-products in the external medium when microorganisms use sugars from the medium as biological oxidants.

Osmoregulation: in many plants, polyol contents correlate well with the osmotic stress caused by the environment–dissecation, high salinity or high sugar concentration. Being readily sythesised and readily removed (by respiration or by sythesis into starch), or being compatible, even in high concentrations, with enzymes and other proteins, have been pointed as the main reasons why polyols have evolved as osmotic protective agents. They may also be more than simple inert solutes: they can possibly mimic the role of water, due to their highly hydroxylated nature, in the biopolymers of the cell cytoplasm maintaining a functional hydration of the enzymes and membranes; a protein "hydrated" with polyol may have its tolerance to high salt concentrations increased.

Cryoprotection: two possible roles are lowering the freezing point of the tissue and protecting the enzyme system if freezing takes place.

Transport and storage: transport of polyols takes place either between two symbiotic partners or within a plant itself. Mannitol acts mainly as a short-term storage compound, while arabitol behaves as a long-term storage compound.

[128, 192, 193]

Besides the roles described above, mannitol may also have a role in the plant protection against pathogens or act as activated oxygen species, thereby preventing peroxidation of lipids and resulting in cell damage. [192]

Polyols have been identified in the aerosol from various environments (e.g. [125, 190, 189, 177, 134]). Of all the polyols reported, arabitol and mannitol are generally the most abundant.

Table 3.6: Concentrations of polyols reported in the bibliography, in ng m^{-3}.

Compound	*Sources*	*Reported concentrations*
Sorbitol (dulcitol)	Bacteria [131] Lichens [132] Soil biota [17]	0.4-1.9/0.2-2.1/0.7-1.4 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) 3-26 (TSP, Sapporo, Japan [17, 189]) 2-10.4 ($PM_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 4-9 (TSP, Gosan, Korea, April-May 2001 [189]) 1.4-7.8 (TSP, Chichi-jima, China, April-May 2001 [189]) 1 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 0.0-1.7/0.3-2.6 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Xylitol	Fruits, berries, hardwood [194] Soil biota [17]	0.9-21.4 ($PM_{2.5}$, Hong-Kong [186]) 2.4-103.1 (Bulk aerosol, woods in Germany [194]) 2-22 (TSP, Sapporo, Japan [17, 189]) 1.5-9.6 ($PM_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 3-22 (TSP, Gosan, Korea, April-May 2001[189]) 1.5-8.1 (TSP, Chichi-jima, China, April-May 2001[189]) 1 ($PM_{2.5}$, Pacific and offshore East Asia, April-May 2001[189])
Mannitol	Fungi [129] Lichens [132] Yeasts and other small fungal spores /fungal fragments [185, 56] Soil biota [17]	1.1-19/<4.2 (PM_{10}/$PM_{2.5}$ Oslo, urban background, fall [134]) 9.0-30/0.81-4.3 (PM_{10}/$PM_{2.5}$ Oslo, curbside, fall [134]) 0.86-14/2.1-4.6 (PM_{10}/$PM_{2.5}$ Elverum, suburban, winter [134]) 12-24/1-2.9 (PM_{10}/$PM_{2.5}$ Elverum, suburban, summer [134]) <10/<0.87 (PM_{10}/$PM_{2.5}$ Birkenes, rural [134]) 3.8-52.3/3.8-46.8/11.2-31.5 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) <16.6 ($PM_{2.5}$, Hong-Kong [186]) 0.9-10.2 (PM_1, Howland experimental forest [127]) 11.2 (day)/<72 (night) (TSP, Amazonia [195]) 1.28-29 (day)/0.62-12 (night) ($PM_{2.5}$; summer, K-puszta [56]) 1.94 (summer)/0.69 (fall) (PM_1; Hyytiälä, Finland [55])

Compound	*Sources*	*Reported concentrations*
		7-20 (PM_{10}, Tel-Aviv, winter [187]) 9.58-24.38/23.69-101.79 ($PM_{2.5}$/$PM_{>2.5}$, Amazonia, July 2001 [185]) 1.6-23 (PM_{10}, Melpitz, Germany [190]) <0.5-88 (PM_{10}, Hyytiälä, Finland [190]) 620-2150 (TSP, savannah fire [85]) 7.8-70/31-220 (PM_{10}, Gent, winter/summer [126]) 9.9-50.1/4.7-55.9 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Arabitol	Fungi [129] Yeasts and other small fungal spores /fungal fragments [185, 56]	2-11/<2.6 (PM_{10}/$PM_{2.5}$ Oslo, urban background, fall [134]) 7.8-24/1-3.2 (PM_{10}/$PM_{2.5}$ Oslo, curbside, fall [134]) 1.5-8.4/1.2-5.9 (PM_{10}/$PM_{2.5}$ Elverum, suburban, winter [134]) 17-24/1.1-3 (PM_{10}/$PM_{2.5}$ Elverum, suburban, summer [134]) 0.48-19/<0.89 (PM_{10}/$PM_{2.5}$ Birkenes, rural [134]) <57.4/4.5-24.4/5.4-13.6 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) 0.7-6.6 (PM_{1}, Howland experimental forest [127]) 1.29-25 (day)/0.69-11 (night) ($PM_{2.5}$, summer, K-puszta [56]) 1.34 (summer)/0.79 (fall) (PM_{1}, Hyytiälä, Finland [55]) 5-45 (PM_{10}, Tel-Aviv, winter [187]) 3.8 (TSP, Chichi-jima, China, April-May 2001 [189]) 7.08-25.65/16.07-93.44 ($PM_{2.5}$/$PM_{>2.5}$, Amazonia, July 2001 [185]) 4.2-35 (PM_{10}, Melpitz, Germany [190]) 1.4-241 (PM_{10}, Hyytiälä, Finland [190]) 6.3-59/45-260 (PM_{10}, Gent, winter/summer [126]) 9.2 -32.2/6.3-38.6 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Erythritol	Lichens [132] Soil biota [17]	18.5-155/3.1-15.3/0.5-3.3 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) 1.0-28.2 ($PM_{2.5}$, Hong-Kong [186]) 0.4-0.87/1.13-2.46 ($PM_{2.5}$/$PM_{>2.5}$, Amazonia, July 2001 [185]) 0.8-3.7 (PM_{10}, Melpitz, Germany [190]) <0.03-1.5 (PM_{10}, Hyytiälä, Finland [190]) 2.3-39.1/2.5-27.7 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Inositol	Soil biota [17]	<9.3/- (PM_{10}/$PM_{2.5}$ Oslo, urban background, fall [134]) <2.8/0.82-1.4 (PM_{10}/$PM_{2.5}$ Oslo, curbside, fall [134])

Compound	*Sources*	*Reported concentrations*
		1.5-5.1/2-3.2 ($PM_{10}/PM_{2.5}$ Elverum, suburban, winter [134])
		1.8-3.8/0.6-0.9 ($PM_{10}/PM_{2.5}$ Elverum, suburban, summer [134])
		<1.8/<1 ($PM_{10}/PM_{2.5}$ Birkenes, rural [134])
		<2.1/<0.7/0.1-0.2 ($PM_{2.5}$, Amazonia dry/transition/wet period [177])
		3-104 (TSP, Sapporo, Japan [17, 189])
		8-82 (TSP, Gosan, Korea, April-May 2001 [189])
		0.16-0.48/2.59-3.29 ($PM_{2.5}/PM_{>2.5}$, Amazonia, July 2001 [185])
		1.0-6.9 (PM_{10}, Melpitz, Germany [190])
		<0.07-3.5 (PM_{10}, Hyytiälä, Finland [190])
		1.3-17.2/3.0-97 (PM_{10}, Gent, winter/summer [126])
		0.5-9.3/0.2-3.5 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Glycerol	Soil biota [17]	6.6-35.8/1.3-5.6/0.8-2.4 ($PM_{2.5}$, Amazonia dry/transition/wet period [177])
		0.7-61.2 ($PM_{2.5}$, Hong-Kong [186])
		3-24 (TSP, Sapporo, Japan [17])
		22-52 ($PM_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188])
		4-50 (TSP, Gosan, Korea, April-May 2001 [189])
		2.5-24 (TSP, Sapporo, Japan, April-May 2001 [189])
		5.3-7.4 (TSP, Chichi-jima, China, April-May 2001 [189])
		6-32 ($PM_{2.5}$, Pacific and offshore East Asia, April-May 2001 [189])
		<0.06-0.41/1.14-4 ($PM_{2.5}/PM_{>2.5}$, Amazonia, July 2001 [185])
		0.5-21/1.1-10.3 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Threitol		1.4-24.0/0.3-2.7/0.1-0.4 ($PM_{2.5}$, Amazonia dry/transition/wet period [177])
		0.2-6.2/0.1-4.5 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])

3.5.7 Anhydrosugars

The varying temperature and aeration conditions during burning determine the molecular alteration and transformation of the organic compounds emitted from biomass fuel [141].

Wood, and cellulosic materials, do not burn directly. The general thermal reactions of cellulose decomposition on heating or exposure to an ignition source can be divided into primary and secondary reactions, according whether they directly affect the cellulosic substrate or one of the intermediate reaction products. [196, 139]

The main primary reactions are temperature dependent, at a temperature below 300°, the dominant reactions are:

- reduction of the degree of polymerisation by bound scission,
- elimination of water (dehydration),
- formation of free radicals,
- formation of carbonyl, carboxyl and hydroperoxyde groups,
- evolution of CO and CO_2 and
- finally, production of a highly reactive carbonaceous char.

[196, 139]

This first pathway consists of three steps: initiation of pyrolysis, propagation and product formation. The initiation period apparently involves the formation of free radicals facilitated by the presence of oxygen or inorganic impurities. Subsequent reactions of the free radicals could lead to bond scission, oxidation and decomposition of the molecule to produce char, water, CO and CO_2. [139]

At a temperature over 300°, other reactions take over:

- cleavage of molecules by transglycosylation,
- fission,
- disproportionation and
- finally, production of a mixture of tarry anhydrosugars (levoglucosan is the main component) and lower molecular weight volatile products.

[196, 139]

In this pathway, depolymerisation by transglycosylation takes place when the molecule has gained sufficient flexibility (activation) and produces levoglucosan (1,6-anhydro-β-D-glucopyranose), small portions of its furanose isomer (1,6-anhydro-β-D-glucofuranose) and 1,4:3,6-dianhydro-α-D-glucopyranose as well as randomly linked oligosaccharides. The intermolecular and intramolecular transglycosylations are accompanied by dehydration, followed by fission and disproportionation reactions in the gas phase, and further decomposition and condensation in the solid phase to produce a mixture of gases and volatile products and a ”stable” carbonaceous char. [139]

Products of the primary reactions, if not rapidly removed from the heated environment, may further react and decompose to provide a series of secondary compounds of low molecular weight. Tar-forming reactions accelerate rapidly and overshadow the production of

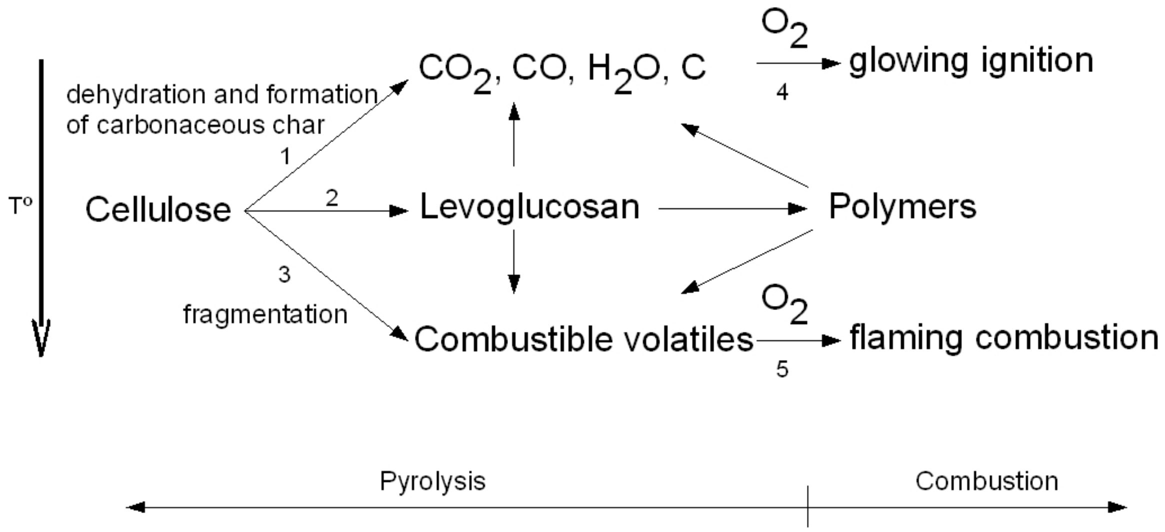


Figure 3.2: The general reactions involved in pyrolysis and combustion of cellulose based on [196, 139]

char and gases. In the tar, levoglucosan is the main compound, with 1,6-anhydro-β-D-glucofuranose and their transglycosylation products. In addition, dehydration products of the glucose units (3-deoxy-D-erythrohexosulose, 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde (furfural), other furan derivatives, levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glycerohex-3-enopyranos-2-ulose), 1,5-anhydro-4-deoxy-D-hex-1-ene-3-ulose, and other pyran derivatives) are found as minor compounds. These dehydration products are important as intermediate compounds in the char formation. On further heating, fission (fragmentation) of the sugar units at higher temperatures accompanied by dehydration, disproportionation, decarboxylation and decarbonylation provides a variety of carbonyl, carboxyl and olefinic compounds, as well as water, CO, CO_2 and char. [139]

The combustible volatile products react with oxygen in the gas phase and give rise to flaming ignition (reaction 5 of Figure 3.2), while oxidation of the char residue in the solid phase leads to glowing or smouldering combustion (reaction 4 of Figure 3.2). [196]

The chemical composition, rate of formation and heat of combustion of the pyrolysis products are affected by the variations in composition of the substrate, the time and temperature profile, and the presence of inorganic additives or catalysts. [139] In the same way that levoglucosan derives from the D-glucose units of the biopolymer (either cellulose or hemicelluloses), its stereoisomers, mannosan and galactosan derive from the mannose and galactose units of hemicelluloses (see 3.2.5). [85, 197]

The major saccharide species identified in the atmospheric aerosol so far is levoglucosan. Anhydrosugars such as levoglucosan, mannosan, galactosan and 1,6-anhydroglucofuranose are formed in pyrolysis processes of cellulose and hemicellulose containing materials (wood, straw, paper) (see Figure 3.3) [196].

Levoglucosan was found to be the most abundant of the identified organic compounds in wood burning emission $PM_{2.5}$, accounting for 3-30 % of the fine particle organic compound mass emitted (100±40 mg/gOC) [198, 87, 88]. These very high emission rates make levoglu-

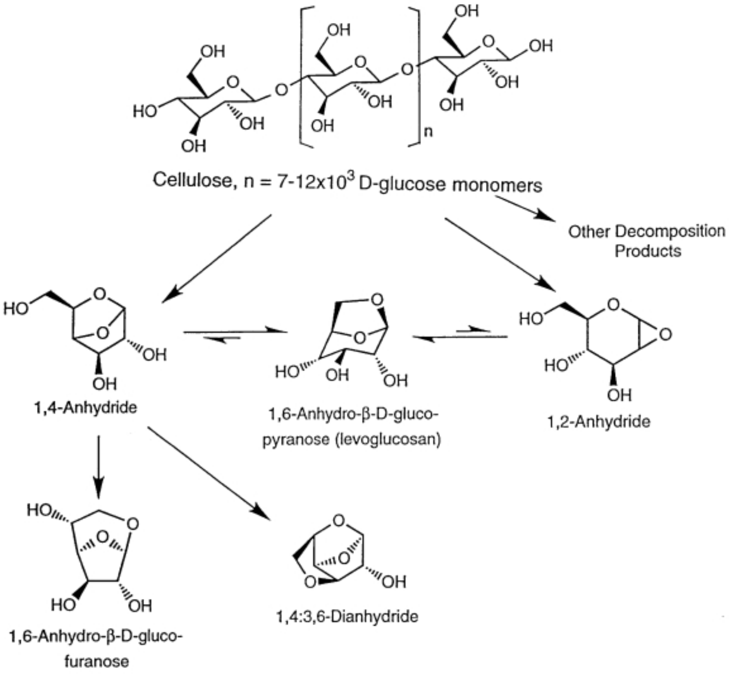


Figure 3.3: The products of the cellulose pyrolysis (T 300°C) [124]

cosan a good candidate for use as a molecular marker for biomass burning, which can be an important source of particulate matter in the atmosphere in certain communities during the cold season [199, 136, 200, 137].

Another required property is the stability in the atmosphere. Levoglucosan shows no decay over 8 hours exposure to ambient conditions and sunlight (Locker, 1988, as cited by [72]). It has also been shown that, with respect to the reaction mechanisms of acid catalysed hydrolysis possible in the aqueous chemistry of atmospheric droplets, levoglucosan is stable up to 10 days [201]. Another hint that levoglucosan is stable for long periods in the atmosphere is that it has been detected over the ocean, where the biomass combustion sources are remote [89, 90]. However, recent research has pointed some issues about levoglucosan stability under certain conditions. Holmes and Petrucci [170] and [171] observed oligomerisation of levoglucosan, used in aqueous solutions as a proxy for biomass burning aerosol, in the presence of OH radicals for both Fenton and acid-catalysed pathways. The products of these reactions are pointed as possible intermediates, which incorporate into new compounds through reactions with other species within aerosols (acid-catalysed, OH oxidation, photooxidation) to potentially form HULIS. Robinson *et al.* [202] studied the sensitivity of the source apportionment (SA) approach chemical mass balance (CMB) model to such variability. They found that the amount of ambient OC apportioned to biomass smoke varied by more than a factor of 2, depending on which source profiles are used in CMB. Thus, the use of different biomass smoke profiles to be used in CMB (e.g. hard and softwood, burning in a stove or open fire) is recommended by the authors.

An additional characteristic that makes levoglucosan a suitable tracer for wood smoke is its uniqueness to biomass combustion (e.g. [89]). Other tracers have been proposed for biomass burning: gas phase methyl chloride [203]; potassium (e.g. [204, 205] whose occurrence in the aerosol is also notably due to other sources, such as meat cooking [206], cigarette smoke [207] and refuse incineration [100, 99, 101] and whose emission rate is highly variable and has to be empirically determined for each situation [205]); methoxyphenols (whose concentrations were reported to be lower as expected, thus indicating a poor atmospheric resistance) [89, 138, 208, 209]; dehydroabietic acid (a resin acid derivative) [90], retene [5], various organic acids [208], and black carbon measured at different wavelengths [81] All of these proposed tracers, as well as levoglucosan, show a considerable variability in their emission factors. This variability is due to the fuel composition and structure, fire intensity aeration, ambient an vascular moisture, smouldering versus flaming phase and the surroundings. The variability of levoglucosan emission does not correlate with that of $PM_{2.5}$, and may thus affect source apportionment estimates [208]. Other carbohydrate polymers (e.g. starch) also produce levoglucosan upon thermal alteration, but the temperatures attained in cooking, baking or toasting are not sufficient to pyrolize carbohydrates to levoglucosan.

The other anhydrosaccharides, mannosan, galactosan and 1,6-anhydroglucofuranose, all levoglucosan isomers and also exclusive to biomass burning, are not emitted in such high quantities as levoglucosan. Recently, Schmidl *et al.* [109] have suggested the potential of those substances for differentiating the contribution of hard and softwoods to the PM_{10} load. The ratio between levoglucosan and mannosan in the particulate emissions from the burning of woods commonly used in Austria (softwoods: spruce and larch, hardwoods: oak and beech) was found to be high for hardwoods (typically 14-15) and lower for softwoods (3.6-3.9). Briquettes from softwoods had a ratio of 2.5. [109]

Levoglucosan has been studied not only in wood burning samples but also in the ambient air. Numerous studies have detected its occurrence, in biomass smoke highly impacted plumes as well as in remote, rural, suburban and urban air samples (e.g. [201, 82, 89, 138, 90, 210, 83, 85, 187, 211, 212, 213, 214, 215].

Table 3.7: Concentrations of anhydrosugars reported in the bibliography, in ng m^{-3}.

Compound	*Sources*	*Reported concentrations*
Levo-glucosan	Wood burning, e.g. [124]	0.26/0.032 ($PM_{2.5}$, impacted/non-impacted by biomass burning, Northern Europe [216]) 3.4-458 ($PM_{2.5}$, Hong-Kong, various sites, year-long [217]) 284-7903/89.9-893/9.6-160 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) 1.06-26.9/6.71-59.8 ($PM_{2.5}$, urban and mixed/rural, daytime, Summer, Lower Fraser Valley [214]) 7.63-34.5/1.07-77.9 ($PM_{2.5}$, urban/mixed and rural, night-time, Summer, Lower Fraser Valley [214]) 860-6091/<171 ($PM_{2.5}$, smoke/post smoke impacted ambient air, Montana [215]) 3930-16000/<470 (PM_{10}, winter/summer Australia [218]) 1.0-55.1 ($PM_{>1}$, Howland experimental forest [127]) 0.12-9.8%of WSOC/0.03-4.9%of TOC (PM_{10}, New Zealand [219]) 4.1-269.8 ($PM_{2.5}$, Hong-Kong [186]) 10.0 (summer)/<29.1 (fall) (PM_1, Hyytiälä, Finland [55]) 3.5-27 (day)/<6.2-95 (night) ($PM_{2.5}$, summer, K-puszta [56]) 120-34000 (TSP, haze episodes, Malaysia [213]) 1.3-6 ($PM_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 8-74 (TSP, Gosan, Korea, April-May 2001 [189]) 6.4-56 (TSP, Sapporo, Japan, April-May 2001 [189]) 0.5-1.2 (TSP, Chichi-jima, China, April-May 2001 [189]) 0.2-40 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 500-74190 (TSP, savanna fire [85]: primarily smouldering fire, not detected over primarily flaming fires) 7.73-32.91/<0.04-4.79 ($PM_{2.5}/PM_{<2.5}$, Amazonia, July 2001 [185]) 1182-6900/39.9-2660 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125]) 446-4106/0.4-13.2 ($PM_{2.5}$, Amazonia, dry/wet season [220]) 121-1133/4.1-34.6 ($PM_{2.5}$ Gent, Belgium, winter/summer [220]) 96-1900/9.1-27 (PM_{10}, Gent, winter/summer [126])

Compound	*Sources*	*Reported concentrations*
		166-358 ($PM_{2.5}$, Southeastern U.S., various sites [83]) 106/2390/2980 ($PM_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138]) 0.0008-0.15 (TSP marine aerosol [89])
Mannosan	Wood burning, e.g. [124]	23.7-543/3.3-69.6/0.4-7.9 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) 333-1086 ($PM_{2.5}$ smoke impacted ambient air, Montana [215]) <10.4 ($PM_{>1}$, Howland experimental forest [127]) 0.2-1.1 ($PM_{2.5}$, flights over the Korea Straight, Yellow Sea, East China Sea, Sea of Japan, April 2001 [188]) 0.2-4.2 (TSP, Gosan, Korea, April-May 2001 [189]) 0.2-15 (TSP, Sapporo, Japan, April-May 2001 [189]) 0.2-2.8 (TSP, Pacific and offshore East Asia, April-May 2001 [189]) 0.08-0.84/<0.05-0.10 ($PM_{2.5}$/$PM_{>2.5}$, Amazonia, July 2001 [185]) 21-259/<2.5 ($PM_{2.5}$, Amazonia, dry/wet season [220]) 17.3-153/0.70-7.9 ($PM_{2.5}$ Gent, Belgium, winter/summer [220]) 10-290/2.0-3.9 (PM_{10}, Gent, winter/summer [126]) 6.0-371/1.7-127 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125]) 7/171/322 ($PM_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138])
Galactosan	Wood burning, e.g. [124]	7.7-261/1.4-32.2/<2.4 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) <491 ($PM_{2.5}$ smoke impacted ambient air, Montana [215]) <2.6 ($PM_{>1}$, Howland experimental forest [127]) 0.4-3.8 (TSP, Gosan, Korea, April-May 2001 [189]) 0.6-2.4 (TSP, Sapporo, Japan, April-May 2001 [189]) <0.04-0.37/<0.04-0.12 ($PM_{2.5}$/$PM_{>2.5}$, Amazonia, July 2001 [185]) 7.6-61.5/<1.19 ($PM_{2.5}$, Amazonia, dry/wet season [220]) 4.4-44.2/<1.31 ($PM_{2.5}$ Gent, Belgium, winter/summer [220]) 4.9-115/0.67-1.17 (PM_{10}, Gent, winter/summer [126]) 2.3-148/1.6-44.6 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125]) 4.1/96/144 ($PM_{2.5}$, urban/urban/background, winter, San Joaquin Valley, US [138])
1,6-anhydro-gluco-	Wood burning [17]	16.3-435/6.8-41.9/1.1-4.9 ($PM_{2.5}$, Amazonia dry/transition/wet period [177]) 0.5-195 (TSP, Santiago, Chile [17]) 135-4005 (TSP, Kuala Lumpur, Malaysia [17])

Compound	*Sources*	*Reported concentrations*
furanose		0.3-3 (TSP, Gosan, Korea, April-May 2001 [189]) 0.3-2 (TSP, Sapporo, Japan, April-May 2001 [189]) 5-248/1.9-115 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Xylosan	Wood burning [125]	2.5-155/0.4-27.5 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
Arabinosan	Wood burning [125]	0.1-23.5/0.0-5.4 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])
N-acetyl-2-amino-glucosan	Wood burning [125]	0.4-38.7/0.2-15.0 (PM_{10}, Amazonia, Pasture/Forest site, burning and dry-to-wet season [125])

3.6 Effects of the atmospheric aerosol

3.6.1 Health risks

Particulate air pollution can affect the health of the entire population. Moreover, within the general population, there are subgroups that have increased susceptibility to the adverse effects of poor air quality. Such subgroups include those identified by age (children or the elderly), socioeconomic status, and the presence of diseases, such as asthma and chronic obstructive pulmonary or cardiopulmonary diseases. Those with specific genetic features might also be at increased risk. [221, 222, 223]

Research on the health effects of PM exposure requires both observational studies of real-world exposures among free-living subjects (epidemiology) and experimental studies of controlled exposures of well-characterised subjects (toxicology and clinical research). While most of the PM-related health effects were first demonstrated by epidemiologic studies, recent experimental studies have both complemented and extended these studies to new areas of research [224]. That reasearch has shown effects mainly for the respiratory and cardiovascular systems, but PM also affects the auditive system [225].

Epidemiological results consistently show a relationship between ambient particulate levels and health issues such as increased morbidity and mortality [226, 227, 228, 229, 230]. Though, the actual effects of the atmospheric aerosols on human health are still to be fully understood and quantified [117, 222, 229], and questions about the influence of confounders (other co-pollutants, weather, social and demographic factors) are still to be answered [229].

The health effects of both $PM_{2.5-10}$ and $PM_{2.5}$ are, to some extent, distinct, but both fine and coarse aerosol are a concern [231, 232, 233, 234, 235, 236]. However, it is thought that naturally derived particulate matter is more benign than particulate matter of anthropogenic origin, posing a low risk to health for the general public. This has been verified for blown dust aerosol [237], though some studies have proved otherwise [232, 238, 239, 240], owing probably to the higher content of aeroallergens in dust PM [133].

The effects of the exposure to ambient particulate matter can be divided into acute and chronic (which are greater than simply the accumulation of acute effects) [224], reaching the respiratory (upper and lower) and cardiovascular systems. Long-term exposure to PM can utterly lead to reduction in life expectancy, owing mainly to cardiopulmonary mortality and probably to lung cancer. [1] The biochemical mechanisms and molecular processes by which airborne aerosol affects the human lung-heart axis are still to be fully resolved, as are the parametrics determinant to those mechanisms. While chronic effects are most probably related to a multi-stage process [224], acute response of the organism are mainly related to:

- direct mechanisms [246],
- cytotoxic, mutagenic and genotoxic outcomes, triggered by an immunological (inflammation), neural or direct response [247, 248, 249], involving inflammation and oxidative stress [249],
- infection [244],
- an allergic response to aeroallergens [133].

Table 3.8: Acute and chronic health effects associated with exposure to particulate matter [241, 242, 221, 243, 244, 245, 1, 238].

Acute
lung inflammatory reactions
adverse effects on the cardiovascular system
hypertension
nasal inflammation
pneumonia
exacerbation of respiratory tract illnesses: asthma and rhinitis, hospital admission for chronic obstructive pulmonary disease (bronchitis, ...)
Chronic
reduction in lung function in children and adults
impairment of normal lung growth
coronary heart disease for people with chronic respiratory disease
development of allergic airways disorder (asthma and rhinitis)
increase in lower respiratory symptoms
increase in chronic obstructive pulmonary disease (bronchitis, . . .)
cancer
reduced birth weight

PM health effects mechanisms

The particle encounters, in the respiratory system, both alveolar macrophages (AM) and epithelial cells (EpC), creating, at that level, an oxidative stress due to the induced production of reactive oxygen species (ROS). [246, 224]

The complex PM mixtures of variable composition are likely to have more than one intracellular target (and therefore more than one mechanism of ROS production and oxidative stress). The in vitro experiments suggest a variety of possible mechanisms, including direct effects of particle components and indirect effects due to pro-inflammatory mediators released from particle stimulated macrophages nearby, or to neural stimulation involving the response of the autonomic nervous system to pulmonary irritants after particle deposition in the lungs. [246, 224, 249]

ROS may be produced indirectly due to pro-inflammatory mediators: upon contact with the cells, PM cause an inflammatory reaction leading to the production of ROS and the release of cytokines. Cytokines act as a network between cells, serving the purpose of communication between cells, and funtion as a signaler of the foreign body so that EpC can produce ROS just by the input of cytokines from AM or other EpC cells. Direct generation of ROS (without immunological nor neural response) are due to compounds such as transition metals or organics, bacterial endotoxin and free radicals at PM surface that enter the cell after diluted and act on the intracellular sources of ROS.

ROS have, at the intracellular level, cytotoxic effects such as apoptosis and necrosis, they are also responsible for oxidative DNA damage resulting in mutagenic and genotoxic effects. [224, 250, 251, 246, 249, 252, 253]

Cytokines, the immunological response to inflammation, when released in the circulation can, besides triggering the formation of ROS, be linked to cardiac arrhythmias and thrombosis as well as artherosclerosis. This effect is however objected due to the short half-lives of cytokines in the blood [224]. In a same way, it has been reported that lung oxidants (ROS) may be involved in heart outcomes [246].

ROS may be further released by a neural mechanism: after particle deposition, the C-fibers in the lung and other receptors detect the initial irritation of airways and alveoli by PM and the signal is transmitted by the afferent arm of the Vagus nerve to the respiratory centers. This signal stimulates the sympathetic nervous system and inhibits the parasympathetic nervous system. A decrease in the efferent arm of the Vagus nerve is associated with a decrease in heart rate variability, especially high frequency variability, and an increase in heart rate, associated with the incidence of adverse coronary events and death. [224]

PM induce the expression of receptor for viruses and bacteria at invasion sites, increasing their density in the lungs [244], thus leading to an infection risk that may outcome in infections such as pneumonia. Fungal spores fragments, pollen grains and antigens are present in PM [48, 115, 38] and may therefore potenciate allergic reactions.

Mutagenic and genotoxic effects may also originate in the single components of PM (without the intermediate action of ROS) and their effects on lipids and proteins. [254].

Direct mechanisms of PM upon distant organs happen when the particle goes beyond the respiratory system and enters the blood circulation. The blood and plasma properties are then altered posing a possible threat to the heart.

PM parameters involved in health effects mechanisms

Studies have shown that particles with different origins induce different responses in the respiratory tract cells [247, 255]. Various PM parameters, chemical, physical and biological, have been proposed as the pathogenic agents that start the adverse health mechanisms. Linking the exposure-response coefficients from epidemiological studies (little spatial variation) with the aerosol composition (major geographic variation) provided little support for the idea that any single major or trace component of the PM is responsible for the adverse effects [256]. Yet, at the molecular level, many in vivo and in vitro studies have investigated the potential role of aerosol chemistry in its health effect [257, 258, 259]. Potential key parameters are organic funtional groups [260, 250], the strong acid fraction [261], benzene [262], free radicals at the PM surface [246] and transition and soluble ionisable metals (iron, nickel, vanadium, copper) [222, 246, 263, 255]. The acidity delivered by the aerosol (mainly the sulphate aerosol) has been proposed as the cause of adverse health effects. [224] Reactive metal ions are able to produce an oxidative lung injury due to the formation of reactive oxygen and nitrogen species. [224] In the case of organic compounds, including benzene and PAHs, because of which fossil fuel and biomass burning have caused severe concerns [72], Karlsson *et al.* [247] found that the genotoxicity of PM was significantly reduced after extraction with dichloromethane, dimethyl sulfoxide and water, but not with acetone and hexane, so that the genotoxicity of PM was caused both by adduct-forming polyaromatic compounds and oxidizing substances as well as the insoluble particle-core. Confirming this finding, Poma *et al.* [260], in an in vitro study on cultured macrophages, found that, in a same mass dosis, fine black carbon particles were consistently less genotoxic than the fine atmospheric particles, suggesting that the contaminants adsorbed on them (i.e. carbon-containing organic compounds in addition to metal oxides and metal salts) are involved in genotoxicity. For such genotoxic mechanisms, it has been shown that airborne particulate mixtures need to be metabolically converted before exerting their genotoxic potential [264].

The issue of the PM physical or biological parameters is more unclear due to the scarcity of data. [256] However, it is known that ultrafine particles have a higher inflammation potential than larger PM. They are also more susceptible to penetrate into the blood, deposit in cardiac tissue, and cause cardiac disorders, such as arrhythmia, and death. [224] Also, bacterial endotoxin has also been proposed as responsible for PM toxic inflammatory effects, but only in alveolar macrophage and not in epithelial cells [265, 224]. Aeroallergens present in the aerosol may trigger allergic reactions when deposited in the respiratory system.

3.6.2 Effects on the radiative balance: direct effect on climate and effect on visibility

Aerosol particles directly affect the climate by two mechanisms: they can scatter and absorb solar (short wavelength) radiation, or they can scatter, absorb and emit thermal radiation (long wavelength). [267]

scattering of solar radiation increases the albedo of the atmosphere, thus reducing the amount of solar radiation reaching the surface (negative direct radiative forcing)

absorption of solar radiation may exert a negative top-of-the-atmosphere (TOA) direct RF over dark surfaces such as dark forests or oceans, or a positive TOA effect if the aerosol is over bright surfaces such as desert, snow, ice and clouds

absorption of terrestrial radiation is thought to be small because the aerosol optical depth decreases at longer wavelengths and because aerosols are mainly present in the lower troposphere, where the surface temperature approximatively equals that of the atmosphere (that is the temperature of the particles) which governs the emission of warm bodies

[268, 8, 269, 2]

The interactions between aerosols and solar radiation do not only affect the climate but also visibility. Radiation absorption by aerosols (and gases as well) is responsible for coloured atmospheres, while reduction in visibility is mainly due to light scattering. [6] Scattering of solar shortwave radiation is responsible for the reduction in visibility, with the difference that the effect on climate is due to radiation scattered upwards, while scattering in all directions affects visibility. [8]

In the absence of particles, the visual range of a Rayleigh atmosphere would be over 200 km, due to scattering by air molecules. In fact, under those conditions, the visibility of most distant objects near the surface would be limited by the curvature of the earth and the orography. The visual range in the boundary-layer atmosphere is reduced mainly by the presence of aerosol particles (dust, smoke, and haze) and hydrometeors. Hydrometeors are large droplets or crystals of water (5μm) and they occur as rain, fog, clouds, and snow. [270, 269, 14]

Key parameters in determining the RF are the aerosol optical properties (a function of wavelength and relative humidity) and the atmospheric loading and geographic distribution of the aerosol (a function of time). [2]

The aerosol characteristics affectig the aerosol direct interactions with solar and terrestrial radiation are:

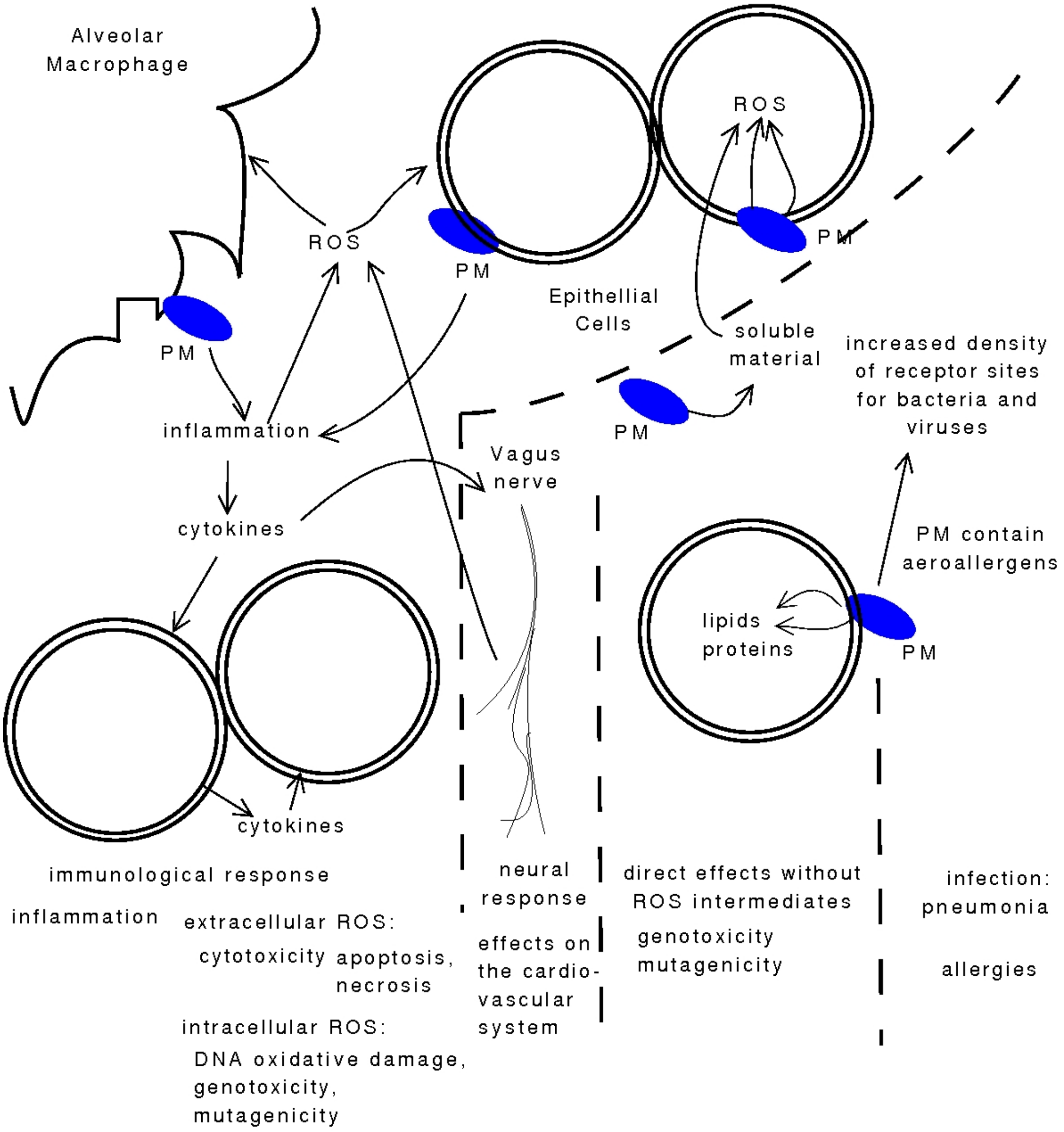


Figure 3.4: The mechanisms by which particulate matter affects health, based on [222, 260, 261, 224, 266]

aerosol size: smaller particles interact with shorter wavelength radiation, while large particles interact with longer wavelength radiation.

aerosol chemistry: sulphates, nitrates and organics are the species considered to contribute substantially to the aerosol hygroscopic growth (affects the backscattering); dark matter such as black carbon may increase the aerosol capability to absorb radiation.

aerosol abundance: the absorption of long wavelength radiation will only be substantial if, besides being large, the aerosol is abundant enough.

[268, 8, 271, 267]

3.6.3 Effects on the radiative balance: effects on the hydrological cycle and indirect effects on climate

Indirects effects of aerosols on the earth's radiative balance are linked with their ability to affect the number, density and size of cloud condensation nuclei (CCN) and ice nuclei (IN). This may change the amount, optical properties and the lifetime of clouds, and hence their reflexion and absorption.

Determining parameters for the indirect effect are the effectiveness of an aerosol particle to act as CCN (a function of size), its chemical composition, its mixing state and the ambient environment. [2]

Due to the large uncertainties inherent of the complexity of the processes and feedbacks involved it is unclear if aerosols indirect effect are negative or positive. [2]

Cloud albedo effect

The cloud albedo effect (also known as the first indirect effect or the Twomey effect) is a microphysically induced effect on the cloud droplet number concentration and hence the cloud droplet size, with the liquid water content held fixed. In this case, the hydrological cycle is not perturbed in a way that feedback mechanisms occur. [2]

In a cloud whose liquid water remains constant, the more but smaller cloud droplets are responsible for an increase in reflection of solar radiation (enhanced albedo). [267]

Cloud lifetime effect

The cloud lifetime effect (also known as the second indirect effect or the Albrecht effect) is a microphysically induced effect on the liquid water content, height and lifetime of clouds. This perturbs the hydrological cycle and feedback mechanisms occur. [2]

The activation of a larger number of aerosol particles limits the size to which drops can grow for an available cooling rate. The number of drops which grow large enough to initiate the collision-coallescence process is decreased. [15] Thus, more but smaller cloud droplets, in a cloud whose liquid water increases, reduce the precipitation efficiency, increasing the cloud lifetime and hence its reflectivity [267].

Effects on ice-clouds

The role of atmospheric ice formation in precipitation is not yet fully understood [2]. Nevertheless, it is known that [15]:

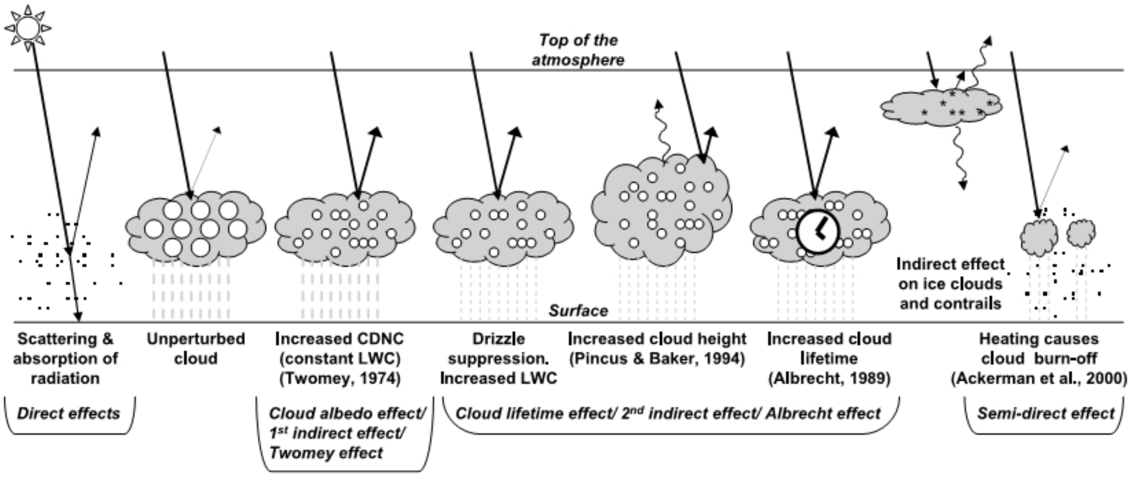


Figure 3.5: Direct and indirect effects by which particulate matters affects the earth-atmosphere radiative balance and hence the climate [2]

1. The size of ice hydrometeors, which tend to be much larger than liquid ones, lead to an increased precipitation and impact radiative balances.

2. For both upper and lower level clouds in the troposphere, the ice iniciation process is presumably dependent on aerosols, though the nucleation can proceed via different pathways and from a variety of nucleating chemical properties. In the heterogenous processes of ice formation, the chemistry and the concentration of the heterogenous nuclei (the aerosol) is of prime importance.

3. It is plausible that a significant fraction of ice nucleating aerosols are from an anthropogenic origin.

Because it perturbates the hydrological cycle, these effects involve feedback mechanisms [2].

Semi-direct effect

The semi-direct effect is the mechanism by which absorption of shortwave radiation by tropospheric aerosols leads to heating of the troposphere altering the relative humidity and the stability of the troposphere, thereby influencing cloud formation and lifetime. It modifies the hydrological cycle leading to the occurrence of feedback mechanisms. [2]

3.6.4 Effects on ecosystems

Atmospheric aerosols are major carriers in the biogeochemical cycle of sulphur, nitrogen, trace metals and crustal elements. They have the ability to fertilize land and the oceans, alter the acidity of water bodies, such as lakes and soils, and impact plant life by direct and indirect mechanisms. [270, 14]

There have been few studies of dust contribution to freshwater ecosystems. Primordially, dust brings nutrients and acidity-altering constituents to the rivers and lakes. These inputs have probably little expression unless the river is slow flowing or a series of waterholes (common situations in arid and semi-arid places). [16]

Apart from internal sources of nutrients (vertical mixing and recycling), the atmosphere, through the wet and dry deposition of aerosols, may constitute an important pathway for nutrients to the photic zone of the open sea where there is little riverine input. [272] In the remote, high-nutrient, low-chlorophyl oceans, phytoplankton, the basis of the trophic chain in the oceans, has its growth limited by soluble iron. Dusts are the main source of iron in the oceans, thus impacting on phytoplankton growth. [273, 274] This was confirmed by geological records. Also, a link to climate is possible: high dust periods being related to lower atmospheric CO_2 concentrations (due to the phytoplankton growth implying an increased photosynthesis) and lower temperatures. [16]

This input of nutrients and promotion of primary production may result in blooms, which disrupt the ecosystem. [272, 14, 16] Aerosol deposition may as well bring toxicity to various organisms within the marine ecosystems with the input of arsenic and antimony [275], lead [276], and polycyclic aromatic hydrocarbons [277], among others.

Turbulence is the key factor determining the dry deposition of particulates. Roughness, as wetness, of the surface can dramatically increase turbulence, and this at large and small scales. [278] Indirectly, particulates may reach the substrate from the plant leaf, either by runoff after rainfall or during leaf-fall. In this case, particle size is not so important, while particle chemistry will potentiate chemical changes in the substrate that will affect the vegetation. This is mainly observed for soils, and this in a large variety of habitats, but can also happen to bark or other substrates supporting epiphyitic communities. Impacting not only plants but also other organisms. [278]

As an example of the extreme importance of turbulence in the dry deposition of particles, at the large scale, forest canopy, by increasing the roughness of the surface, are more efficient at removing particles than baren land. At the small scale, plants having stomatas slightly elevated above the epidermal cell will cause local turbulence and increase dry deposition. [278]

Dust deposition plays a role in soil evolution, altering soil fertility. Dust may enrich surface soils and other substrates with a wide range of nutrients (P, K, Mg, Na, Ca, Fe, Cu, Mn and Mo). The saharan Harmattan dust is a strong nutrient contributor to the ecosystems of various kinds of forests such as in coastal Ghana, in Catalonia across the Mediterranean or in the Amazon, across the Atlantic [279, 16]. Besides the input of nutrients, dust deposition may as well alter soil acidity. This has been observed e.g. close to limestone quarries. [278] As consequence of the nature of the particulate matter contribution and its spatial and temporal pattern are indirect effects on plants which are supported by the substrates, such as alteration of community composition. [16, 278]

Plants play an active role in air pollutant removal [7], in a dry deposition process where soils and the build environment, and even the oceans, are also important. Wet deposition can also bring aerosols to soils and plants. (see 3.3)

Particulates do affect plants if they are deposited either on plant surface or on the soil, in three principal processes:

- Direct deposition onto leaf surface
- Blocking leaf stomata and/or uptake into leaf tissues

- Deposition onto substrates (e.g. soil) and indirect effects via changes in substrate chemistry

[278]

Particle size is the key factor determining whether a particle will or will not enter the stomata of the plant leaf. The size of the stomata is generally in the range from 8 to 10 μm in diameter. Given their size, particles can be either excluded, lodged into or pass through the stomata. Plants whose surface possess a cuticle (most plant leaves, though not bryophytes and lichens) won't suffer chemical damages from particulates retained on the surface. Thus, the chemistry of particles small enough to enter the stomata is of interest, with the exception of cement dust, which is so caustic that it dissolves the cuticular layer. Also, since most plant leaves have their stomata on the lower leaf surface, settling of particles will generally have small impact, while turbulance around and below the leaf is needed to lead to stomatal impacts. [278]

Vegetation has a wide range of responses to particulate pollution:

Physiological: direct physical action of the presence of particulates

Injury: active chemistry or toxic properties of particulates, mainly following entry into leaf tissue

Growth and reproduction: change in the fitness of the individual plants in natural communities, leading to a change in its composition or impacts on crop yields in managed systems

Indirect responses: changes indirect adverse effects of pests and pathogens and in bacterial and fungal communities, depending on the particulate and species properties

Changes to substrate chemistry: change in soil pH, input of nutrients

[278, 279]

3.6.5 Effects on the built environment

Aerosols, from anthropogenic pollution, but also marine salt, are a major issue on the weathering of various kinds of outdoor and indoor stones, forming damaged layers on their surface, altering their aspect and finally leading to surface erosion, discoloration, gypsum crust development, splitting and cracking. Bindings (e.g. mortar) also suffer decay by similar processes. [280, 281, 282, 283, 284, 285] Particular attention has been devoted to the study of carbonate stones with low porosity (i.e. marble and limestone) in view of their use in the construction of many famous monuments. In these cases, black crusts forming in areas sheltered from intensive rainwater run-off are indicative of visual damage. Such damage layers are the accumulation areas where the wet and dry deposition of atmospheric gas and aerosol occurs on the material surface along with the precipitation of products of reactions between the stone materials and the gas and aerosol. [281] The chemical processes provoking stone degradation are salt or water crystallisations and acid-base chemical dissolution reactions. [283]

The presence of salts, either deposited from solution (wet deposition) or when they absorb water (dry deposition), in combination with movement and evaporation of water forms solutions of soluble salts in the stone. The mechanical stress on the porous structure leads to disaggregation and crumbling. [284, 31]

Table 3.9: The responses of vegetation to particulate matter.

Physiological	blocking of stomata alters transpiration rates raised leaf temperature, affecting metabolic functions shading resulting in reduced photosynthesis cell structural damage or toxicity leads to metabolic interferences
Injury	cell plasmolosys cell destruction bark peeling dieback of branches and death of trees leaf lesions
Growth and reproduction	reduced vegetative and reproductive growth increased growth for young trees, reduced grows for older ones
Indirect responses	adverse effects of pests and pathogens increase or decrease of bacterial communities increase or decrease of fungal communities
Substrate chemistry	changes in soil pH leads to changes in communities composition deposition of mineral dust brings an input of nutrients

Upon wash-out and rain-out, the atmospheric aerosol may produce anion (Cl^-, SO_4^{2-} and NO_3^-) enriched rainwater, as well as increase its acidity through the dissolution of cations such as NH_4^+ or H^+. These alterations result in a Ca^{2+} release (loss of $CaCO_3$ thickness) from stone to reaction ions and products, via the 'carbonate-CO_2-bicarbonate' reaction where the water and hydrogen ion loading effects are significant, as well as the limestone type, but the nature of the anion is not, under a given wetting and drying regime. [283]

In the case of dry deposition, Primerano *et al.* [286] have investigated the sulphation of calcareous stones by oil fly ash. They found that the pollutant transfer mechanism operates via the absorption of humidity from the atmosphere, made possible by the hygroscopic nature of the ashes. This absorbed humidity activates the reaction of bisulphates and hydrolisable metallic ions contained in the ashes. The basic calcareous stone material tends to neutralise the resulting acidity with the reaction of calcium carbonate and sulphuric acid, forming calcium sulphate. The compostition of the fly ash is then responsible for the crust colouration (with carbonaceous material resulting in a black colour)

Main aspects determining the degree of weathering on stones are:

stone surface geometry: loss from complex, sculptural surfaces is several times greater than from flat, vertical surfaces of comparable petrography and exposure history.

stone porosity: stones with greater porosity are more vulnerable (e.g. limestone suffers an increased weathering when compared to marble, a metamorphism of limestone with lower porosity).

stone chemistry: e.g. selenite, i.e. gypsum stone, has a far more stable black crust than other kinds of stones and has undergone a deceleration in their weathering since the anthropogenic acidification of the atmosphere.

orientation: orientation in relation to prevailing winds is a major variable in the effect of air pollution on the build environment. It determines the exposure to precipitation and thus the wetness of the surface as well as the accumulation of wet deposition and its washout.

[280, 281, 287, 284, 288, 289]

Bioaerosols may also be a vector for bacterial or fungal stone decay [290].

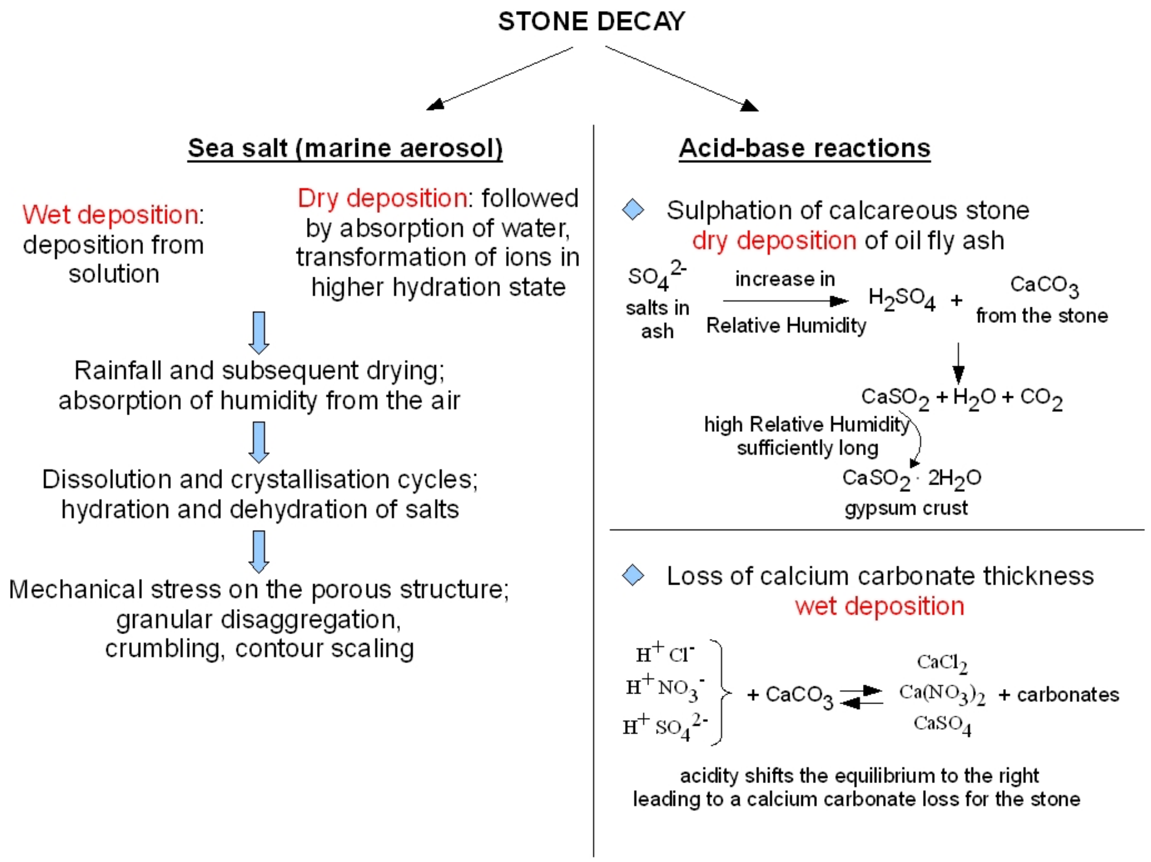


Figure 3.6: The effects of particulate matter on the build environment [280, 281, 282, 287, 283, 284, 285, 286, 291, 31]

Part II

Methods

Chapter 4

Sampling and sampling sites

4.1 The CARBOSOL project

The CARBOSOL (A Study of the Present and Retrospective State of the Organic Versus Inorganic Aerosol over Europe) project deployed an integrated approach combining radiocarbon measurements with bulk measurements of organic carbon and elemental carbon as well as levoglucosan and cellulose tracers to provide a bulk source apportionment of the carbonaceous and non-carbonaceous aerosol.

The sampling sites included in the CARBOSOL are located in a West-East transect covering western Europe, stretching 4000 km from the Atlantic oceanic background to the central european lowlands. Aerosol sampling took place continuously for approximately two years in 2002-2004. Time resolution was one week.

Azores

The Azores (AZO) sampling station was located in the Terceira island (397 km^2, 60,000 inhabitants), in the eastern group of the Azorean archipelago. The island is located on the Terceira rift, a geological structure at the junction of the Eurasian, African and American tectonic plates. It is a volcanic island with the highest point at the Santa Bárbara stratovolcano (1021 m a.s.l.) on its west side. The main tree variety on the island is the *Cryptomeria japonica*, a species introduced a little more than 100 years ago endemic to Japan, where its pollen is a major cause of hay fever. The aboriginal Laurel forest plants are now very minor. [292, 293] The aerosol was sampled over a cliff overlooking the ocean, at an altitude of 50 m above sea level (a.s.l.), continuously between July 2002 and June 2004. Main transport influence is from the Northern Americas and, to a minor extent, Europe and Africa. The air reaching the station has usually travelled over the ocean for several days and the pollution from local sources is generally diluted. Therefore, the station is considered representative of background oceanic air. The area surrounding the sampling site is used for cattle grazing and horticulture. Aerosol was sampled by sucking air at a flow rate of 1.1 m^3 min^{-1} through quartz fibre filters (Whatman QM-A, 10 x 8 inches). The sampler stood 1.5 m above the ground and was run with an Anderson PM$_{10}$ inlet to remove particles larger than 10 μm. The filter holder had a Tisch 2.5 μm impactor stage which separates particles larger and smaller than 2.5 μm. Only PM$_{2.5}$ particles were chemically characterised.

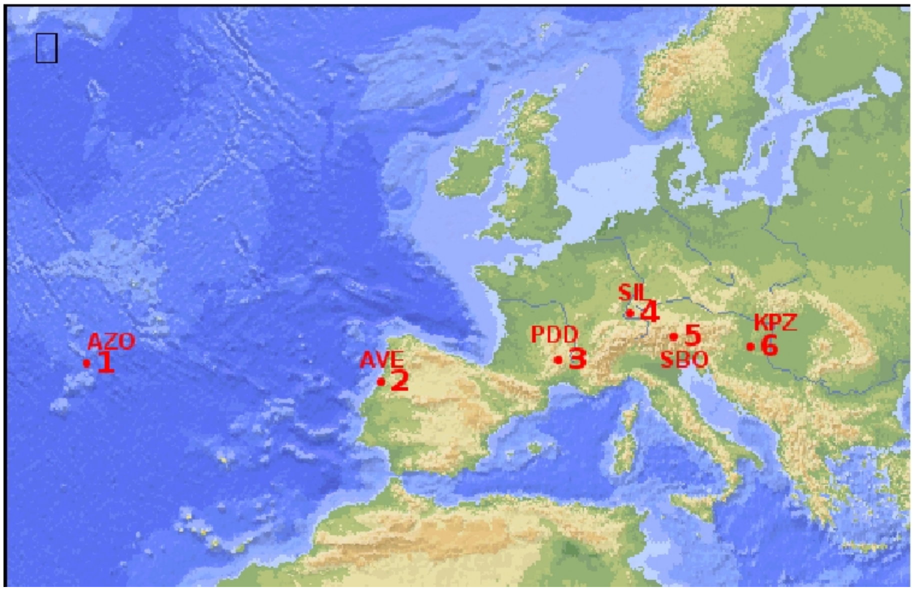


Figure 4.1: Location of the CARBOSOL sampling sites forming a West-East transect over the European continent

Aveiro

The AVE site (rural coastal site with maritime influence, 47 m a.s.l.) was located 10 km inland from the north Atlantic ocean in a rural area some 6km S-E of Aveiro (55,291 inhabitants). The region is characterised with a mixed eucalyptus (*Eucalyptus globullus*) (a species endemic to Oceania and introduced as a fast growing species for the paper and pulp industry and today one of the main tree species) and maritime pine *Pinus pinaster* [294] interspaced with patches of agricultural fields where the exploitation is typically of small scale, and mainly of maize (in spring and summer) and horticultural products. Sampling was performed at 2.5 m above the ground using a system similar to the AZO one and during the same period of time. As for the Azores site, only $PM_{2.5}$ was chemically charaterised, except for an intense wildfire period in Summer 2003 where the coarse fraction as well was characterised.

Puy de Dôme

The Puy de Dôme (PDD) volcano, in the French Massif Central, is located in the centre of a system of inactive volcanoes called Chaîne des Puys. The PDD site is located at the Microphysics and Chemistry station run by the Observatoire de Physique du Globe de Clermont Ferrand (OPGC) on the top of the Puy de Dôme mountain in Central France (1450 m a.s.l.). In winter the site is very often under free tropospheric conditions. Typical activities in the area are intensive agriculture, cattle husbandry and forest management. A forest inventory for the region (Auvergne region) states that half the forested area consists of coniferous species and the other half of deciduous ones [295]. Aerosol was sampled at a flow rate of 1.1 m^3 min^{-1} on circular quartz-filters (Gelman Pallflex Tissuquartz) with 15 cm diameter (Digitel filter holder). The air inlet was located 6 m above the ground and equipped with a heated rain/snow shelter (Digitel). It was assumed to collect particles up to 10 μm. The sampling

Figure 4.2: The Schauinsland (left) and Puy de Dôme (right) observatories

took place between October 2002 and August 2004.

Schauinsland

The Global Atmosphere Watch (GAW) station run by the German Federal Environmental Agency (SIL station for the CARBOSOL campaign) is situated on a mountain ridge (1205 m asl) in the Black Forest of south-western Germany (federated state of Baden-Württemberg). The black forest has a mainly oceanic climate. The geology of the area is dominated by granite and gneiss (N and E) and sandstone (S and W), and the potential natural vegetation is mainly a mixed forest of beech and fir, with minor contributions of oak, pine and spruce. However, the historical utilisation of the forest as well as wildfires have made this mainly deciduous composition evolve into a forest dominated by conifers. Due to its faster growing rate and its being more profitable, spruce has replaced beech in many places. [296] In Baden-Württemberg, deciduous trees cover 42% of the forested area, while conifers cover 55%, though, around the site, conifer forests and meadows are the dominant landscapes. The area is surrounded by coniferous forests (50%), meadows (40%) and some agricultural fields (10%). The sampling took place at 12 km N-E of the city of Freiburg in the Rhine valley. Usually, the station is situated above the ground-level atmospheric inversion layer of this densely populated region. Strong thermal convections occurring during the Summer may transport air masses from the Rhine valley to the SIL site. Aerosol sampling took place 4 m above the ground at a flow rate of 0.9 m^3 min^{-1} on 15 cm diameter circular quartz-filters. The air inlet was similar to the PDD one and samples from October 2002 to August 2004 were analysed.

Sonnblick

The Sonnblick Observatory (SBO), located on a mountain peak (3106 m a.s.l.) in the main ridge of the Austrian Alps, is operated by the Austrian Central Institute for Meteorology and Geodynamics. It is frequently above the atmospheric mixing layer, is supplied with electricity

Figure 4.3: The Sonnblick observatory

and has no local sources of exhaust fumes [297]. The observatory is located in the Salzburg area, where conifers are the main tree species (81%) [298]. Atmospheric aerosol sampling took place on the roof platform of the observatory from October 2002 to August 2004. The sampler, equipped with a $PM_{2.5}$ inlet, was a high volume sampler (Digitel) operated at a flow rate of 0.5 m^3 min^{-1} with quartz fibre (Pall Gelman Science 2500 QAT-UP) 15 cm diameter filters.

K-puszta

The KPZ station is run by the Hungarian Meteorological Service and the University of Veszprém, as part of the GAW and EMEP networks. It is located in the great hungarian plain some 15 km N-W of the city of Kecskemét (150,000 inhabitants) and 60 km S-E of the capital Budapest (1,9 mn inhabitants). Forests (62 % coniferous trees, mainly *Pinus nigra*) and clearings surround the sampling site. Aerosol (PM_2) was sampled 7 m above the ground at a flow rate of 0.6 m^3 min^{-1} (Sierra-Andersen impactor) on quartz fibre filters (Whatman QM, 20 x 25 cm) between July 2002 and May 2004. To collect enough material for conducting all analysis, even at remote oceanic and mountain sites, weekly sampling was applied to avoid problems related to detection limits of the deployed analytical methods. Due to the long sampling period, alteration of aerosol may have occurred on filters during sampling. It can, however, been assumed that, during sampling, equilibrium between gas and particulate phase would govern the behaviour of the filtered aerosol similarly to what happens in the atmosphere. Furthermore the large mass of particles collected would reduce potential adsorption of semi-volatile organic compounds on active sites of the quartz fibres surface, as result of their rapid saturation.

To reduce contamination by organic material, quartz filters for PDD, SIL and SBO were pre-fired in factory, whereas for AZO, AVE and KPZ, filters were pre-treated by heating in a furnace during several hours at 500-700°C in laboratory. After the thermal treatment, filters were wrapped in thermally treated and cleaned aluminium foil.

Table 4.1: Sampling sites of the CARBOSOL campaign, altitude in meters above sea level, classification following Van Dingenen *et al.* (2004) [299].

Site	*Altitude m.a.s.l.*	*Coordinates*	*Classification*
AZO	50	38 ° 38' N 27 ° 2' W	marine background
AVE	47	40 ° 34' N 8 ° 38' W	rural background lowland
PDD	1450	45 ° 46' N 2 ° 57' E	natural continental background
SIL	1205	47 ° 55' N 7 ° 54' E	rural background mountain
SBO	3106	47 ° 3' N 12 ° 57' E	natural continental background free troposphere in winter
KPZ	136	46 ° 58' N 19 ° 35' W	rural background lowland

After sampling, filters were folded in two, with the exposed side face to face, wrapped in aluminium foil and immediately transported to the laboratory in charge of the sampling site, where they were stored at -20°C. Batches of sampled filters and filter blanks were divided into several fractions, enclosed into heated treated aluminium cylinders, and sent by express mail to the various laboratories participating in the analytical work.

For the determination of saccharide species reported here, punches of several weekly filters corresponding to one month were pooled together. Therefore, the time resolution for those compounds is one month.

4.2 The AQUELLA project

Until 2004 the legal framework for PM in Austria referred to the total suspended particles (TSP). However, with the transposition of the European Union 1999/30/EC directive (April 22^{nd}, 1999), motivated by health issues of fine particles (see 3.6.1), the preocupation shifted towards PM_{10}. This resulted in the Immissionsschutzgesetz-Luft (*Law for the ambient levels protection - Air*, IG-L). In the directive, PM_{10} is defined as *particulate matter with a 50% cut-off diameter of 10 micrometers.* As limit values for the public health protection the IG-L states a yearly PM_{10} average of 40 $\mu g m^{-3}$ and a daily average of 40 $\mu g m^{-3}$ coupled with exception criteria.

The AQUELLA (Bestimmung von Immissionsbeiträgen in Feinstaubproben, *Determination of source contributions to ambiente PM levels*) projects are aimed to the identification of the different PM sources in Austria and to the determination of their contributions. The projects are commissioned by the various Austrian federated states, as it is the scope of the 1999/30/EC directive and the IG-L. The sampling sites included in the AQUELLA projects are all part of the air quality monitoring networks operated by the Austrian federated states. The samples treated in the scope of this work

The ambient particulate matter was sampled daily through 2004 using hi-vol samplers

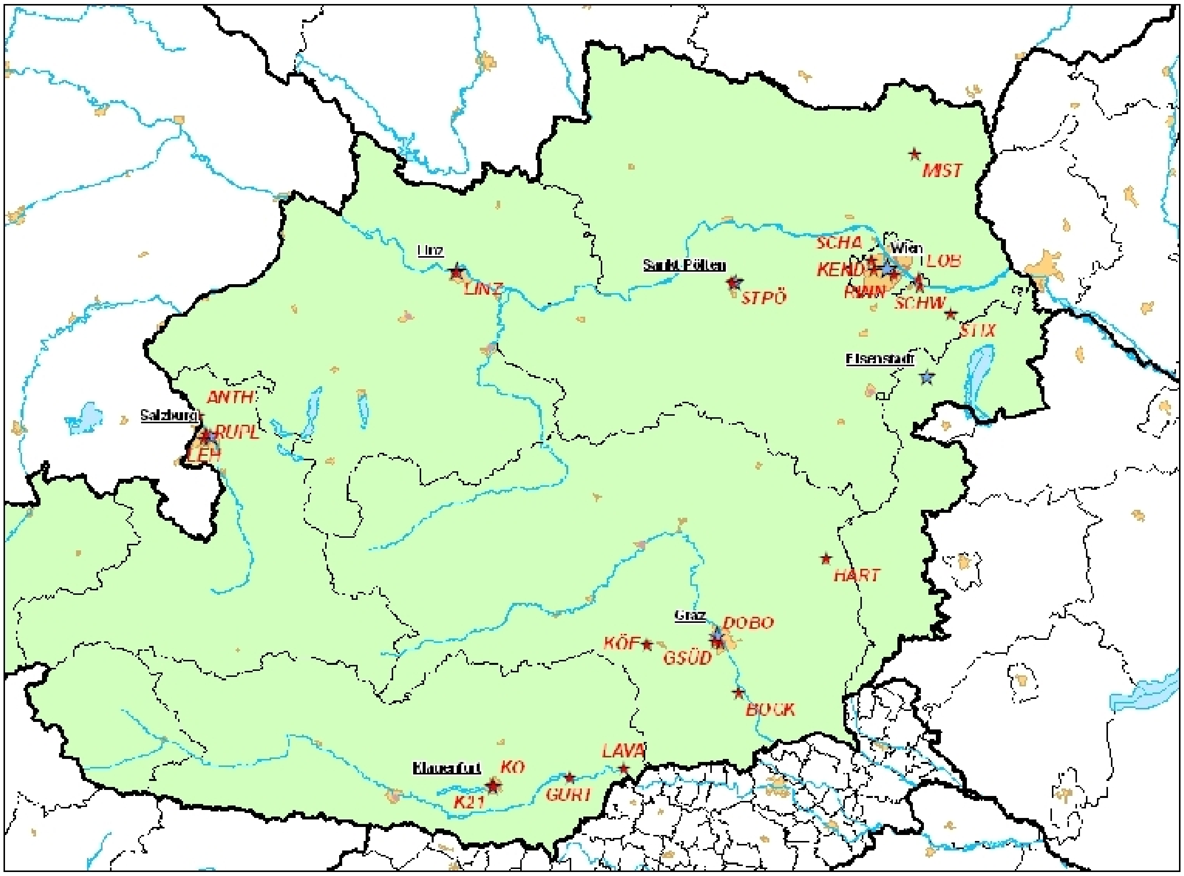


Figure 4.4: Location of the AQUELLA sampling sites in eastern Austria

(DHA-80, DIGITEL elektronik AG, Hegnau, Switzerland) on quartz fibre filters (Pallflex 2500QAT-UP, 15 cm diameter, PALL Life Sciences, USA) for 24 hours (approximately 700 cubic meters per filter). Gravimetric measurements were conducted by the local authorities who run the sampling network. Filters were weighed after and before sampling, and had been previously conditioned in a clean room with controlled temperature and humidity (20C±1°C; 50%±5%). For chemical analysis, pools of aliquots of filters (24 hours continuous sampling) were made.

4.2.1 Vienna sampling sites

Vienna, the capital of Austria, located next to the Danube river, has 1.8 million inhabitants. It lies surrounded by plains in the North, East and South-East, and by woody hills in the West. Four sites from the Vienna monitoring network were selected for this campaign, two with background characteristics and two impacted by traffic. Schafberg (SCH) and Lobau (SCH) are the two background sites. The former is located at the north-west end of the city, in a park-type residential area and the latter lies within a national park (Donau Auen). Rinnbckstrasse (RIN), close to a highway, and Kendlerstrasse (KEN), alongside a busy street, are the traffic-impacted sites. The four sites are located in a NW-SE transect over the city (Figure 4.5).

4.2.2 Salzburg sampling sites

Salzburg has 150,269 inhabitants and is the fourth largest city in the country. Salzburg stands approximately 300 km West of Vienna. It lies along the Salzbach River and is surrounded by mountains at the northern border of the Alps (Figure 4.4). The sampling site located at Rudolfsplatz (RU) is representative for highly traffic-impacted conditions. Lehen (LE) is another site located in the city centre, though in a residential area and not as much impacted by road traffic. Anthering (AN) is a sampling site situated outside the city and representative for background conditions.

4.2.3 Styria sampling sites

Styria is a federated state within the republic of Austria with a population of 1,203,986. The sampling sites of the AQUELLA campaign for that federated state were located either in the city of Graz or around it. Graz (287,723 inhabitants) is the second largest city of Austria and the capital of the federated state of Styria. It is located some 200 km south of Vienna on the banks of the Mur River (Figure 4.4). The city lies south east of the Alps, which shield the city from prevailing westerly winds and give the climate some Mediterranean influence. It is located in a basin with only one opening, to the South, which often gives the city's atmosphere stagnant characteristics. The sampling sites form a N-S transect (Figure), with two sites within the city, impacted by traffic (Don Bosco, DB and Graz Süd, GS, this last one with more residential characteristics), and one background site outside the city (Bockberg, BB) (Figure 4.7). The sampling site of Don Bosco (DB) is situated inside the city center. The Graz Süd sampling site is located in a residential area within the city of Graz. Bockberg is the background sampling site of the AQUELLA-Styria project. It is situated on a hill (445 m a.s.l.) 28 km outside the city of Graz, to the south.

Figure 4.5: Location of the AQUELLA sampling sites in the city of Vienna. Clockwise from the top-left: SCH, RIN, KEN and LOB

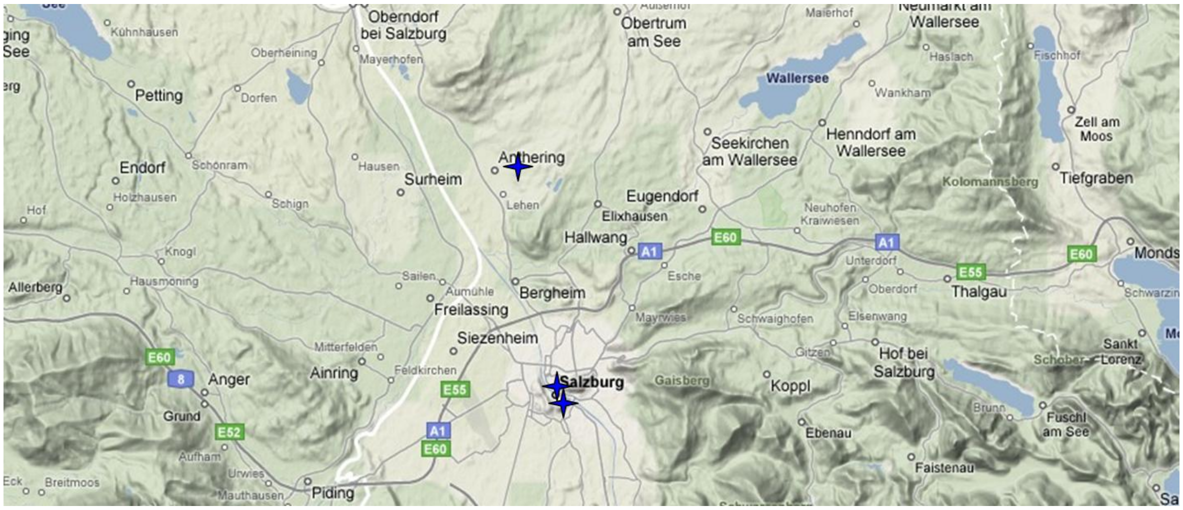


Figure 4.6: Location of the AQUELLA sampling sites in the city of Salzburg and its surroundings

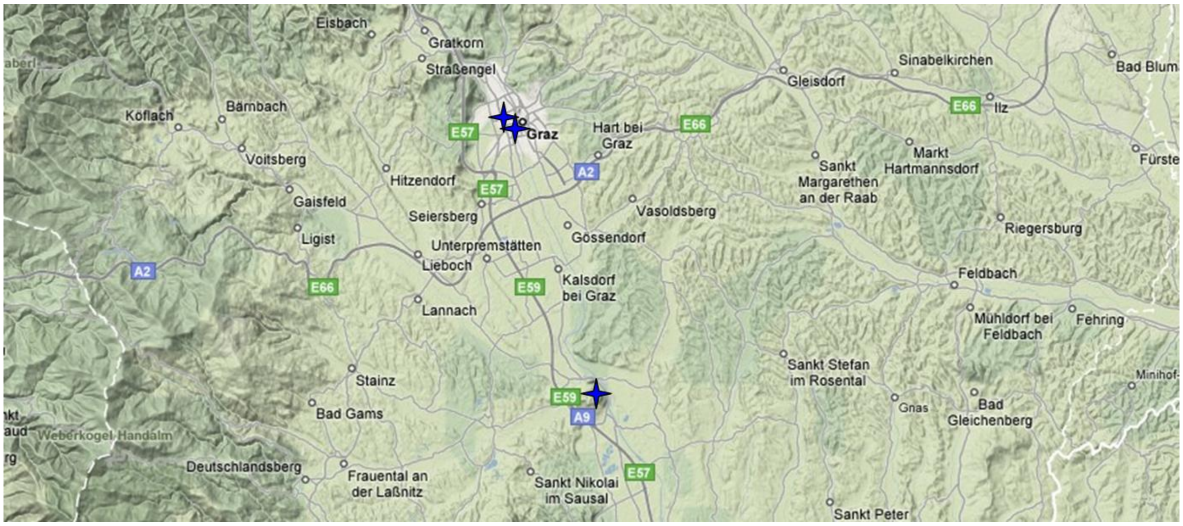


Figure 4.7: Location of the AQUELLA sampling sites in the city of Graz and its surroundings

Figure 4.8: Location and pictures of the AQUELLA sampling sites in the city of Salzburg and its surroundings

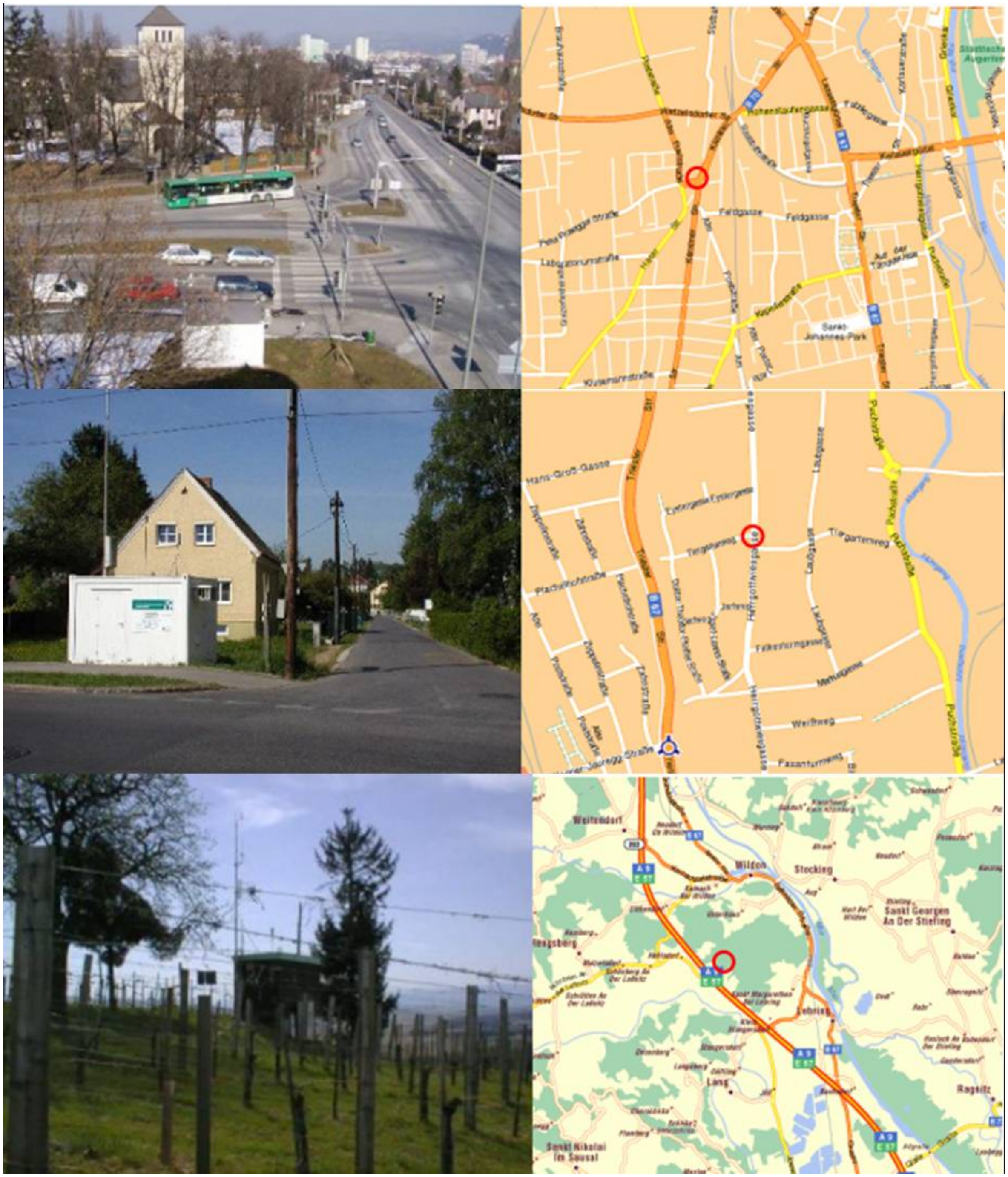


Figure 4.9: Location and pictures of the AQUELLA sampling sites in the city of Graz and its surroundings

Chapter 5

Determination of saccharides in atmospheric aerosol using anion-exchange HPLC and pulsed amperometric detection

Methods applied so far for analysis of atmospheric saccharides are based either on derivatisation (silylation) and determination with gas chromatography (GC) with various detection techniques, such as various types of Mass Spectrometry (MS), Time-of-Flight (TOF) or Flame Ionisation Detection (FID) (e.g. [124, 138, 210, 126, 220, 190, 211, 17, 300, 214]) or on HPLC separation coupled with ultraviolet (UV), electrochemical, various types of MS or aerosol charge detection (e.g. [85, 301, 302, 303, 304, 186]. The use of high-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD) has recently been proposed for the determination of levoglucosan [305], nevertheless, the reported method was restricted to biomass burning samples. A review on the currently applied methods appeared lately by Schkolnik and Rudich (2005) [306].

Compared with the widely used GC-MS methodology, the determination of primary sugars, sugar polyols and anhydrosugars by HPAE-PAD has the advantage of omitting the multi-step derivatisation, and thus being less time, cost and labour intensive. After extraction in Milli-Q water with the help of ultrasonic agitation, the sample solution is injected in a Dionex CarboPac PA1 column. At high pH, carbohydrates are actually weak acids and ionisable; it is then possible to separate them using the principle of ion chromatography. The column used is optimised for the separation of mono- and disaccharides by high pH anion exchange chromatography (HPAE) coupled with Pulsed Electrochemical Detection (amperometry) (PAD). HPAE-PAD is extremely selective and specific for carbohydrates because:

1. pulsed amperometry detects only those compounds that contain functional groups that are oxidisable at the detection voltage employed (in this case, sensitivity for carbohydrates is orders of magnitude greater than for other classes of analytes).
2. Neutral or cationic sample components in the matrix elute in, or close to, the void volume of the column. Therefore, even if such species are oxidisable, they do not usually interfere with analysis of the carbohydrate components of interest.

[307, 308]

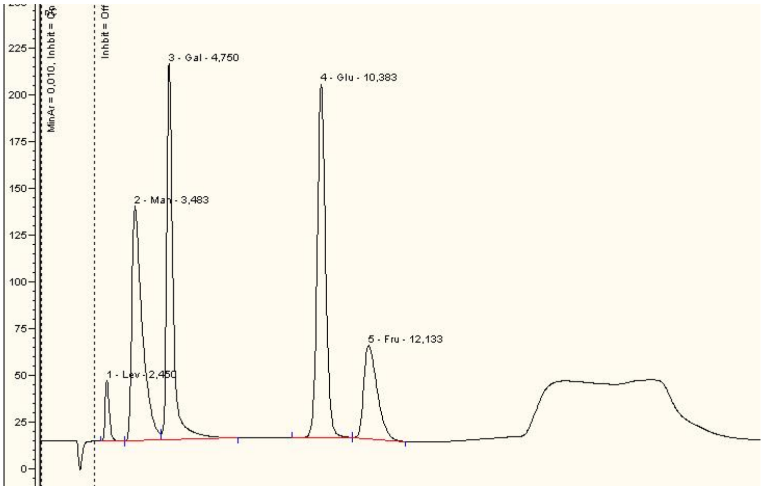


Figure 5.1: Chromatogram of the separation of five saccharides with a Dionex CarboPac$^{\mathrm{TM}}$PA-10 column

The method developed showed a good resolution, and a selective detection, as well as it proved to be reliable and reproducible for the compounds and purposes considered. The results achieved are comparable to those obtained with another method (GC-FID), but the use of HPAE-PAD for the determination of saccharides in the atmospheric aerosol has the advantage of being both faster and more simple when compared with other published methods.

5.1 Method development

5.1.1 Separation - Choice of the ion-exchange column

Carbohydrates are very weak acids. At high pH, they are at least partially ionised, and thus can be separated by anion-exchange mechanisms. However, anion-exchange chromatography cannot be performed at high pH with classical silica-based columns, because they are chemically not stable at high pH, but an alkali-stable polymer resin anion-exchange column, such as the Dionex CarboPac$^{\mathrm{TM}}$PA-10 can be used instead. The method described in the Dionex Technical Notes 20 and 21 [307, 308] was tested to analyse the sugar content of atmospheric aerosols. The Dionex CarboPac$^{\mathrm{TM}}$PA-10 was used, as recommended, with a mobile phase of aqueous sodium hydroxide solution increasing from 3.6 to 4.8 mM NaOH over 15 min to measure three anhydrosugars (levoglucosan, mannosan, galactosan) and two primary monosaccharides (glucose and fructose) (Figure 5.1). The whole was followed by a cleaning step (250 mM NaOH, 10 minutes). Some of the filters analysed were sent to the university of Antwerp to be analysed by GC-FID [126, 220] for a method intercomparison. The results (see Figure 5.3) showed a quite good concordance for samples of the cold season, but a great discordance for samples of the warm season, where the HPAE-PAD method measured values much greater than those measured by the GC-FID method. A possible overlap of other aerosol saccharidic compounds was suspected. Besides the five compounds already included in the analysis (levoglucosan, mannosan, galactosan, glucose and fructose), a set of most commonly reported saccharides in aerosol (2-methyltetrols, primary sugars and polyols) were tested in order to assess the possibility of co-elution:

2-methyltetrols: 2-methyerythritol and 2-methylthreitol

primary monosaccharides: xylose, arabinose, galactose, mannose

primary disaccharides: sucrose, maltose, trehalose (mycose)

polyols: glycerol, erythritol, xylitol, arabitol, sorbitol and mannitol

Other saccharides found in aerosol samples are inositol and 1,6-anhydroglucofuranose, which were not tested but are not expected to occur commonly nor at significant concentrations, and some di- and trisaccharides, expected to elute mainly during the cleaning step. This allowed to see that the method failed to separate some compounds: levoglucosan and arabitol overlapped completely (Figure 5.2); mannitol and mannosan overlapped partially.

Three solutions were then considered to start the development of a method which could allow the determination of the sugars (the main goal were the anhydrosugars) without interferences:

- modify the detection in order to selectively detect only one of the compounds which co-elute
- modify the mobile phase in order to reach a satisfying separation
- finally, change the stationary phase.

Carbohydrates are detected by measuring the electrical current generated by their oxidation at the surface of a gold electrode. In order to overcome problems associated with the removal of oxidation products from the electrode, and to improve the sensitivity, a pattern of changing potentials is applied to the electrode. In the first step, a voltage is applied between the gold working electrode and the solution, which is high enough to cause electron-transfer reactions thereby oxidising the carbohydrate molecules adsorbed on the electrode surface. As the application of a potential produces, in addition to the analyte oxidation current, also an initial capacitative charging current, the cell current is measured after a short time delay that allows the charging current to decay. The analyte oxidation current is measured by integrating the cell current (read against an Ag/AgCl electrode) over the integration time. The detector response is then measured in Coulombs (charge = current time). After the integration time, a sequence of two different potentials is used, a first potential is applied to clean the gold working electrode surface from the reaction products, and then a second one to equilibrate the electrode so that the cycle can start again. The equilibration time allows analyte molecules to accumulate under diffusion control, on the electrode surface, thus enhancing the sensitivity. The waveform requires a total of 500 ms, and data can be collected at 2 Hz. (Figure 5.4) The measurement potential was varied between -25 and 300 mV (Dionex standard is 100 mV) to evaluate whether a potential could be found at which only one compound would be detected. All compounds of this class showed the same behaviour, implying that one potential can be selected for the detection of all compounds, but that selective detection is not possible (Figure 5.5).

Assuming that, when levoglucosan and arabitol elute together, the area of the peak equals the sum of the areas of both compounds and knowing that the sensitivity of the detector response varies when the measuring potential is changed, it is possible, at least theoretically, to

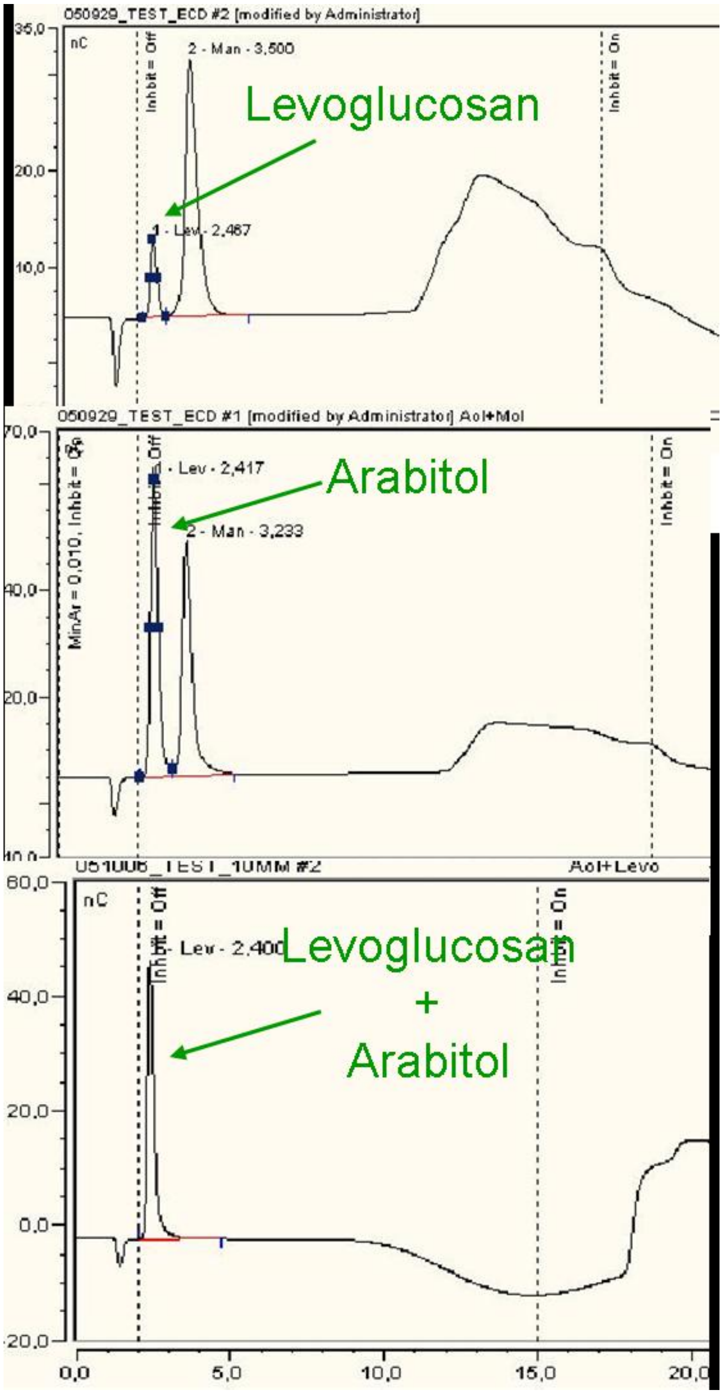


Figure 5.2: Arabitol and Levoglucosan overlap completely when using the Dionex PA-10 column

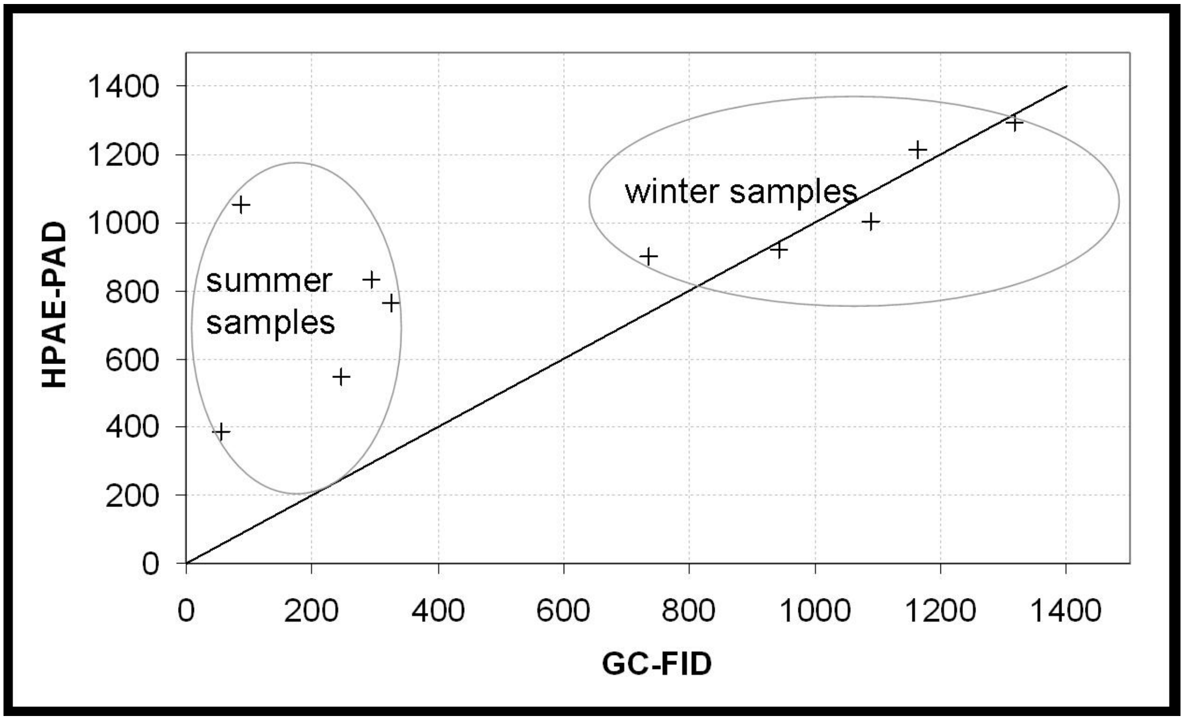


Figure 5.3: Comparison between the GC-FID and HPAE-PAD (with Dionex PA-10 column) results.

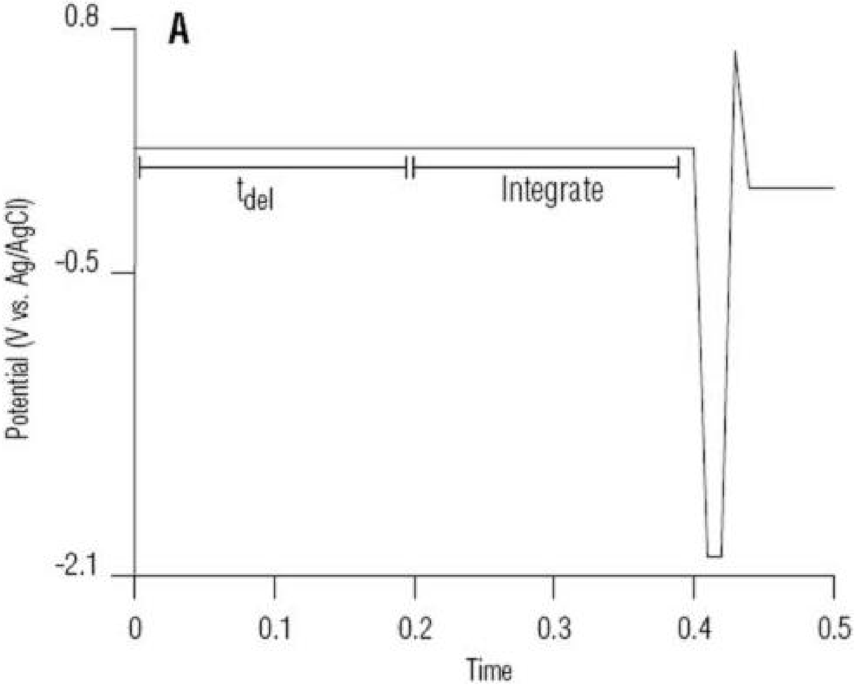


Figure 5.4: Waveform of potentials used to determine the current from the redox reaction.

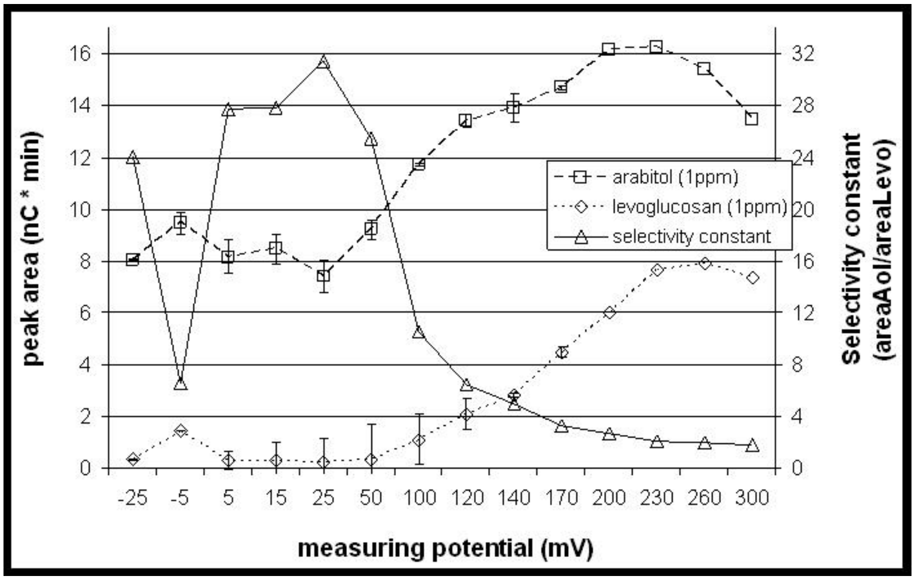


Figure 5.5: Detector response as a function of applied measuring potential for arabitol and levoglucosan. The selectivity constant is the ratio between the arabitol and the levoglucosan areas.

determine the concentrations of both compounds when analysing one sample at two different measuring potentials.

$$A_{total} = A_{Levoglucosan} + A_{Arabitol} \tag{5.1}$$

and A, the area of the peak, is proportional to C, the calibration of the analyte:

$$A = a \times C + b \tag{5.2}$$

$$\text{thus} \begin{cases} \mathrm{A}_{total}^{pot1} = (a_{Levo}^{pot1} \times C_{Levo} + b_{Levo}^{pot1}) + (a_{Arab}^{pot1} \times C_{Arab} + b_{Arab}^{pot1}) \\ \mathrm{A}_{total}^{pot2} = (a_{Levo}^{pot2} \times C_{Levo} + b_{Levo}^{pot2}) + (a_{Arab}^{pot2} \times C_{Arab} + b_{Arab}^{pot2}) \end{cases}$$

Where C is the concentration, $a_{Levoglucosan}$, $b_{Levoglucosan}$, $a_{Arabitol}$ and $b_{Arabitol}$ are the parameters of the calibrations of levoglucosan and arabitol (separately) for both $potential1$ and $potential2$.

A_{total} for both $potential1$ and $potential2$ is the area of the peak for the respective measurement (at measuring potentials 1 and 2). We have then a system of two equations with two unknowns $C_{Levoglucosan}$ and $C_{Arabitol}$.

This methodology, however, proved inaccurate and with low repeatability with both standards (Table 5.1) and samples. The low repeatability of the signal when consecutively switching between potentials is the likely cause of this lack of accuracy and repeatability.

The modification of the mobile phase, varying the NaOH concentration, and therefore the pH, did not bring any separation improvement. Thus, another stationary phase was tested: the Dionex CarboPac$^{\mathrm{TM}}$PA-1 column. Changing to a PA-1 column resulted in a partial separation of the overlapping compounds, and also offered a broader operational pH range.

Table 5.1: Determination of Arabitol and Levogluocsan using a dual potential method.

Potentials (mV)	*Calib. range (ppm)*	*Concentration (ppm)*	*error arabitol (%)*	*error levoglucosan (%)*
100-200	0.2 - 0.5 - 1	1	1.5	16
		0.5	1.4-2.5	4.7-18
		0.75	3.6	17
140-230	1 - 2.5 - 5	2	4.5	12
		4	1.9	5.1
140-230	0.5 - 2 - 4	1	3	25
		1.5	3	11
		2.5	3.6	9
		3.5	0.07	0

5.1.2 Chromatographic separation

Exchange of the different compounds between the eluent and the stationary phase can be controlled by adjustment of the pH, in this case, by changing the sodium hydroxide concentration. While a continuous gradient is often used to achieve separation of complex mixtures, it was found to be more efficient in the current work to use a step programme to elute the different classes of saccharides. Sodium hydroxide concentrations between 0.1 and 150 mM were tested on the CarboPac$^{\text{TM}}$PA-1 column. The separation was better for concentrations in the range of 0.1–0.5 mM, but since the sensitivity of detection by pulsed amperometry for carbohydrates is lower at a lower pH, a concentration of 0.5 mM was selected for the analysis of the sugars alcohols and the anhydrosugars. As too low, a hydroxide concentration is difficult to control, resulting in variable retention times, the lowest practical value was 0.5 mM (Figure 5.6). For the primary sugars, which are more strongly retained by the column, the eluent pH could be raised without any loss in selectivity or in sensitivity. The NaOH concentration used for this step was 20 mM. Addition of methanol to modify the polarity of the eluent was evaluated in an attempt to improve the separation of the difficult pair, arabitol and levoglucosan, but was not successful. Small improvements in chromatographic performance can also be achieved by adjustment of the flow rate. Figure 5.7 shows the variation in column performance, for four of the saccharides, including levoglucosan, as a function of eluent flow rate. The adopted value of 1 mL min^{-1} is probably close to the optimum, since higher flows would require too high an eluent pressure.

5.1.3 Peak deconvolution

The resulting chromatograms (Figures 5.8 and 5.9) show good separations for most compounds, but still a partial overlap can be seen for the peaks of arabitol, usually associated with lichens and fungal spores, and levoglucosan, accepted as a useful marker for wood smoke. To achieve complete analysis, PeakFit$^{\text{TM}}$software (Systat) was used where the shape of the peaks of the different overlapping compounds is expressed in terms of a range of parameters within a type of modified Gaussian curve. The use of a modified Gaussian curve was necessary because the peaks are not symmetrical, but show some tailing, which means that peak

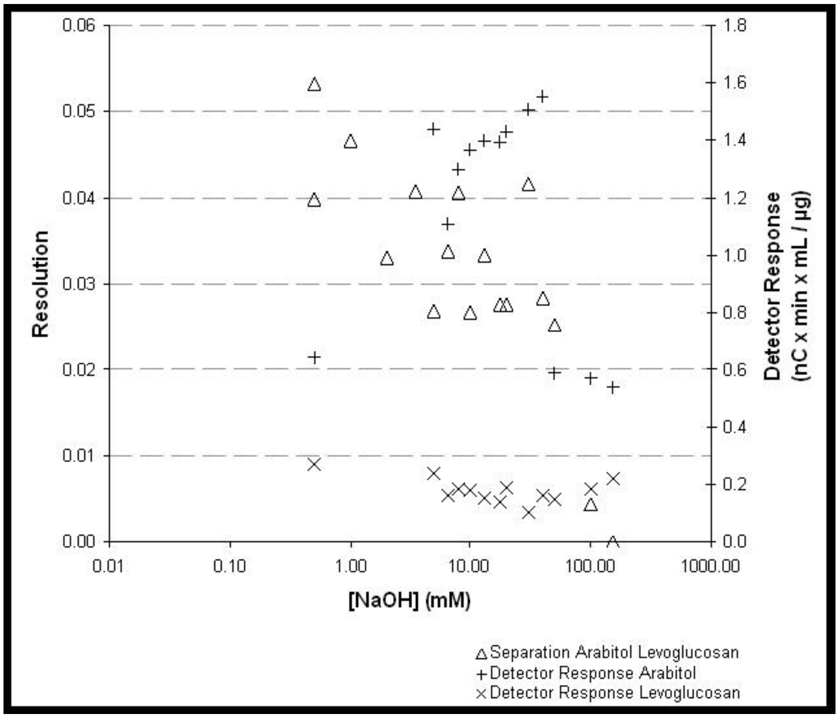


Figure 5.6: Peak separation and detector response as a function of eluent composition: $Resolution = \frac{T_{levloglucosan} - T_{arabitol}}{\frac{T_{levloglucosan} + T_{arabitol}}{2}}$.

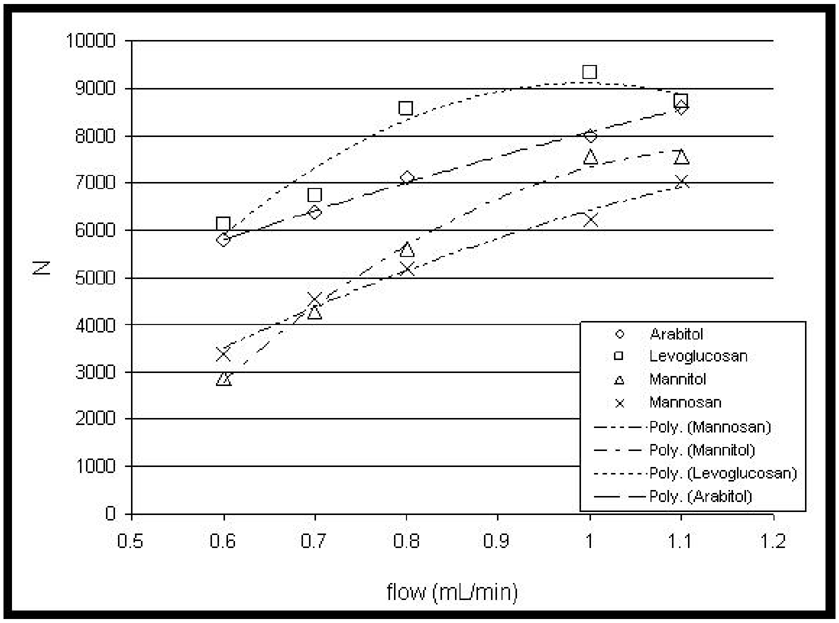


Figure 5.7: Column performance (number of theoretical plates, N) for four saccharides as a function of eluent flow rate

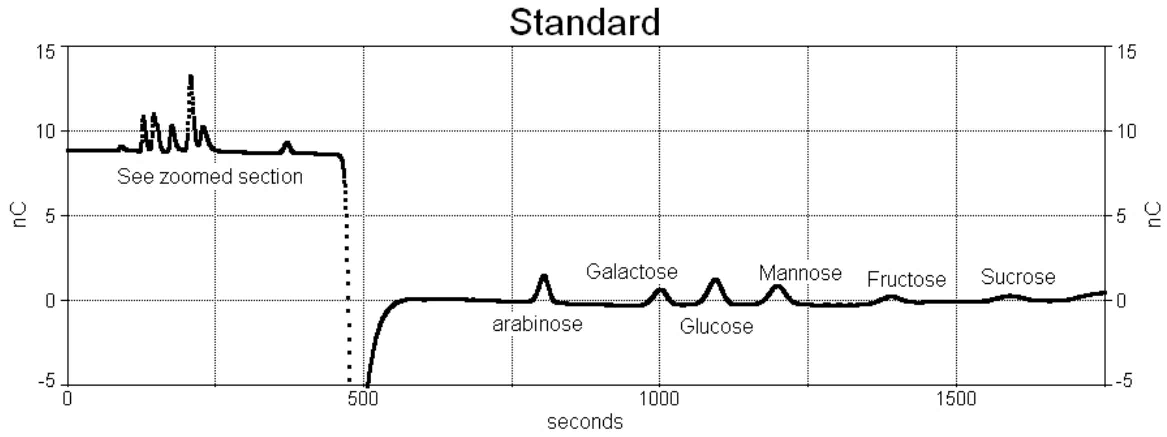


Figure 5.8: Chromatogram for the 13-component saccharide mixture: xylitol, arabitol, sorbitol, arabinose, galactose, glucose, mannose, fructose and sucrose: 0.5 μg mL^{-1}; levoglucosan, mannitol, mannosan: 1 μg mL^{-1}; galactosan: 0.25 μg mL^{-1}

fitting with a simple Gaussian peak-fit was not satisfactory, and peak height measurement was simply wrong. The ranges for the different parameters are obtained via the injection of standards that do not contain both of the overlapping compounds (non-overlapping standards). The parameters are checked with standards that contain both the overlapping compounds (checkstandards). If the concentration of the compounds within the check standards, calculated with the calibration curve from the non-overlapping standards, is as expected, than we assume the ranges for the parameters are right. Once these ranges for those parameters obtained and validated, one can fit a curve, which respect those parameters, to the experimental data of samples. The mannitol–mannosan pair was resolved by the eluent pH programme, though because of tailing of the mannitol peak, deconvolution using the PeakFit$^{\text{TM}}$software was also used to obtain more accurate results.

Figure 5.10 shows that levoglucosan can be determined precisely in the presence of arabitol by this approach. The circles represent calibration points based on solutions containing only levoglucosan. The crosses show corresponding points for the same levoglucosan concentrations, measured with the deconvolution software, but with arabitol also present, at a comparable concentration. The dotted line is the best fit for the mixed standard calibration line. The figure also shows results for two other integration techniques: a simple Gaussian (not tailed) deconvolution and a valley-to-valley integration (integrator). These two techniques are not adequate, as shown. Three sugars listed in Table 1 but not observed in the chromatograms shown in Figure 5.8 are maltose, trehalose and xylose, reported to originate from soil [17]. Maltose could be analysed by adding an additional gradient step to the programme since it elutes later than the other compounds. Xylose elutes between mannose and fructose, while trehalose does between mannosan and galactosan. However, as they were not detected in the selected samples tested for this purpose, their analysis was not included in the method adopted for routine analysis in the AQUELLA (Austrian Aerosol Sources) projects.

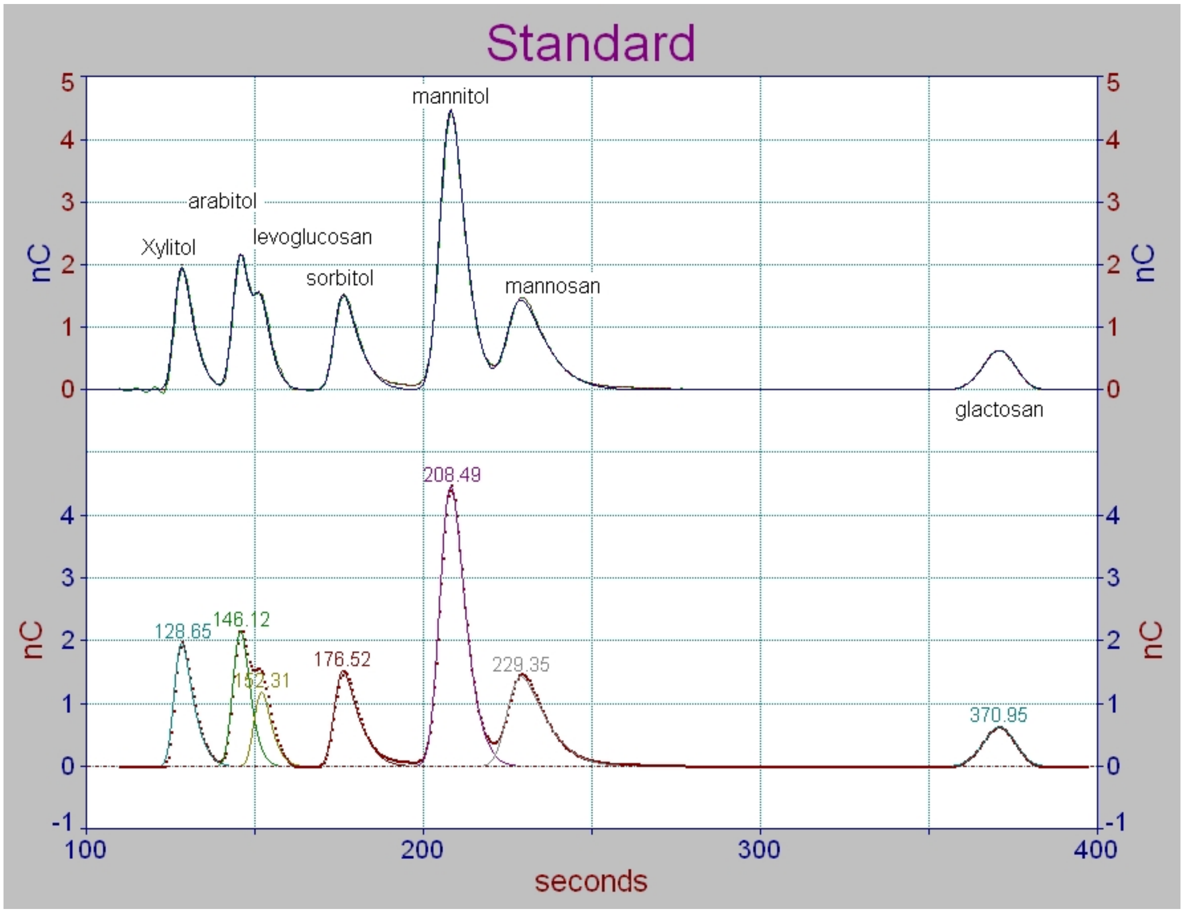


Figure 5.9: Expanded initial section of the chromatogram showing the polyols and the anhydrosugars, plus the peak deconvolution output. The inferior graph shows how the deconvolution software fits the peaks while the above one shows how the fitted data matches the experimental data

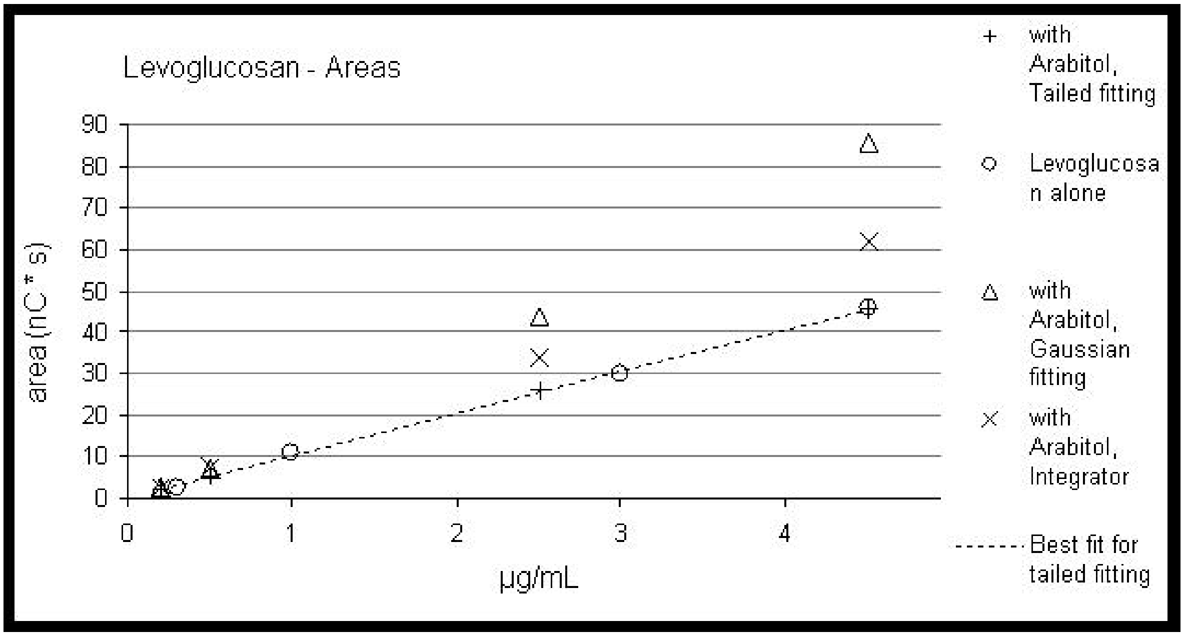


Figure 5.10: Levoglucosan calibration with additional points from mixtures, showing the results of different peak deconvolution methods. Common points have the following concentrations (levoglucosan:arabitol in μg mL^{-1}: 0.2:0.08; 0.5:0.2; 1:2.5; 2:4.5)

5.2 Method validation

5.2.1 Limits of detection

The limits of detection (LOD) were assessed as those concentrations giving a peak signal equivalent to three times the standard deviation of the lowest standard, above the blank. Those sugars eluting early in the run, such as xylitol (in step 1) and arabinose (in step 2), gave the sharpest peaks and the lowest LOD of 0.004 and 0.005 μg mL^{-1}, while the others were in the range 0.01–0.03 μg mL^{-1}. Mannosan, which gives a broader, tailing peak, showed a LOD of 0.05 μg mL^{-1} (see Table 5.2). The limits of detection are thus determined by the measurement step, and not by blanks or contamination. When applied to filters carrying PM trapped from 720 m^3 of air pumped at 30 L h^{-1} over 24 h, from which normally a section of 1/32 of the whole 150-mm diameter filter is extracted in 2.4 mL of ultra-pure water, these limits of detection correspond to 5 ng m^{-3} for mannitol, 3.6 ng m^{-3} for levoglucosan and 1 ng m^{-3} for arabitol. As levoglucosan levels measured in urban aerosols (Vienna, Graz and Salzburg) were typically 40–50 ng m^{-3} in summer and 500–1500 ng m^{-3} in winter, the method is more than sensitive enough for this purpose.

5.2.2 Repeatability

A set of standards (13 sugars at five calibration levels in the range 0.1–5 μg mL^{-1} for levoglucosan and 0.04–2 μg mL^{-1} for arabitol) was run in triplicate to assess the measurement performance. To assess procedure performance, five filter pieces, each of 4.5 cm^2 stamped out of one filter from a high-volume sampler, were extracted separately with 3 mL of ultra-

Table 5.2: Limits of detection (LOD) and quantification (LOQ).

replicate areas	Xol	Lev	Sol	Man	Gan	Aol	Mol
1	0.994	0.735	0.395	1.360	0.720	2.043	2.022
2	0.964	0.669	0.325	1.398	0.740	2.441	2.261
3	0.946	0.618	0.399	1.618	0.763	2.475	2.328
4	0.907	0.553	0.295	1.343	0.826	2.365	2.187
5	0.984	0.551	0.315	1.903	0.859	2.150	2.048
6	0.953	0.616	0.414	1.821	0.818	2.145	1.921
$\mu g\ mL^{-1}$	*0.04*	*0.1*	*0.04*	*0.1*	*0.04*	*0.04*	*0.1*
average	0.958	0.624	0.357	1.574	0.788	2.270	2.128
st dev	0.031	0.071	0.051	0.245	0.055	0.180	0.156
rsd	0.032	0.113	0.143	0.156	0.069	0.079	0.073
LOD(ppm)	0.004	0.034	0.017	0.047	0.008	0.010	0.022
LOQ(ppm)	0.012	0.102	0.051	0.140	0.025	0.029	0.066

replicate areas	Ase	Gse	Glu	Mse	Fru	Suc
1	0.067	0.025	0.053	0.035	0.006	0.012
2	0.066	0.029	0.033	0.037	0.008	0.019
3	0.066	0.03	0.037	0.039	0.013	0.016
4	0.067	0.024	0.043	0.027	0.013	0.018
5	0.06	0.036	0.03	0.029	0.011	0.014
6	0.067	0.035	0.051	0.029	0.012	0.02
$\mu g\ mL^{-1}$	*0.04*	*0.04*	*0.04*	*0.04*	*0.04*	*0.04*
average	0.066	0.030	0.041	0.033	0.011	0.017
st dev	0.003	0.005	0.009	0.005	0.003	0.003
rsd	0.042	0.166	0.230	0.152	0.274	0.187
LOD(ppm)	0.005	0.020	0.028	0.018	0.033	0.022
LOQ(ppm)	0.015	0.060	0.083	0.055	0.099	0.067

Six replicates of the lowest level in the standards calibration range for the 13 sugars considered, areas in $nC \times s$ for the anhydrosugars and the polyols and in $nC \times min$ for the primary sugars.
$LOD = Concentration \times rsd$ and $LOQ = 3 \times LOD$.

Table 5.3: Correlation data for comparison of techniques (HPLC and GC-FID).

	Arabitol	Levoglucosan	Mannitol
Slope	0.83	1.03	1.03
Correlation R^2	0.96	0.99	0.70

Numbers of samples were 23 for levoglucosan and 15 for arabitol and mannitol.
Samples represented various yearly periods and thus concentration ranges were wide: 15–45 μg mL^{-1}, 20–80 μg mL^{-1}, and 10–200 μg mL^{-1} for arabitol, mannitol and levoglucosan, respectively.

pure water and injected to assess the overall procedure repeatability. One 13.6 cm^2 aliquot was extracted with 9 mL ultra-pure water and this extract was injected five times to assess the measurement repeatability. From the 13 sugars investigated, 6 could be identified in the real sample: arabitol, mannitol, sorbitol, levoglucosan, mannosan, and glucose. The average relative standard deviation was 3.5% for all the sugars except for sorbitol (7%) for which the measured signal was only about 10% of that of the lowest level standard. There was no significant difference in the repeatability between injections of the same extract and injections following different extractions. The repeatability of the data handling procedure explained in 5.1.3 was also tested. The chromatogram of a real summer sample (arabitol: 33 ng m^{-3}; levoglucosan: 35 ng m^{-3}) and the corresponding standards were submitted 10 times, on different days, to the peak deconvolution procedure. The relative standard deviation was 0.6 and 0.9 % for arabitol and levoglucosan, respectively. The difference between the maximum and minimum computed areas was 2.3 and 2.7 % of the maximum computed area for arabitol and levoglucosan, respectively.

5.2.3 Recovery

Previously baked and equilibrated blank filters (4.5 cm^2 each) were spiked with mixtures of the 13 sugars, extracted and analysed. In the range 5–15 μg of each sugar (in the 3 mL extract) the recoveries were in the range 95–108%, averaging 102% over ten extractions. At a much lower level of 0.2 μg each sugar (around twice the LOD) the recoveries were still in the range 80–120%. Also, a filter aliquot was successively extracted three times in order to check for extraction efficiency on a real sample. Between extractions, care was taken to leave as little water as possible inside the vial. The second extraction yielded a peak only for both arabitol and levoglucosan, but below the quantification limit. No peak was observed for the analysis of the third extract.

5.2.4 Comparison with another method

A comparison was conducted by analysing a number of real samples by the method described here and a GC-FID method developed at the University of Antwerp, for arabitol, levoglucosan and mannitol. Figure 5.11 shows the correlation graph for levoglucosan, as an example. Only in two samples out of 23 did the levoglucosan values differ by more than 20%, and only in one sample out of 15 for mannitol, and four out of 15 for arabitol. The average differences were 16, 9 and 15% for arabitol, levoglucosan and mannitol, respectively. Table 5.3 summarises the correlation data for these comparisons.

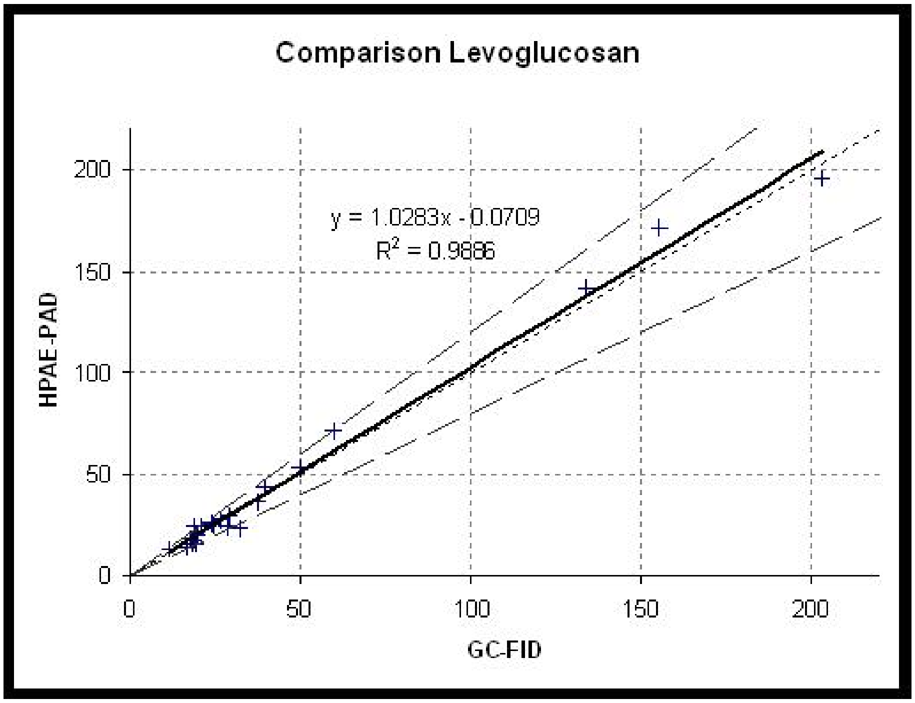


Figure 5.11: Comparison between the GC-FID and HPAE-PAD (with Dionex PA-1 column) results, concentrations in ng m^{-3} (dashed lines represent ± 15%.)

5.2.5 Stereoisomers

Of the compounds considered in method development (the 13 sugars included in routine analysis: xylitol, arabitol, levoglucosan, sorbitol, mannitol, mannosan, galactosan, arabinose, galactose, glucose, mannose, fructose and sucrose) and the other componds tested (glycerol, erythritol, xylose, maltose, trehalose (mycose), 2-methyerythritol and 2-methylthreitol) some are structural isomers. Those are glucose, galactose, mannose and fructose ($C_6H_{12}O_6$), arabitol and xylitol ($C_5H_{12}O_5$), sorbitol and mannitol ($C_6H_{14}O_6$), sucrose, maltose and trehalose ($C_{12}H_{22}O_{11}$), arabinose and xylose ($C_5H_{10}O_5$), levoglucosan, mannosan and galactosan ($C_6H_{10}O_5$). The method development above showed that no co-elution problems could occur from this kind of isomerism.

Problems with stereoisomers could, however, arise (e.g. D- and L-glucose not having the same retention time). Enantiomers (stereoisomers that are nonsuperimposable complete mirror images of each other) (mainly annotated as D- and L-, or (+)- and (-)-), should show no differences in retention times since the only property that differs from one form to the other is the ability to rotate plane-polarised light. Anomers (α- and β-), which are diastereoisomers, have different chemical properties. Since both forms are interchangeable in aqueous solutions, two different peaks for the same sugar should be noticed if those actually had different retention times. Since this was not the case, it is assumed that anomers of the same compound do not have different retention times.

Thus, though not all different forms of enantiomers and anomers were tested, it is known that such isomers do not have different retention times. In real samples, all the different forms (anomers and enantiomers) are present in the peak of the compound.

Chapter 6

Determination of cellulose in atmospheric aerosol

This determination was carried using an enzymatic procedure. The biodegradation of cellulose is an essencial step in the carbon cycle, by which the carbon balance of the biosphere is maintained. The enzymes which perform this function are collectively known as cellulases. The term 'cellulase' usually refers to a mixture of enzymes rather than a single enzyme. These are produced by a variety of microorganisms (bacteria, fungi, ...) and also by higher plants and some invertebrate animals. [309]

Cellulases' main functions are to serve as morphogenic agents (weaken the cellulose-rich cell wall in preparation for growth, differentiation or abcissions), as invasive agents (facilitate the penetration of pathogens into the plant) or as digestive agents (permit cellulose to be used as carbon source). [309]

Total cellulose refers to all the cellulose present in the sample; not only to that one not encapsulated by lignin and available for the enzymatic reaction. Total cellulose was derived from the determined free cellulose which accounts for 72% of the total cellulose [49]. All the results presented hereafter refer to total cellulose.

Free cellulose present in ambient aerosol was determined by the enzymatic method described by [49], excluding the alkaline peroxide pretreatment step to remove lignin. This step proved to make the quartz filter crumble, resulting in the loss of the sample.

After sampling, part of the quartz fibre filter (analysis areas reaching from 4.5 to 6.3 cm^2, depending on the number of days being pooled together) was analysed.

On a first step, the quartz fibre filter was eluted with 2.4 mL of a 0.05 M citric acid solution (pH of 4.8), containing 0.05% of thymol to prevent bacterial growth, during 45 minutes, in a ultrasonic bath. The cellulose was then saccharified by two enzymes: a *Trichoderma reesei* cellulase and an *Aspergillus Niger* cellobiase (respectively a volume of 8 μL and 0.8 μL diluted to 80 μL each was added) during 24 hours at the temperature of 45°C. pH and temperature are the ideal for the enzymatic saccharification reaction.

The D-glucose yield of the enzymatic reaction was previously tested using weighed solid cellulose standards. After stopping the saccharification by denaturising the enzymes (10 minutes in an 80°C bath - minimum) and centrifuging, the supernatant was collected in order to determine D-glucose.

D-glucose was determined using a modified test-combination by Boehringer Mannheim GmbH / R-Biopharm. Glucose was phosphorylated to glucose-6-phosphate (G-6-P), through a reaction with adenosine-5'-triphosphate (ATP) catalysed by the hexokinase (HK) enzyme. Subsequently, the evolved G-6-P was oxidised by NADP (reaction catalysed by the enzyme Glucose-6-Phosphate dehydrogenase–G6P-DH) to gluconate-6-phosphate, with the formation of NADPH, which was stoichiometrically proportional to the amount of D-glucose originally present.

$$D - Glucose + ATP(+HK) \longrightarrow G - 6 - P + ADP \tag{6.1}$$

$$G - 6 - P + NADP^{+}(+G6P - DH) \longrightarrow gluconate - 6 - phosphate + NADPH + H \tag{6.2}$$

A series of reagent blanks was performed with every batch of samples. The increase in NADPH was measured by absorbance at 340nm (absorption maximum for NADPH), read against distilled water. The concentration of D-glucose can be calculated as follows:

$$C = \frac{V \times MW}{\varepsilon \times d \times v} \times \Delta A_{D-glucose} \tag{6.3}$$

where V is final Volume in mL
MW is the molecular weight of glucose
ε is the extinction coefficient of NADPH at 340 nm (6300 l $\times$ mol^{-1} $\times$ cm^{-1})
d is the light path, in cm
v is the sample volume, in mL

Since the glucose not yielded by the enzymatic reaction was measured along with the product of the saccharification, cellulose values needed to be corrected. Glucose present in aerosol samples was measured by means of a High pH Anion Exchange separation column coupled with Pulsed Amperometric Detection (HPAE-PAD) (see Chapter 5), the result of this analysis was subtracted to the result of the enzymatic breakdown of cellulose analysis.

6.1 Method optimisation and validation

6.1.1 Test of the D-glucose determination

The D-glucose determination was tested using D-glucose standards at low concentrations. Plots of the D-glucose determined (y-axis) and the D-glucose actually in the sample (x-axis) for two different experiments (16 determinations at 8 concentration levels and 12 determinations at 4 concentration levels) are plotted in figure 6.1. Correlations were high in both cases (0.94 and 0.99), with slopes close to unity (0.99 and 1.05). Also, for the experiment shown on the left of figure 6.1, the extinction coefficient ε for D-glucose was calculated using the slope of the plot of the signal read against the D-glucose concetration. The slope (signal over concentration in mg L^{-1}) was 0.03311. The computed ε, using the above equation, was then 6590 $\frac{L}{mol \times cm}$, close to the theoretical value of 6300. In another experiment, with only 5 data points, the calculated ε was 6109 $\frac{L}{mol \times cm}$.

6.1.2 Procedure optimisation

Parameters such as volume extraction, extraction time and mixing during digestion were tested. Results are displayed in Table 6.1. The starting point was 15 minutes extraction time, 3 mL extraction volume and no mixing. Results showed that the method was optimised for 2.4 mL (higher signal and better repeatability with sufficient extraction solution present

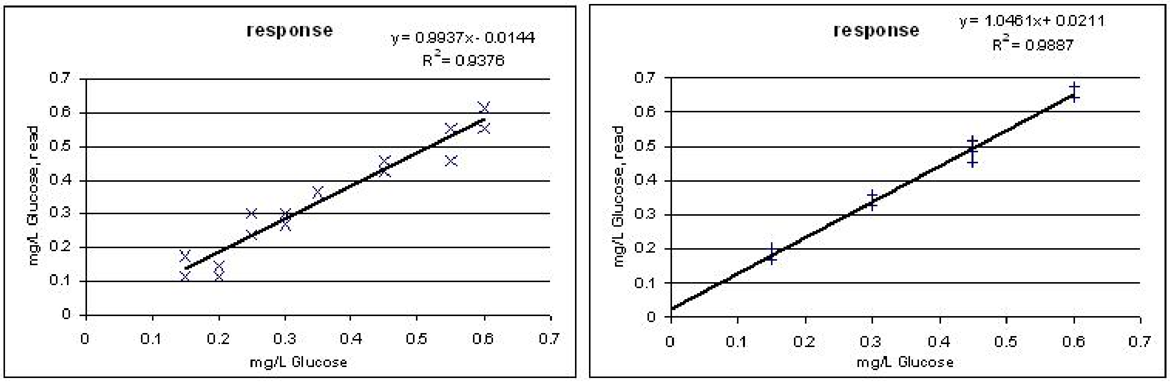


Figure 6.1: Tests of the D-glucose determination

to cover the whole material), 45 minutes extraction time (both 30 and 45 minutes are better than 15 minutes and are not significantly different in terms of rsd but 45 minutes was chosen for showing better rsd within blanks) and no mixing.

Also, Student's t-test was applied on the mixing, volume and the two time tests. For those tests, a normal distribution of the variables and equal variances between pairs of datasets were assumed. As shown on Table 6.1, the two different means obtained for each test were not statistically (95%) different.

6.1.3 Whole procedure repeatability – real samples

The repeatability of the whole procedure was tested analysing different aliquots from the same filter extracted separately (different extraction) and aliquots of the same extract (same extraction).

Same extraction relative standard deviations were expected to be very low, and were indeed when tested with a 15 minutes extraction (0 and 2.4%). Due to this very high repeatability, this test was not carried further. For the final settings, different extraction relative standard deviations for samples analysed in same batches was 7.16%, while for analysis in different batches (2 × 4 measurements), it was 7.62 and 15.9.

Relative standard deviation values were rather high in both cases (same extraction and different extraction), but this was not a surprising result. Cellulose itself is heterogeneous in nature, different parts of its constituent fibrils displaying widely different accessibilities to the same reagent. [75]

Also, a standard addition test was conducted. Results are shown in figure 6.2. The data points correlate well ($R^2 = 0.85$) and at the origin (0 μg Cellulose added), the y-axis value is 1.177 μg Cellulose. The raw sample (without added cellulose) was measured 6 times, the result is 1.37 ± 0.215 μg Cellulose (average ± standard deviation). However, the slope of the linear regression is not one. This could be due to the method's variability, but also to possible matrix effects which would hinder the use of a calibration curve. This is not the case in this determination, where an average saccharification efficiency is used.

Table 6.1: Cellulose optimization and repeatability tests.

	EV mL	ET min	rsd DE %	rsd BW DE %	rsd SE %	*n*	*t*	*DF*	*theoretical 95% t*
	2	15	16.2			2			
	2.5		26.6			3			
	3		14.0			3			
	9	15			2.4	3			
	9				0.0	3			
time 1	3	15	48.40	8.75		8	*0.103*	*14*	*2.14*
		30	23.28	5.61		8			
mixing	3	30	14.53	2.62		8	*0.032*	*30*	*2.04*
non-mixing			19.17	2.70		9			
SA	3	30	15.69	2.82					
volume	3	30	8.41	4.03		9	*-0.118*	*16*	*2.11*
	2.4		6.46	3.67		9			
time 2	2.4	30	6.52	12.95		6	*1.46*	*22*	*2.07*
	2.4	45	7.16	1.87		7			
different batches	2.4	45	7.62			4			
			15.97			4			

EV is the extraction volume, ET the extraction time and rsd is the relative standard deviation (relative to the blanks when BW is indicated).
DE is different extraction and SE stands for same extraction.
n is the number of samples
t is the Student's *t* statistic, calculated for equal sample sizes and equal variances (*time 1* and *volume*) and for unequal sample sizes and equal variance (*time 2* and *mixing/non-mixing*).
DF are the corresponding degrees of freedom.
theoretical 95% t is the inverse of the Student's *t* distribution for 5% probability and the corresponding degrees of freedom. SA are the results of the repeated measurments of the sample (no cellulose added) used for the standard addition test.
Punch areas were 6.3 cm^2, except for the *same estraction* experiments where the punches area were tripled, as was the extraction volume.

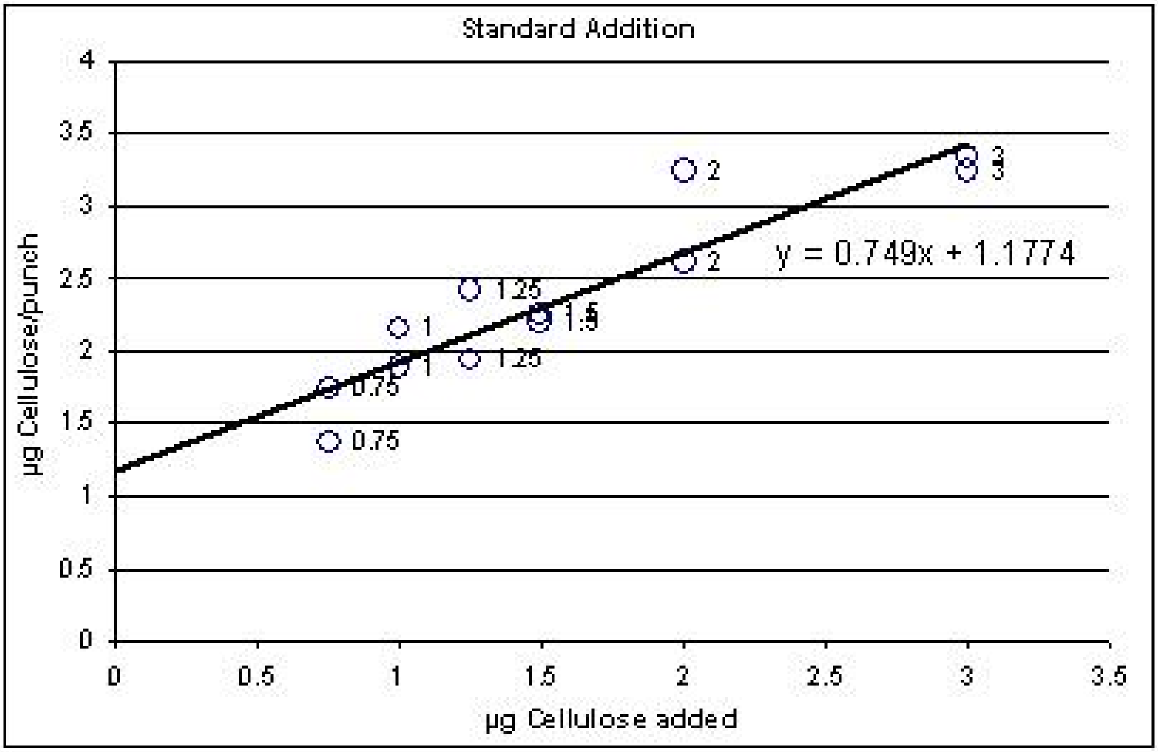


Figure 6.2: Test of standard addition for cellulose. Added mass of cellulose (in μg) is indicated by each data point.

Chapter 7

Other methods used

7.1 Carbon determinations

7.1.1 CARBOSOL samples

Carbon determinations used in the CARBOSOL project were done using a thermal-optical method as explained by Pio *et al.* (2007) [310]. The system included a quartz tube with two heating zones, a laser, and a nondispersive infrared (NDIR) CO_2 analyser. Filter samples were first exposed to HCl vapors for several hours to remove carbonates. The filter was then transferred within the first heating zone, which can be heated up to 900°C. The second heating zone, filled with cupric oxide (CuO), was maintained at 700°C. Quantitative combustion of volatilised carbon to CO_2 was achieved in the second heating zone, where O_2 is added. During heating, the blackness of the filter is monitored by measuring light transmittance through the filter sample with a pulsed laser beam. The transmittance initially decreases with heating due to charring of organic matter, and then increases again, as the char is combusted. The cut-point between OC and EC is defined as that point in the thermogram at which transmittance has returned to the value it had before charring. [111, 310]

7.1.2 AQUELLA samples

The determination of total carbon (TC) was done measuring the CO_2 evolved from the combustion, in oxygen and at 1000°C, of all the material on the filter. Non-dispersive IR photometry (NDIR, Maihak) was used for this determination. The same apparatus was used to determine elemental carbon (EC), but the filters were previously heated at 340° C so that it was free of all the organic matter [311]. Carbonate carbon (CC) was determined as the last form of carbon to be released as CO_2 in the thermo-optical gradient temperature method method, at temperatures higher than 550° C [312, 313]. Organic carbon (OC) was computed as the difference between TC and the sum of elemental and carbonate carbon (EC+CC).

Part III

Results

Chapter 8

The CARBOSOL project

The aerosol collected on filters at six background european sites (as explained in 4.1) were analysed by different project partners within the CARBOSOL framework. For the saccharidic analysis, however, the first method used proved inaccurate (see 5.1). After the method improvement had led to a method with a satisfying performance, it was necessary to reanalyse the filters. Because of time limitations, the weekly original time resolution had to be dropped in favour of a monthly one. This was done by filter pooling: aliquots of filters (one week continuous collection) were pooled together into monthly samples (aliquots from up to six filters). Filters whose start and end date did not belong to the same month were allocated to the month within which they had sampled more time.

8.1 Assessing the impact of biomass combustion on the European aerosol background using levoglucosan levels

The results presented in this section have been published as *Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background* by Hans Puxbaum, Alexandre Caseiro, Asunción Sánchez-Ochoa, Anne Kasper-Giebl, Magda Claeys, András Gelencsér, Michel Legrand, Susanne Preunkert and Casimiro Pio, in Journal of Geophysical Research, Vol. 112, D23S05, doi: 10.1029/2006JD008114, 2007.

The author's task in the referred publication was to analyse the samples for saccharidic compounds using the method explained in Chapter 5 as well as preparing text, figures and tables for the publication.

8.1.1 Field blanks and detection limits

For deriving the detection limit (LOD) of the complete analytical procedure and to check for potential contamination during the shipping, storage, sampling and assembling of the filter holder, field blanks were taken along with the samples at every sampling site. The detection limits were determined by taking three times the standard deviation of the field blanks and normalising them to an average air volume collected for the weekly samples. This volume varies between the sampling sites. The average sampled volumes were 10081 Nm^3 for AZO, 10691 Nm^3 for AVE, 8025 Nm^3 for PDD, 7380 Nm^3 for SIL, 3019 Nm^3 for SBO and 4457 Nm^3 for KPZ. The practical detection limits achieved for levoglucosan determinations at the CARBOSOL sites, based on 3 standard deviations of the variation of field blank samples was in the range of 0.7–0.2 ng/m^3 air equivalent (for weekly samples with 3000–10000 m^3 sample volume) and aliquots of 0.7–1.3% of the filter area for the determination of levoglucosan.

The measurement of the field blank filters was done prior to the method development described in 5.1. When applying the method detection limits reported in 5.2.1 to the volumes above and considering the average areas of the filter aliquots pooled together for analysis, the procedure LOD (in ng m^{-3}) can be calculated as follows:

$$LOD_{procedure} = LOD_{method} \times EV \times \frac{Total\ area\ (cm^2)}{Pooled\ area\ (cm^2)} \times \frac{1}{Sampled\ volume\ (m^3)} \tag{8.1}$$

EV is the extraction volume (mL). LOD$_{method}$ is the LOD of the analytical method as given in Table 5.2 (μg mL^{-1}). The total area is the sum of the areas of the filters (one week continuous sampling) whose aliquots are pooled together into monthly samples. The pooled area is the sum of the area of the punches from the filters (one week continuous sampling) analysed together. The overall procedure LODs were in the range 0.45–2.69, 0.62–3.70 and 0.11–0.66 ng m^{-3} for levoglucosan, mannosan and galactosan, respectively (see Table 8.1). Note that since average values were used, these LODs are just an indication. Indeed, it is possible that for a single pool, though the analysis result (in μg analyte per mL of extract) was above the analytical method LOD (reported in Table 5.2), the final computed values (in ng m^{-3}) was below the procedure LOD calculated as explained here.

For these measurements, filter aliquots of the weekly samples were pooled together into monthly pools (punches from up to 6 weekly samples). Only 9 out of 133 monthly pools were below the LOD (3 out of 21 at AZO and 6 out of 23 at SBO).

8.1.2 Levoglucosan annual averages at the CARBOSOL sites

Table 8.2 summarises the average, minimum and maximum values, as well as summer and winter averages for levoglucosan at all six sampling sites. These values vary considerably between the sampling sites and the seasons (Table 8.2). Three sites are situated at low altitude level and three at high altitude level. At low level are the Atlantic background site AZO, the coastal semiurban site AVE and the central European rural site KPZ. At the Atlantic background sampling site AZO, the lowest concentrations of levoglucosan were observed. The biannual average at AZO was around 5 ng/m^3 with a range of <1.1–19 ng/m^3. At the two other low-level sites, AVE and KPZ, the concentration levels of levoglucosan were around a factor of 60–100 higher than at the Azores. At AVE, the biannual average was 517 ng/m^3, with a range of 20–1651 ng/m^3, while at KPZ the biannual average was 309 ng/m^3, with a range of 13–922 ng/m^3.

The highest biannual average concentration of levoglucosan at the mountain sites was observed at SIL, a rural site at the lowest elevation of these sites (1205 m a.s.l.). Here, the biannual average was 24 ng/m^3 with a range of 7–56 ng/m^3. At the next higher site PDD (1450 m a.s.l.), an average of 17 ng/m^3 with a range of 2–47 ng/m^3 was noted, while at the free tropospheric background site SBO (3106 m a.s.l.), an annual average of 8 ng/m^3 with a range of <1.2–56 ng/m^3 was observed. The SBO sampling site is representative for the free troposphere, in particular during the cold season [297].

The remote Atlantic site AZO and the free tropospheric site SBO exhibit some similarities with regard to the concentrations of levoglucosan. In particular, the average of the biannual data set for SBO is relatively close to that of AZO. The winter averages are at SBO around a factor of 2 higher than at AZO, while summer averages are around a factor of 5 higher.

Table 8.1: Limits of detection (LOD) expressed as ambient air concentrations (STPC) (ng/m^3) for the six CARBOSOL sampling sites.

	method LOD (ppm)	AZO	AVE	PDD	SIL	SBO	KPZ
avg sampled volume		31140	45856	30948	31551	11754	16154
avg analysed area		4.2	3.0	4.3	3.3	4.3	3.5
avg total area		1404	1738	593	678	609	1506
n ° of pools		21	24	20	24	23	21
n ° of pools < LOD		3	0	0	0	6	0
Xylitol	0.004	0.13	0.15	0.05	0.08	0.14	0.31
Levoglucosan	0.034	1.10	1.28	0.45	0.67	1.24	2.69
Sorbitol	0.017	0.55	0.64	0.23	0.34	0.62	1.35
Mannosan	0.047	1.51	1.76	0.62	0.93	1.70	3.70
Galactosan	0.008	0.27	0.31	0.11	0.16	0.30	0.66
Arabitol	0.010	0.31	0.36	0.13	0.19	0.35	0.75
Mannitol	0.022	0.71	0.83	0.29	0.43	0.80	1.74
Arabinose	0.005	0.16	0.19	0.07	0.10	0.18	0.40
Galactose	0.020	0.64	0.75	0.27	0.39	0.73	1.58
Glucose	0.028	0.89	1.04	0.37	0.55	1.01	2.18
Mannose	0.018	0.59	0.69	0.24	0.36	0.67	1.44
Fructose	0.033	1.06	1.24	0.44	0.65	1.20	2.61

The average sampled volume is the average of the sum of the sampled volumes for each weekly sample which are pooled together.

The average analysed area is the average of the sum of areas of the sample aliquots which are pooled together into monthly pools.

The average total area is the average of the sum of the weekly filter areas which are pooled together into monthly pools.

The extraction volume was 3 mL.

n ° of pools < LOD is the number of pools below the detection limit for levoglucosan.

Table 8.2: Levoglucosan concentrations for the CARBOSOL campaigns.

	AZO	AVE	PDD	SIL	SBO	KPZ
average	5.2	517	17.0	24.4	7.8	309
minimum	<1.1	19.6	1.6	7.2	< 1.2	13.0
maximum	19.2	1651	46.5	55.5	55.6	922
summer	2.0 (2.3)	31.5 (76.3)	7.1 (11.4)	12.3 (16.9)	10.2 (5.5)	21.1 (66.3)
winter	6.6 (8.5)	1290 (957)	18.3 (21.6)	33.7 (32.0)	12.4 (9.9)	653 (576)
w/s	3.3 (3.7)	41.0 (12.5)	2.6 (1.9)	2.7 (1.9)	1.2 (1.8)	31 (8.7)

Summer: First number is the average of June, July and August; number in brackets is the 6 month average (April–September).
Winter: First number is the average of December, January and February; number in brackets is the 6 month average (October–March).
w/s is the winter/summer ratio.

SBO receives air masses from lower levels during the warm season [314], which leads to higher background levels, than the lateral transport from the continents to the Azores.

Winter/summer ratios were highly variable between the sites. At AVE and KPZ, a strong winter dominance was observed with a winter/summer ratio of 41 and 31, respectively. At AZO, winter values were around three times higher than summer ones, while at the elevated sites, winter levels were 1.2–2.7 times higher than summer ones. The winter/summer ratio decreases with increasing elevation (Table 8.2).

8.1.3 Seasonal variation of the atmospheric levoglucosan concentration

The annual cycles of levoglucosan at the CARBOSOL sites are presented in Figure 8.1. More or less pronounced seasonalities with winter or early spring maxima were observed at all sites, except for SBO. AZO is a maritime background site with very small local emission sources; hence the observed levoglucosan concentrations were low. However, a seasonality with a winter maximum was observed in the first year of the biannual cycle, whereas in the second year hardly any seasonality was evident. The wintertime increase may originate from local effects or from long-range transport.

At the AVE site, the most pronounced seasonal variation of all sites was observed for levoglucosan, with highest concentrations in winter and lowest ones in summer (Figure 8.1). AVE is a coastal semi-urban place, with moderate winter temperatures of around 10°C. The use of wood for domestic heating is common on the countryside in northern Portugal. For KPZ the seasonal variation is also pronounced, with winter maxima and summer minima (Figure 8.1). The winter/summer ratio as shown in the previous subsection is lower than in Aveiro (31 compared to 41).

At the elevated sites PDD and SIL, the seasonal cycles of levoglucosan were also quite pronounced, with maxima in early spring (March). The annual cycle at SBO showed unexpected peaks in December 2002 and March 2003 (Figure 8.1). Either a local influence from the valley below the Sonnblick Observatory, or transport events may have triggered such elevated levels.

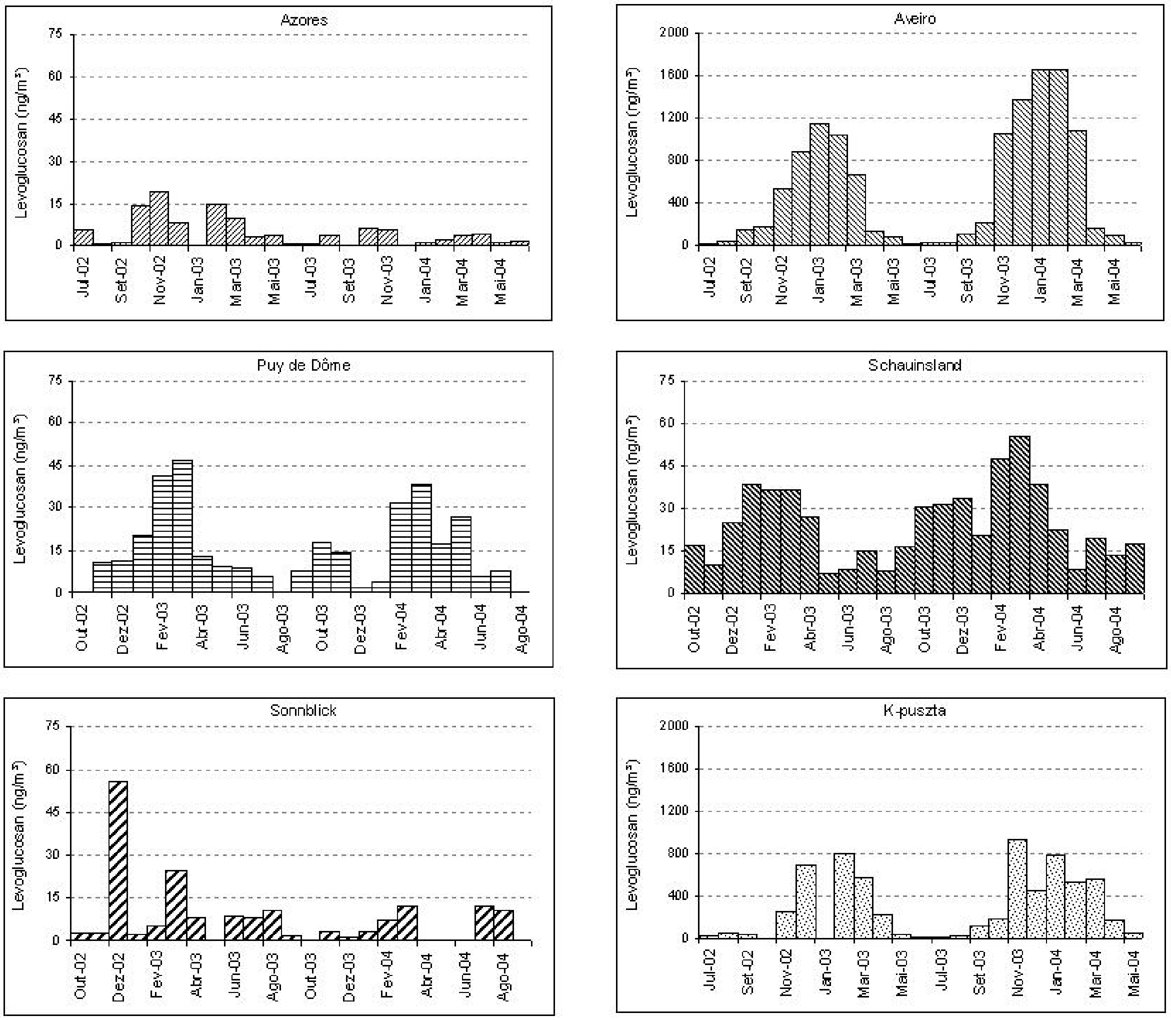


Figure 8.1: Annual cycles for levoglucosan at CARBOSOL sites.

8.1.4 Contribution of Levoglucosan-C to OC

The average contribution of levoglucosan-C to OC for the CARBOSOL sites is summarised in Table 4. The biannually averaged contribution of levoglucosan-C to OC for all sites varied between 0.7% (SBO) and 3.2% (AVE). The higher contributions of levoglucosan-C to OC were found at the more polluted low-level sites (AVE and KPZ). At AVE and KPZ, elevated contributions were expected because of the closeness to sources. At the more remote sites, the levoglucosan-C in OC fraction is in a narrow range between 0.7% (SBO) and 0.9% (PDD). The respective fraction at the AZO site is similar to the elevated SIL site. The relatively weak variation of levoglucosan-C to OC ratios at the remote sites indicates that biomass smoke is a ubiquitous constituent in the European background aerosol. In particular during winter, the relative fraction of levoglucosan-C in OC is in a range of 1.3–6.1% at the CARBOSOL sites (Table 8.4). During summer the relative fraction is between 0.1 and 0.5%.

8.1.5 Contribution of Biomass Smoke to OC and OM

Concentrations of levoglucosan in fine particle ($PM_{2.5}$) emissions from fireplace combustion of wood and for wood stoves in different regions of the United States were reported by Fine and co-workers and Schauer and co-workers. [87, 88, 315, 316, 198] Schmidl *et al.* [109] reported levoglucosan concentrations in PM_{10} emissions from wood stove combustion of common austrian woods. The results of these studies are summarised in Table 8.3. The conversion factor $\textit{Biomass smoke OC} = \textit{levoglucosan} \times 7.35$ (recommended value for the U.S. [88]) was used for all sites, except AVE. For AVE we employ the factor 6 which is on the lower range of the assumed variability of the factor. This decision was made because of the different make-up of the portuguese forest in regard the central-european forest, namely the important presence of eucalyptus, which has a low OC/levoglucosan ratio (see Table 8.3). [142, 198]

Table 8.3: OC and levoglucosan in fine particulate matter from different types of biomass combustion compiled from recent studies

	fuel	*OC*	*levoglucosan*	*ref*
US conifers	apache pine	47^c	41^a	[141]
PM_2	california redwood	3^c	11^a	
	Douglas fir	3^c	16^a	
	Eastern white pine	35^c	57^a	
	Lodgepole pine	5^c	15^a	
	Montezuma pine	16^c	28^a	
	Mountain hemlock	3^c	3^a	
	Noble fir	3^c	19^a	
	Pacific silver fir	21^c	41^a	
	Ponderosa pine	1.5^c	3^a	
	Port Orford cedar	32^c	44^a	
	Sitka spruce	11^c	10^a	
	Western white pine	2^c	0.4^a	
US deciduous	Eucalyptus	2^c	30^a	[142]
trees	Oregon maple	25^c	18281^a	

	fuel	*OC*	*levoglucosan*	*ref*
PM_2	Red alder	10^c	9785^a	
	Silver birch	19^c	23229^a	
	Dwarf birch	4^c	2321^a	
Fireplace				[198]
Southern	pine	56	258 (1375^a)	
US	oak	59	234 (706^a)	
PM_{10}	Eucalyptus	44	522 (1940^a)	
Fireplace				[87]
NE–US	hardwood	86-88	109-168	
$PM_{2.5}$	softwood	73-106	52-96	
Fireplace				[88]
S–US	hardwood	74-85	99-159	
$PM_{2.5}$	softwood	100	36-47	
Fireplace				[315]
Mid-W	hardwood	67-103	76-334	
US & W–US	softwood	80-97	10-271	
Wood stove				[316]
US	hardwood	51-59	108-213	
$PM_{2.5}$	softwood	44-78	253-408	
Wood	Beech	51	80 (4^b)	[317, 109]
stove	Oak	49	271 (13.3^b)	
Austria	Spruce	54	198 (11^b)	
PM_{10}	Larch	56	270 (15^b)	
	briquettes	41	246 (10^b)	
Asian	coconut leaves	49	57	[318]
biomass	rice straw	56	33	
	cowdung	49	39	
Wood	biomass briquettes	55	179	
stove	Jackfruit branches	54	82	
recommended averages		ratio OC/ Levoglucosan		
	US	7.35		[88]
	Austria	7.1		[317, 109]
	Portugal	6		this work

OC emission factors in % of PM. Levoglucosan emission factors in mg/g OC, ^{a} in mg/kg wood burned, ^{b} values in % w/w of PM, ^{c} values in g/kg wood burned.

The recommended conversion factor from the Fine *et al.* (2002) [88] data is 7.35. This factor corresponds to a fraction of levoglucosan in OC of 13.6%. To calculate the concentration value of biomass smoke OC, the concentration of levoglucosan is multiplied by 7.35. Table 8.4 shows the derived values of biomass smoke OC for the CARBOSOL sites.

The site with the lowest biannual average of biomass smoke OC is AZO (39 ng/m^3), followed by SBO with 57 ng/m^3, PDD with 125 ng/m^3 and SIL with 180 ng/m^3. Highest biannual averages of biomass smoke OC were obtained for KPZ (around 2300 ng/m^3) and

AVE (around 3100 ng/m^3). The highest single monthly average of biomass smoke OC was around 7700 ng/m^3 during winter in Aveiro, while at KPZ the highest monthly average was around 4800 ng/m^3.

To derive the contribution of biomass smoke to organic matter (OM), biomass smoke OC, as well as aerosol OC has to be converted to allow for the contribution of H, O, and possibly heteroatoms. The conversion factors are not precisely known, neither for biomass smoke OC nor for aerosol OC. From the Fine *et al.* papers [87, 88] on fire place emissions an OC to OM conversion factor of 1.2–1.4 can be derived, while for more primitive fuels the factor is around 1.7–1.8 [318]. As a first-order approximation 1.4 was employed as the conversion factor for biomass smoke from biomass OC and 1.7 conversion of aerosol OC to aerosol OM at background sites [319]. Table 8.4 also presents the average contributions of biomass smoke to OM, maximum and minimum values, as well as the averages of summer and winter periods.

The average contribution of biomass smoke to OM for all the sites ranges between 9 and 36%. The highest contributions were observed at the low-level sites AVE (36%) and KPZ (28%). At the high-level sites, the contribution is between 9% (SBO) and 12% (PDD). At the Azores (AZO), the contribution (12%) is similar to those at the high-level sites. Thus the spatial differences of the contributions of the biomass smoke to OM are less pronounced than the absolute concentrations of levoglucosan.

In winter, the contribution of biomass smoke to OM is generally higher than in summer. Normally in this season the temperatures are very low, the air mass exchange in the atmosphere is slower and higher emissions can be expected during the cold season. The contributions of biomass smoke to OM during winter range between considerable 18% and 68%. At the background (AZO) and mountain sites (SIL, PDD, SBO), winter levels of biomass smoke to OM are in a narrow range of 18–23%, indicating possibly similar regional emissions with respect to wood burning. At the sites that are anthropogenically affected, the contributions of biomass smoke to OM during winter are as high as 47% (KPZ) and 68% (AVE).

The biomass smoke results can be compared to data from other sites. Most available data of biomass smoke contributions to the organic aerosol are currently from receptor model studies in the USA and Asia (see Table 3.2). From these data, it can be derived that wood smoke impacts in small communities in the southeast United States is the overall dominant source for the wintry organic aerosol. As to available data from Ghent, Belgium, the contribution of biomass smoke to organic material (PM_{10}) employing emission data of Fine *et al.* [87] was estimated to be on average 35% during a 1998 winter period [220]. Relative levels of biomass combustion organic matter in the background aerosol as well as at directly wood smoke impacted sites in the eastern United States and Europe seem to be in a similar range (i.e., around 25–65%).

8.2 Saccharides in the aerosol from background sites at a West-East transect in Europe

This chapter deals with the polyols (arabitol and mannitol) and primary monosaccharides (fructose and glucose) concentrations during the CARBOSOL campaign. The concentrations were determined using the method described in Chapter 5. Carbon analysis were conducted at the University of Aveiro [310] see 7.1.1.

Table 8.4: OC from wood smoke (OC_{WS}) and wood smoke contribution to OM (OM_{WS}, in %) for the CARBOSOL campaigns.

OC_{WS} ng/m^3	AZO	AVE	PDD	SIL	SBO	KPZ
average	39	3099	125	180	55	2272
min-max	3-141	117-9903	12-342	53-408	<LOD-408	96-6778
summer	15(17)	189(458)	52(83)	90(124)	75(41)	155(487)
winter	48(62)	7739(5740)	134(159)	247(235)	91(73)	4800(4234)
w/s	3(4)	41(13)	3(2)	3(2)	1(2)	31(9)
$OM_{\%WS}$	AZO	AVE	PDD	SIL	SBO	KPZ
average	12	36	12	10	9	28
min-max	0.5-51	4.0-89	0-40	1.1-25	0-64	1.9-96
summer	2.0(3.8)	5.5(12)	1.1(3.6)	2.0(3.6)	3.8(2.2)	2.6(8.3)
winter	18(21)	68(59)	21(19)	21(16)	23(15)	47(49)
w/s	9(6)	12(4.8)	20(5.3)	10(4.4)	6(7)	18(6)

Summer: First number is the average of June, July and August; number in brackets is the 6 month average (April–September).
Winter: First number is the average of December, January and February; number in brackets is the 6 month average (October–March).
w/s is the winter/summer ratio.

8.2.1 Annual and half-year averages

The glucose two-year average ranged from 2.6 at the oceanic background site Azores to 49 ng m^{-3} at the central European plain site K-puszta. The maximum monthly value observed was 191 ng m^{-3}, at K-puszta, in May 2004.

Defining the months of October to February as the cold season and March through September as the warm one, one can see that the difference in glucose levels between warm and cold season is higher at the high-altitude sites. The difference was not as stressed at K-puszta and practically no difference between cold and warm season was observable at the Azores. The cold season levels at Aveiro were higher than the warm season ones by a factor of 3.6.

The average level for fructose varied from 0.3 to 32 ng m^{-3}. The lowest value was observed at Sonnblick and the highest in K-puszta, where the largest monthly value also occurred: 160 ng m^{-3} in April 2003.

For fructose, the difference between warm (March to August) and cold (September to February) seasons was very well marked (see Table 8.5). At the oceanic site Azores, the mean concentration during the cold season was twice higher than during the warmer months. This was the only site to show higher concentrations in the cold season. Fructose was not detected at all in the samples from the cold season in the remotest site SBO. At AVE, a site with maritime influence, the ratio between warm and cold season levels was of 30%, while it was in the range of 4–15% at the other continental sites.

The elevational distributions of glucose and fructose are shown in Figure 8.2. Continental sites showed a decrease in the glucose concentration with altitude. The same trend for fructose is observed, but SIL average fructose level is slightly higher than at PDD. Though, at the opposed ends of the elevational scale, both remotest sites revealed very low concentrations. The sea-influenced site AVE exhibited a fructose average concentration comparable to that at the remotest sites, and a glucose concentration equivalent to that of the mid-altitude mountain sites.

Bi-yearly averages of arabitol ranged from 2.6 ng m^{-3} in Sonnblick to 11.1 ng m^{-3} in K-puszta (see Table 8.6). The maximum concentration observed was 33.7 ng m^{-3} in Puy de D{ome in July 2003. Defining the months from December to April as the cold period and May to November as the warm one, it was possible to distinguish that the difference between both the cold and warm period was strongest at Puy de Dôme, followed by Aveiro and Schauinsland. The difference was less stressed in K-puszta and Sonnblick, and no difference was observed at the Azores.

The higher bi-annual average for mannitol was observed at K-puszta (17.8 ng m^{-3}), while the lowest occurred at the Azores (1.3 ng m^{-3}). Puy de Dôme exhibited the highest registered concentration, 54.7 ng m^{-3}, in May 2004. Considering the months from November to March as the cold season, and March to September as the warm one, one can verify that the seasonal variation for that annual pattern occurred principally at the high level sites (Table 8.5), while being more moderate at the low-altitude ones.

At the continental sites, the correlation (see Table 8.7) between fructose and glucose was high for PDD, SIL and KPZ (R=0.75–0.97), and moderate for SBO (R=0.55). Combined with the fact that at the mountain sites glucose and fructose both have a wide spring/summer common maximum (spring maximum at KPZ), this points towards a common biological source for both sugars at those sites. Arabitol and mannitol are correlated but some differences, as explained below, may point toward different fungal communities. Correlations between polyols and primary sugars are, at some sites, moderate, indicating a possible partial common origin. When comparing the ratio arabitol/mannitol (Table 8.7), and despite the variation, a difference between the two most remote sites (Azores and Sonnblick) and the other four sites (Aveiro, Puy de Dôme, Schauinsland and K-puszta) can be detected. While the average ratio value was higher for the two most remote sites (2.6 for both Azores and Sonnblick, with a very large variation for Sonnblick, though only 4 out of 14 observation were < 1.0), it was lower and less variable at the other sites. There, a consistent range from 0.63 to 0.78 was observed (for ascospores of four different airborne fungal species arabitol/mannitol ratios between 0.17 and 0.98 were found by Bumberger (2007) [320], Bauer *et al.*, 2008 [321] found a ratio of 0.7 in urban PM_{10} aerosol). This could possibly be due to a more aged aerosol at the Azores and Sonnblick, for which the spores had already been somehow transformed and degraded, or their relative abundance modified by deposition. At the sites with a more consistent ratio, this could possibly translate a local spores population less influenced by transport and its associated transformation, or simply another make-up of the local fungal population. Another explanation for that difference would be that there are other sources than fungal spores accounting for the polyols content of the atmospheric aerosol.

8.2.2 Seasonal trends – sources discussion

At the high-altitude sites, a seasonal trend for glucose can be observed. Figure 8.3 shows a maximum in spring/summer and a minimum in winter, which occurred in both years. Concentrations at PDD and SIL were in the same range. At SBO, glucose levels were lower by approximately one order of magnitude, though the same annual trend was also observed. At the low-altitude sites (Figure 8.4), an annual trend was not so clearly observable. For the Atlantic background site located at the Terceira Island, in the Azores archipelago, glucose concentrations were very low and hardly showed a seasonal trend. The levels exhibited at that

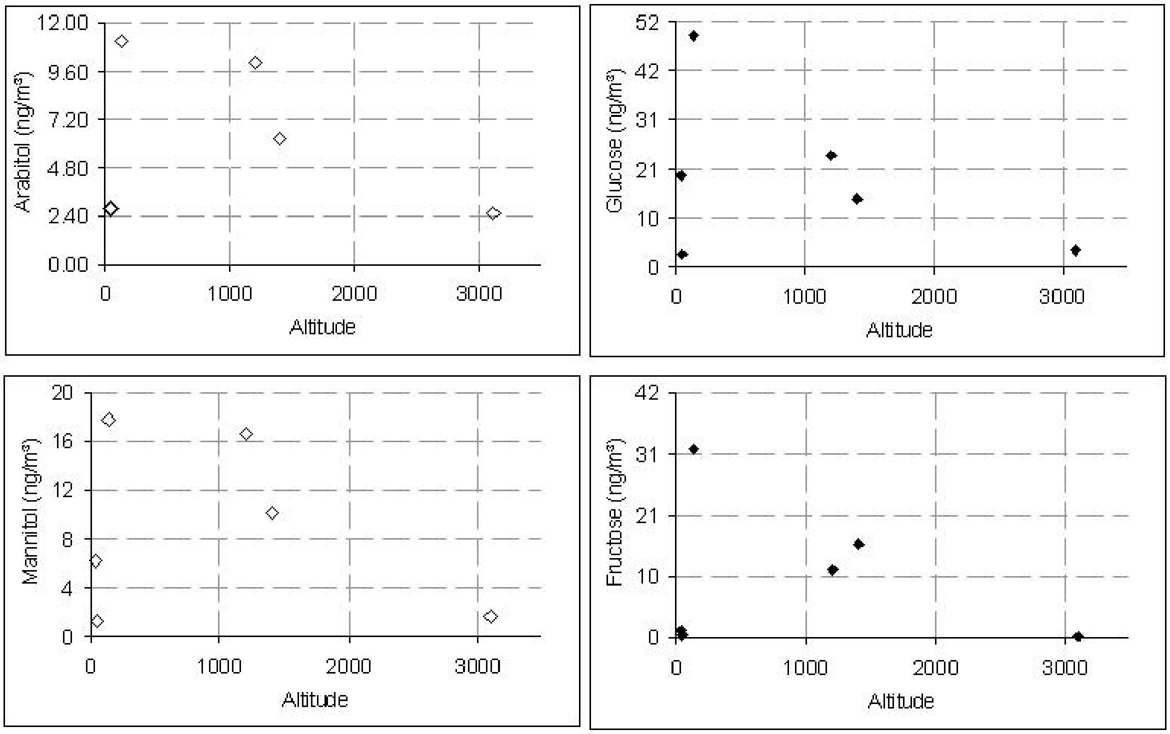


Figure 8.2: Elevational patterns for glucose, fructose, arabitol and mannitol (annual averages) at CARBOSOL sites.

Table 8.5: Glucose and fructose levels during the CARBOSOL campaign.

		AZO	AVE	PDD	SIL	SBO	KPZ
glucose	average	2.63	19.41	14.32	23.67	3.42	48.95
	max	5.70	74.70	67.07	102.95	13.77	190.73
	Oct–Feb	2.48	33.45	3.46	5.57	0.98	24.00
	Mar–Sep	2.71	9.38	24.10	36.60	4.54	64.31
	$\frac{cold}{warm}$	0.92	3.57	0.14	0.15	0.22	0.37
fructose	average	0.52	1.29	15.95	11.53	0.30	32.08
	max	3.77	5.29	104.96	61.28	4.68	156.47
	Sep–Feb	0.72	0.61	1.18	2.73	0.00	8.12
	Mar–Aug	0.36	2.03	30.72	20.33	0.75	53.86
	$\frac{cold}{warm}$	1.99	0.30	0.04	0.13	–	0.15
Glu. and Fru.	% of OC	0.42	0.15	0.58	0.57	0.13	0.64

Table 8.6: Arabitol and mannitol levels during the CARBOSOL campaign.

		AZO	AVE	PDD	SIL	SBO	KPZ
arabitol	average	2.73	2.83	6.24	10.02	2.56	11.11
	max	5.33	12.43	33.70	28.49	8.22	25.29
	Dec–Apr	2.71	0.54	1.10	2.97	1.36	5.38
	May–Nov	2.57	4.17	12.29	16.22	3.96	17.31
	$\frac{cold}{warm}$	0.95	7.74	11.12	5.47	2.93	3.22
mannitol	average	1.31	6.22	10.14	16.59	1.68	17.79
	max	3.78	23.47	54.73	50.70	5.52	54.80
	Nov–Mar	0.73	5.54	2.52	3.07	0.08	18.63
	Apr–Oct	0.51	6.70	17.75	26.25	3.01	17.16
	$\frac{cold}{warm}$	0.69	1.21	7.03	8.55	35.93	0.92
Arab. and Man.	% of OC	0.96	0.23	0.95	1.01	0.34	0.85

Table 8.7: Correlations and ratios between sugars' concentrations during the CARBOSOL campaign.

	AZO	AVE	PDD	SIL	SBO	KPZ
G./F.	5.02±7.57	4.39±4.48	2.02±1.12	5.80±12.3	3.87±2.23	2.92±3.29
min-max	0.07-24.7	0.69-8.14	0.83-4.35	0.75-55.06	2.29-5.45	0.86-8.46
summer	2.7±2.7	0.88±0.26	0.96±0.11	16±23	3.87±2.23	1.4±0.4
A./M.	2.67	0.68	0.63	0.78	2.63	0.72
min-max	1.01-5.75	0.19-1.52	0.12-1.09	0.16-1.68	0.54-12.81	0.16-1.19
G.–F.	0.18	-0.48	0.97	0.75	0.55	0.94
G.–L.^{c}	-0.29	0.74	0.46	0.12	0.85	0.50
G.–L.^{c}	-0.21	0.74	0.12	-0.16	0.85	0.37
G.^{BB}–L.	0.14	0.88	-0.29	-0.39	-0.04	-0.26
A.–M.	0.73	0.74	0.78	0.66	0.76	0.56
A.–G.	0.79	-0.23	0.73	0.28	0.38	0.23
A.–F.	0.38	0.12	0.65	-0.03	0.28	0.13
M.–G.	0.58	0.09	0.62	0.42	0.61	0.16
M.–F.	0.20	-0.04	0.42	0.40	0.19	-0.08
EF$_{BB}$ ^{Glucose}	0.75-19	0.25-0.54	0.17-6	0.69	0.25-3.5	0.14-0.77

G.^{BB} refers to glucose from Biomass Burning only.
Correlations (R) between Glucose and Levoglucosan marked with ^{c} include only cold season months.
A.–Arabitol, F.–Fructose, G.–Glucose, M.–Mannitol, L–Levoglucosan.
EF$_{BB}$ ^{Glucose} is the emission factor of glucose by biomass burning.

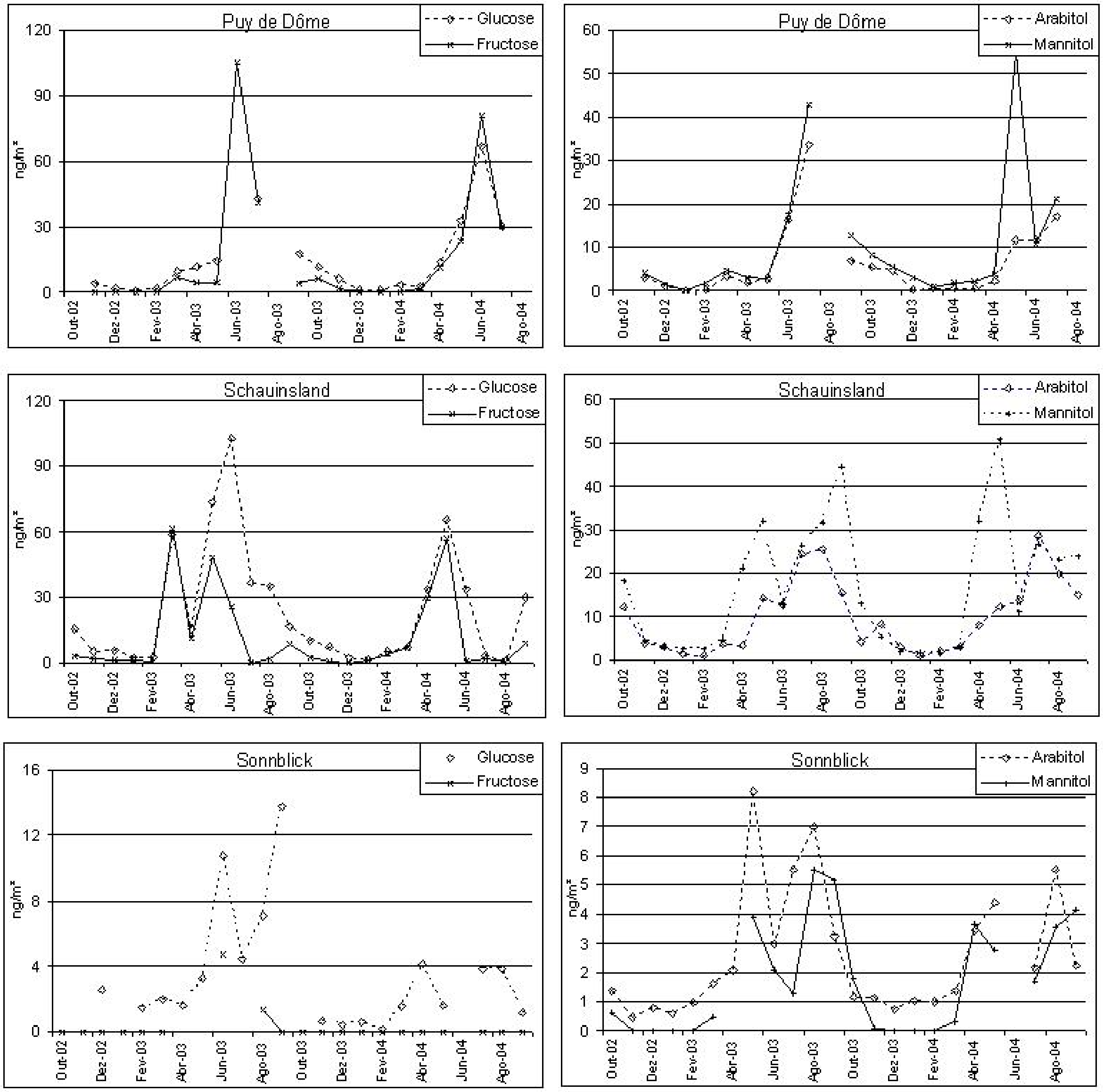


Figure 8.3: Saccharides concentrations in PM_{10} (monthly pools) at the high-altitude sites during the CARBOSOL campaign

site were even lower than those observed at the free troposphere high-altitude background site SBO, this by a factor of approximately 2, on a bi-annual average basis. At the central European site KPZ, where the higher glucose levels were observed, an annual trend was observed. Maxima occurred in May in both years, with lower concentrations during the cold season. At the other low-altitude site, AVE, a totally different seasonal pattern took place, with higher values during the cold season and lower values during the warm season. At that site, glucose concentrations were lower than at KPZ and the high-altitude sites PDD and SIL. At KPZ, fructose concentrations had a first maximum in spring and another, lower one, in August. Fructose concentrations exhibited a minimum during the colder months. Fructose concentrations were much lower at the other two low-altitude sites, AZO and AVE, with a maximum monthly value of only 5.3 ng m^{-3}. Despite such low concentrations, an annual trend was observable, with maxima in the spring and the autumn. At the high-altitude sites, fructose had a spring-summer maximum in its concentration. Levels at PDD and SIL were comparable to those that occurred in KPZ, while SBO had concentrations in the range of those at AVE and AZO. Glucose and fructose peaks in spring are probably due to pollen season.

The arabitol levels at AVE were at minimum during the winter, and started to increase at the beginning of spring to peak during the autumn (October or November). The annual cycle at KPZ is very similar, while at AZO it is very difficult to distinguish a seasonal trend. At those sites, mannitol followed, in general, the same trend as arabitol. At the high-altitude site SBO, the polyols concentrations showed a broad spring-autumn maximum as well; as they did in SIL, though peaking earlier in the year than the low level sites. PDD was somewhat different, with a peak more defined in time.

Three periods are identified where primary sugars peaked in KPZ: April-May, August and November (this last one only in 2003). The higher of them, April-May, is concurrent in time with the *Pinus nigra* flowering season and is concurrent with the onset of a broader spring-summer peak for the polyols. The August peak is coincident with a polyols summer peak. The fact that the primary sugars peaks are more localised in time that the polyols one indicates that the sources are probably different, at least to some extent: fungal spores for the polyols and either other kinds of spores or other PBAP classes for the primary sugars. Pine pollen is too large of a particle to be sampled within PM_2. The resuspension of soil dust, as proposed by Simoneit *et al.* (2004), where pollen fragments could be included, is a possible explanation.

The increase in primary sugars would be owed then to the biological material present on site due to the polinisation. For the November 2003 peak, which was also the main peak for mannitol and a clear peak for arabitol, however, the same fungal spores outburst [47] seems to be the main source.

At SIL, a first peak for glucose and fructose was observed in March 2003. This peak has no corresponding polyols concentration increase and, therefore, is probably not due to fungal spores activity. The date is somewhat early for the pollen season of spruce (not routinely monitored in Germany), the main species in the region. It is, however, coincident with the pine pollen maximum activity, though pine is only a minor species and its pollen a large particle not expected in PM_{10} (though pollen fragments might be part of PM_{10}). May 2003 is the next peak, for all four species, thus indicating the possibility of a common origin. The occurrence of a peak for the polyols at the same time as for the primary sugars indicates that fungal spores is a probable common origin. However, the onset of the 2003 grass pollen season in the nearby city of Freiburg was mid-April (Figure 8.6) showing that different origins are also

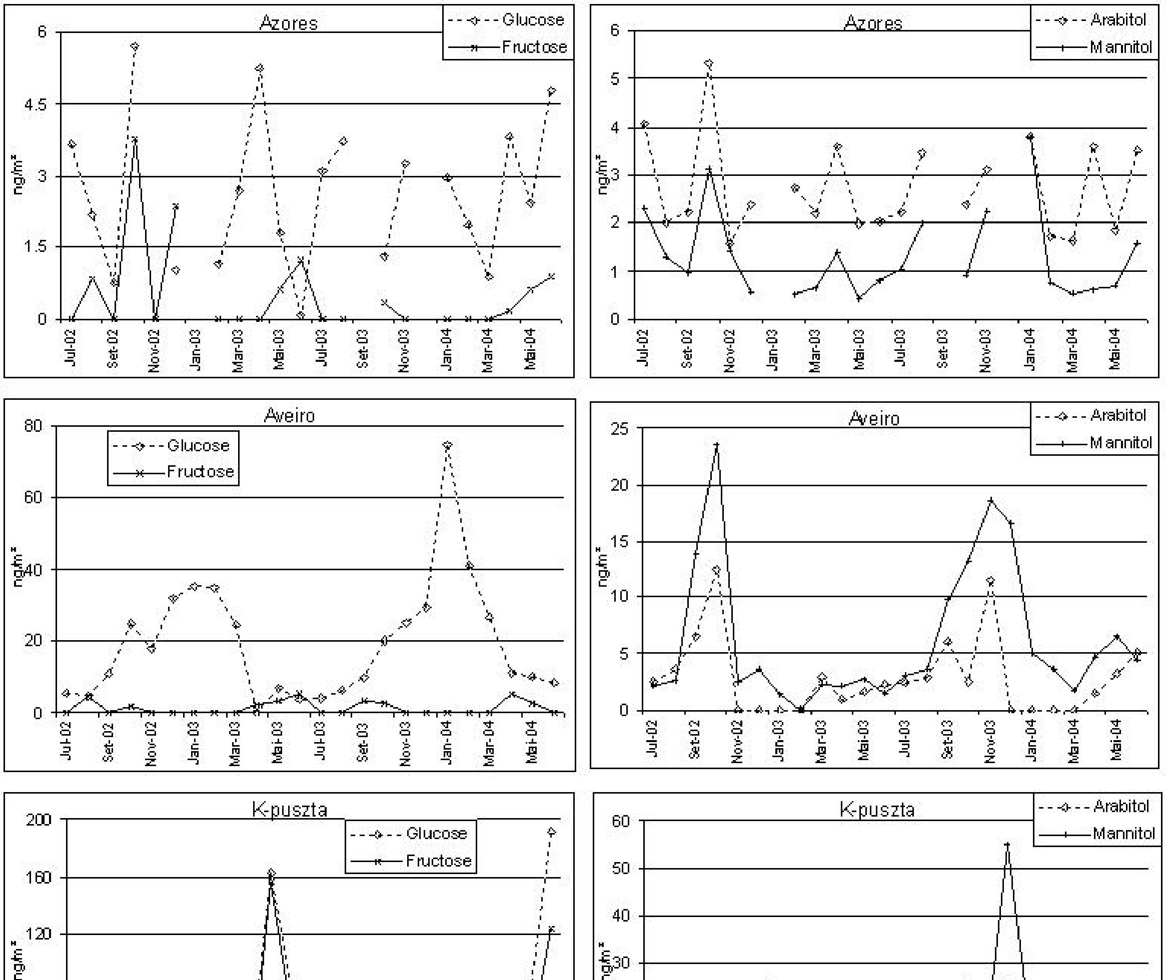


Figure 8.4: Saccharides concentrations in PM_{10} (monthly pools) at the low-altitude sites during the CARBOSOL campaign

plausible. Glucose keeps on growing in June, when polyols and fructose decrease, suggesting, as in March, that biological sources other than fungal spores are responsible. Grass pollen peaked in June in 2003, probably affecting the glucose levels in PM_{10}, or indicating that other species pollen did. Polyols showed a broad maximum in summer. Arabitol peaks in July/August, while mannitol peaks in September. These slight differences between the two polyols indicate different contributing species. The cycles fairly repeated themselves during the following year, the most noticeable difference being the lack of a glucose and fructose peak in March and June. Analysing the meteorological data, plotted in Figure 8.5, it is possible to see that the temperature in March and June in 2003 (4.1 and 17.8°C, respectively) was higher than for the same months in 2004 (0.5 and 11.7°C, respectively). It is then possible that the release of PBAPs causing the glucose peaks for those months in 2003 occurred at a slightly different time in the next year, taking place then later in the warm season. This is confirmed by the grass pollen data (Figure 8.6). Although grass pollen may not be the main contributor to glucose in PM_{10} at that time of the year, the differences in its monthly distribution between 2003 and 2004 can be viewed as a proxy for global pollen and show that the pollen production was more evenly distributed between June and July in 2004 than in 2003. Also, glucose peaked at 103 ng m^{-3} in 2003 but only at 65 ng m^{-3} in 2004, when the temperatures were lower (Figures 8.3 and 8.5)

At SBO fructose only peaked in June 2003, as did glucose, not corresponding to an increase in polyols concentration. The other glucose peaks (September 2003, April 2004 and July/August 2004) are quite in phase with mannitol, but not with arabitol, pointing to different fungal communities contributing to the $PM_{2.5}$ load. The polyols annual cycle at the high alpine site SBO was very similar to that observed at SIL, though mannitol peak does not last as long. This, together with the low concentrations, indicates that the PBAPs occurring at that site are more due to transport than to local production. Indeed, due to its altitude, the SBO sampling site lies far above the tree line and other vegetation is also quite absent. Therefore pollen and spores particles or fragments production in situ is expected to be low, being dependent on mixing and vertical transport from the ecosystems lying at lower altitudes to reach such elevation.

At PDD, the polyols distribution throughout the year is simpler than at the other mountain sites, with both polyols very much in phase, suggesting a less diverse fungal community. Another difference is that there was no polyols increase neither during spring nor autumn (except for mannitol in May 2004). Pollen, as fragments, or other PBAPs are the likely cause for the primary sugars peak in June. Figure 8.7 shows the total monthly pollen (for the genii Betula and Quercus, for the family Poaceae (grasses, Graminae) and the total pollen) mass concentration at the nearby Clermont-Ferrand station. Correlation between glucose and total pollen was very low (R^2=0.02). However, the correlation between glucose concentration and the poaceae pollen concentration was higher (R^2=0.57). Also, the time series were very similar, with the 2003 peak being not as intense as the 2004 one. This is in parallel with the findings at SIL. Glucose was anti-correlated with the other pollen types' concentrations.

Glucose had a totally different seasonal pattern at AVE. Higher $PM_{2.5}$ glucose levels in winter are due to biomass burning and are discussed in the next section. Polyols had higher values at the end of spring and autumn, which is when the leaves of deciduous trees fall, on which some fungal species live as saprophytes. Figure 8.5 shows that relative humidity was higher at the end of 2003 and beginning of 2004 than in the year before. Also, mannitol levels peaked longer at that time, but not arabitol. This is an indication that relative humidity is a factor that controls the discharge of ballistospores.

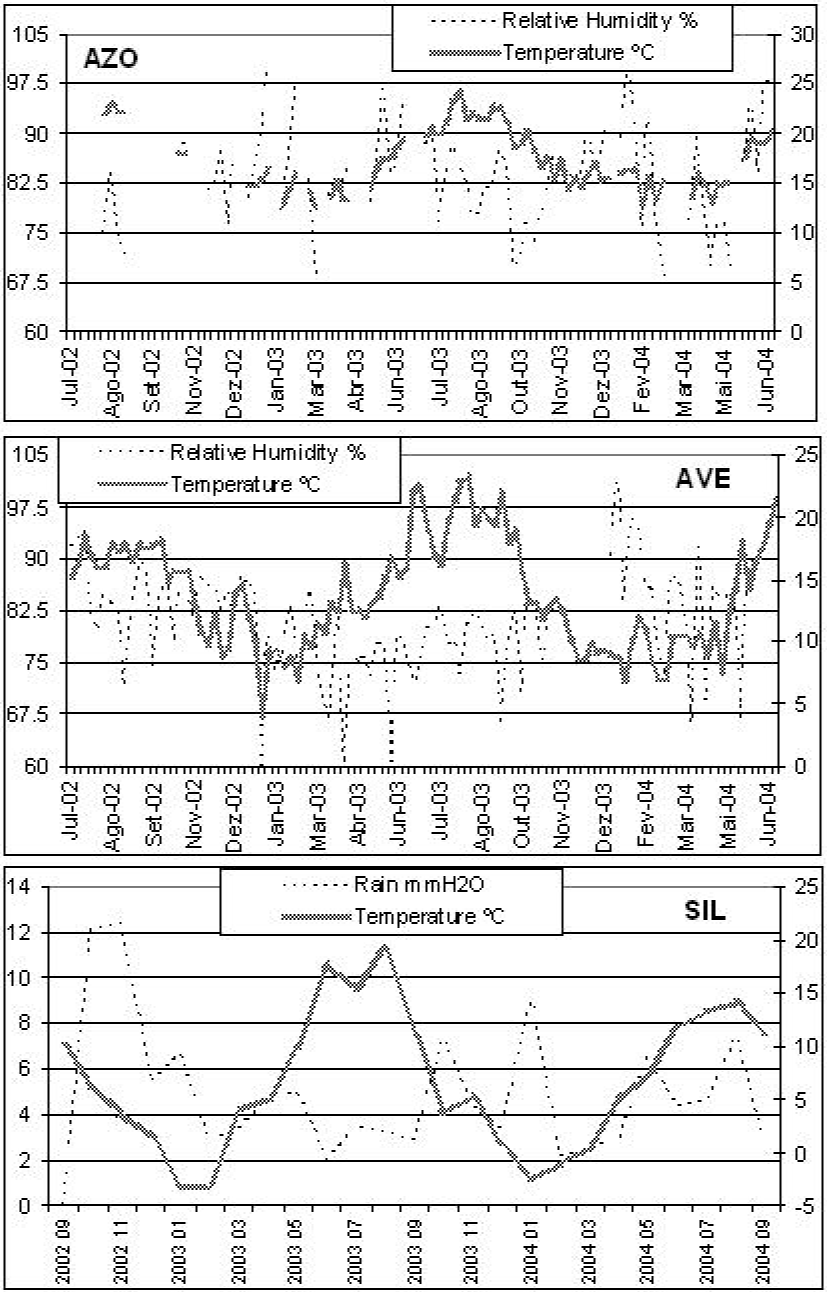


Figure 8.5: Meteorological parameters at the AZO, AVE and SIL sites. AVE and AZO: relative humidity is plotted on the left y-axis, weekly averages. SIL: rainfall is plotted on the left y-axis, monthly averages. Temperature is always plotted on the right y-axis.

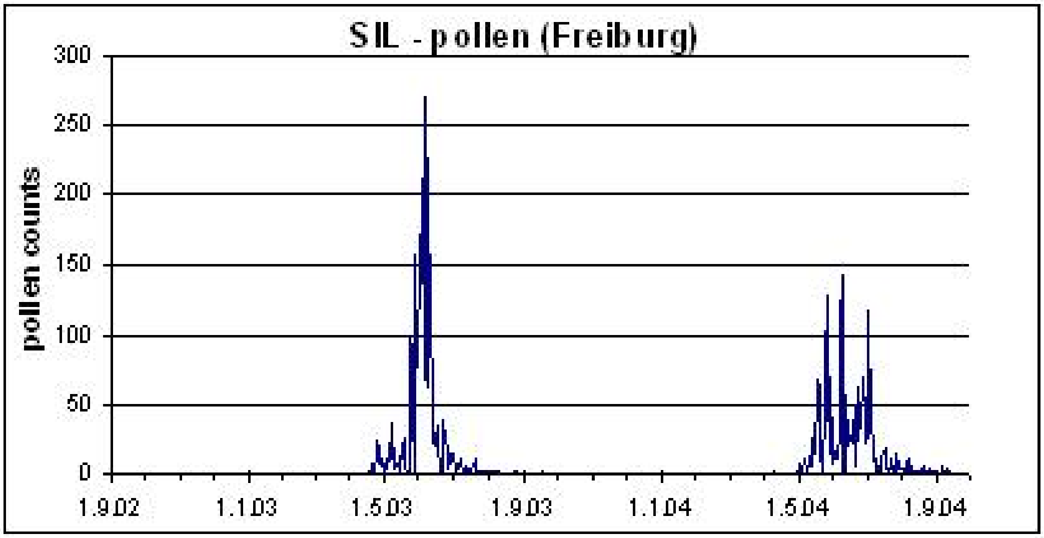


Figure 8.6: Grass pollen (daily values) counts at Freiburg (close to the SIL CARBOSOL station).

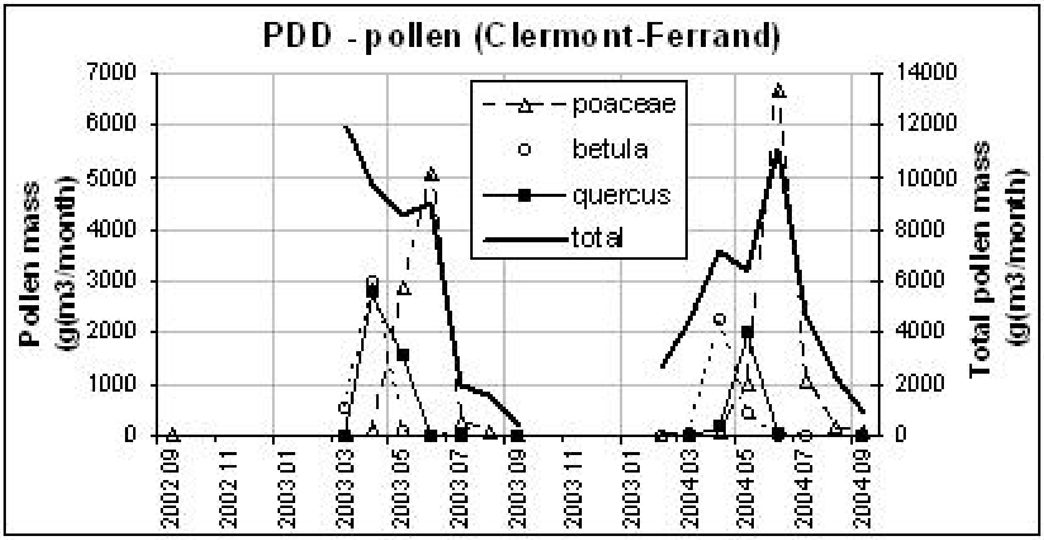


Figure 8.7: Pollen mass concentration (monthly averages) at Clermont-Ferrand (close to the PDD CARBOSOL station).

Concentrations observed at AZO were the lowest and a seasonal pattern is not identifiable. When comparing this oceanic site with the other remote site, SBO, one can see that the levels at AZO were much more constant, being higher than at SBO in winter and lower in summer. This confirms that SBO is influenced by transport from lower altitudes in summer, but lies in the free troposphere in winter. At AZO, there is possibly some continental influence, and the local or oceanic sources are expected to contribute little, though we cannot say they do not exist.

Higher glucose values during the warm season are linked to an increase in the biological activity, with a higher emission rate of primary biological particles. However, at AVE, higher glucose concentrations occurred in the cold season. The likely source for this increase was biomass burning, a source that dominates the aerosol production in the area at that time of the year (see 8.1). The high correlation between glucose and levoglucosan (R=0.88 and R=0.74 for the whole campaign and the cold season, respectively), a tracer for biomass burning, confirms this statement. The difference in the glucose seasonal trend between AVE and KPZ lies in the concentration amplitude of the warmer months. Indeed, glucose concentrations during cold months at KPZ actually reached levels that are comparable with those that occurred at AVE, thus indicating that biomass burning is also an important source of glucose during the winter, and that the biological summer sources of glucose in AVE are not as relevant as they are at KPZ (to some extent, this may also be applied to AZO). Yet, glucose and levoglucosan were anticorrelated at KPZ during the whole campaign (R=-0.26) and only slightly correlated during the cold months (R=0.50). At the mountain sites, on the other hand, no glucose winter peak was observed, pointing towards the lower importance of a wintry biomass burning at the higher elevation sites and thus a less important source for glucose. Also, when comparing winter levels, between PDD or SIL and KPZ or AVE, one can see that they were 20 to 70 times lower at the mountain sites (see 8.1).

8.2.3 Determination of the glucose emission factor by biomass burning

Schmidl *et al.* (2008) [109] referred the occurrence of glucose in aerosol from residential biomass burning, though at levels about one hundred times lower than those for levoglucosan. Using the $\frac{Levoglucosan}{PM_{2.5}}$ factor presented in section 8.1, 6 for Aveiro and 7.35 for the other sites, it is possible to derive the wood burning $PM_{2.5}$ concentration:

$$PM_{2.5}^{Biomasssmoke} = Levoglucosan \times EmissionFactor_{Levoglucosan}^{Biomasssmoke} \tag{8.2}$$

Since even in winter some glucose may originate from biogenic sources, a correction to winter glucose concentrations has to be applied. To the author's knowledge, fructose has not been reported in particulate matter from biomass burning Assuming that the biogenic relationship between fructose and glucose is constant throughout the year, and that the atmosphere of the summer months is free of particulate glucose originated in biomass burning, one can derive a factor for estimating biogenic glucose from the determined fructose values:

$$Glucose_{Biological} = Fructose \times (\frac{Glucose}{Fructose})_{June,July,August} \tag{8.3}$$

and

$$Glucose_{Biomass\ Smoke} = Glucose_{Total} - Glucose_{Biological} \tag{8.4}$$

Knowing the concentration of the particulate matter as well as the glucose concentrations whose origin is wood burning, it becomes feasible to determine the glucose emission factor from that source:

$$Emission\ Factor_{Glucose}^{Biomass\ Smoke} = \frac{Glucose_{Biomass\ Smoke}}{PM_{2.5}^{Biomass\ Smoke}} \tag{8.5}$$

Such methodology has limitations, such as varying biological emitters throughout the year will probably yield to different biological glucose to fructose ratios for different seasons. Biomass burning could also be a considerable source of PM in the summer, namely from agricultural fires or forest fires

Results are displayed in Table 8.7. For all six sites, the lower limits of the calculated range for the glucose emission factor by biomass burning seems reasonable, but the upper limit is clearly an overestimation at AZO, PDD and SBO. At SIL all but one of the ten months to which the methodology described above was applied had negative values for the estimated biomass burning glucose. This was the only site were the emission factor calculated with the correction for biological glucose was different from that calculated without that correction (0.49-15 was the EF range for SIL in the uncorrected case). The ranges found for the less remote, and more impacted by biomass burning, sites AVE ($2.5 \times 10^{-3} - 5.4 \times 10^{-3} \frac{ng\ Glucose}{ng\ wood\ burning\ PM_{2.5}}$) and KPZ ($1.1 \times 10^{-3} - 7.7 \times 10^{-3} \frac{ng\ Glucose}{ng\ wood\ burning\ PM_{2.5}}$) show good concordance. At those two sites, fructose was either not detected or below the detection limit for the colder months, thus the biogenic glucose correction is not important. These results confirm that, as explained in paragraph 8.2.2 from the seasonal trend of glucose and its correlation to levoglucosan, significant glucose emitting biomass burning only occurred in AVE and KPZ. Either because biomass is burned in such low quantities at AZO, PDD, SIL and SBO that the low mass of glucose emitted prevents it to be used as a tracer, or because the biomass burned is different in such a fashion that its emissions' composition leads to these differences. The first possibility is supported by the results from section 8.1, where it was found that biomass smoke constituted 59% and 49% of the total aerosol organic matter in AVE and KPZ, respectively, and around 15–21% at the other four sites. With such a difference between AVE or KPZ and the other sites, and the relatively low glucose emission factor by biomass burning when compared to levoglucosan, high noise is to be expected when applying the described methodology.

8.2.4 Contribution to OC

Glucose and fructose contribution to OC, combined, were up to 2.8%. Bi-annual averages were in the range 0.13-0.58% (see Tables 8.5 and 8.6). The highest value was observed at KPZ and the lowest bi-annual means occurred at AVE and SBO. Arabitol and mannitol had contribution to OC about two times more important (bi-annual averages from 0.23 to 1%), with a maximum monthly value of 1.5% (PDD, May 2004). Unlike their low concentrations, arabitol and mannitol were a quite important molecular fraction of $PM_{2.5}$ OC at AZO (0.96% on average). Figure 8.8 shows that the contribution of the 4 sugars studied to OC kept only the compounds' concentrations seasonality at PDD, SIL and KPZ, as well as at AVE for glucose, mainly due to the glucose originated from biomass burning. At those sites, the sugars contribution to OC roughly follows the annual cycle explained in section 8.2.2. At the most remote sites, AZO and SBO, no yearly seasonality is distinguished.

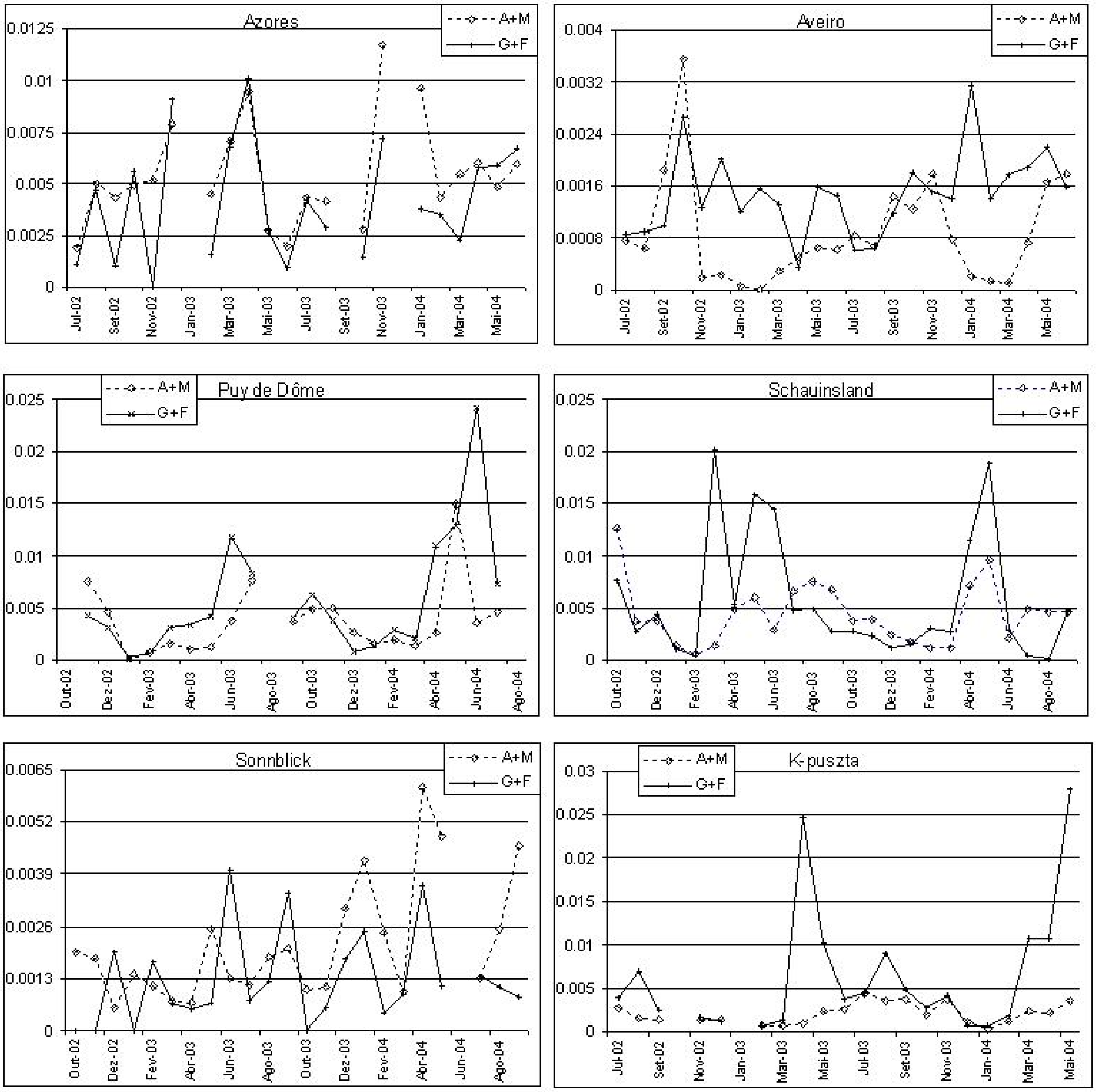


Figure 8.8: Saccharides contribution to OC (A+M refers to arabitol-C and mannitol-C, G+F refers to Glucose-C and fructose-C) during the CARBOSOL campaign

8.2.5 Comparison with other studies

Glucose concentrations observed at AVE, PDD, SIL and KPZ are within the same range as those reported by Carvalho *et al.* (2003) [190] for Melpitz, an agricultural location in Germany, during the early spring, but lower than the values from Pashynska *et al.* (2002) for Ghent [126] (see Table 3.5). Glucose levels at AZO and SBO are of the same order of magnitude as those at Hyytiälä, a remote forest site in Finland, during the summer [190]. Pashyska *et al.* (2002) [126] reported higher glucose concentrations during the warm season for the city of Ghent, as it occurred at all CARBOSOL sites except AVE and AZO. The cold season to warm season ratio for Ghent(0.25 to 0.3) was higher than that for the high level sites, but lower than that for KPZ. Values reported by Carvalho *et al.* (2003) and Pashynska *et al.* (2002) refer to PM_{10}.

At the three continental sites, PDD, SIL and KPZ, glucose levels in summer $PM_{2.5}$ are higher than levels measured by Graham *et al.* (2003) in the Amazonian toward the beginning of the dry season, when the effects of biomass burning are not important [185]. During the cold season, glucose at PDD and SIL is in the lower end of the range of values presented for the biogenic background aerosol of the Amazonian, as at AZO and SBO throughout the year. At KPZ, the warm season, when the glucose values are higher than those reported by Graham *et al.* (2003), is somehow longer than at the mountain sites, spreading from spring to autumn [185]. The concentrations of fructose measured at PDD, SIL and KPZ were in the same range than those observed at Melpitz by Carvalho *et al.* (2003) and, as for glucose, lower than those reported by Pashynska *et al.* (2002) for Ghent [190, 126]. The warm season values at those three continental sites were within the same order of magnitude than those reported for the Amazonian dry period aerosol [177]. During the cold season, they were comparable to the Amazonian wet season values reported by the same authors. At AZO, AVE and SBO, fructose concentrations were comparable to those at Hyytiälä [190] and those reported by Decesari *et al.* (2006) [177] for the Amazonian wet season. As for glucose, Pashyska *et al.* (2002) reported higher fructose concentrations during the warm season for the city of Ghent. This was the case at all CARBOSOL sites but AZO.

Chapter 9

The AQUELLA projects

9.1 Contribution of biomass burning to the austrian aerosol using levoglucosan as a tracer

In this section, besides the analysis of the results obtained by the technique described in Chapter 5, results of the carbon analysis conducted at the Technical University of Vienna on AQUELLA samples are also presented (see 7.1.2).

9.1.1 Blank filters, detection and quantification limits

A set of 101 blank filters were analysed for the whole campaign at the three regions. The three anhydrosugars considered in this section (levoglucosan, mannosan and galactosan) were not detected in any of those filters. Therefore, the detection and quantification limits were calculated using the detection (LOD) and quantification (LOQ) analytical limits of the method, see Table 5.2 [322]. The LOD is defined as three times the standard deviation of the lowest concentration standard, a level that is expected to be close to the actual detection limit [323]. The LOQ is three times the LOD. Those limits (given in μg/mL) were applied to an average extraction volume (3 mL), an average filter portion (1/32) and an average sampled air volume (approximately 750 m^3). Results are reported in Table 9.1. Also, Table 9.2 reports the number of filter pools which were below the quantification limit for each compound and each site, as well as the total number of filter pools considered for the whole year. For calculation purposes, values below the LOD or the LOQ were set to $\frac{1}{2}$ of the respective limit.

Table 9.1: Limits of detection (LOD) and quantification (LOQ) expressed as ambient air concentrations (STPC) (ng/m^3) for levoglucosan, mannosan and galactosan.

	Levo	Manno	Galac
LOD (ng/m^3)	4.5	6.1	1.1
LOQ (ng/m^3)	13	18	3.3

Table 9.2: Number of sample pools below the LOQ for levoglucosan, mannosan and galactosan during the AQUELLA campaigns.

	Levo	Manno	Galac	pools
SCH	1	12	12	51
RIN	0	10	11	52
KEN	3	12	12	52
LOB	0	19	13	48
BB	0	12	8	39
GS	0	8	9	44
DB	0	6	7	44
RU	0	11	6	39
LE	0	12	12	36
AN	0	16	13	40

9.1.2 Anhydrosugars annual averages

The annual average concentration for levoglucosan ranged from 0.12 (in the Viennese background sites SCH and LOB) to 0.48 $\mu g/m^3$ in the densely populated urban residential site GS, in Graz. Concentrations annual averages were the lowest in Vienna (0.12 to 0.16 g/m3), and the highest in Styria (0.25 to 0.48 $\mu g/m^3$). Salzburg had intermediate values (0.15-0.22 $\mu g/m^3$) (Table 9.3). Higher maximum values (individual pools) were also exhibited in Styria, and lower in Vienna, consistent with statistics of the regional of biomass fuels in Austrian countries. Differences between sites within one region were more pronounced in Graz. There, levoglucosan concentrations in the city (GS and DB) were, on an annual average basis, 1.8 times higher than in at the background site (BB). At the other two regions the differences were lower: 1.4 in Salzburg and 1.25 in Vienna, consistent with statistics of the regional of biomass fuels in Austrian countries. This is probably due to the fact that the BB site lies much more far away and is much more isolated from the city than SCH and LOB (in Vienna) or AN (Salzburg). Warm season values are comparable to those measured by [214] at rural, suburban and urban sites in the Lower Fraser valley (Northern America) and by [56] at K-puszta, a rural site in the central European plain (both in Summer and $PM_{2.5}$). Warm and cold season values are in the same range as those measured by [220] and [126] for the European city of Ghent in Belgium.

Table 9.3: Levoglucosan concentrations (μg m^{-3}), levoglucosan/mannosan ratios and correlations between the three anhydrosugars for the AQUELLA campaigns.

		Vienna				Styria			Salzburg		
		SCH	RIN	KEN	LOB	DB	GS	BB	RU	LE	AN
L.	avg	0.12	0.16	0.14	0.12	0.25	0.48	0.41	0.22	0.21	0.15
	min	BQL	0.02	BQL	0.02	0.04	0.04	0.04	0.02	0.01	0.02
	max	0.66	0.83	1.2	0.65	1.3	2.2	1.9	1.1	1.2	0.77
	winter	0.22	0.24	0.23	0.19	0.45	0.86	0.74	0.30	0.33	0.25
	spring	0.05	0.06	0.06	0.05	0.16	0.22	0.18	0.07	0.07	0.06
	summer	0.03	0.04	0.03	0.02	0.08	0.10	0.09	0.05	0.05	0.03
	autumn	0.20	0.30	0.24	0.24	0.36	0.82	0.68	0.40	0.48	0.27
	w/s	8.2	6.1	7.6	8.0	5.8	8.2	8.4	5.9	6.9	8.1
L./M.	avg[a]	5.2(6)	4.1(5.6)	4.2(5.7)	6.4(7.5)	6.4(7.7)	5.0(6.4)	4.8(4.6)	5.6(5.8)	5.4(5.7)	5.7(6)
	min-max[b]	3.7-6.5	2.9-5.7	1.9-6.2	3.3-15	5.7-7.6	2.4-7.3	2.4-7.6	4.2-7.5	3.7-11	3.0-6.3
		(2.7-13)	(2.0-15)	(1.7-18)	(3.3-24)	(2.9-19)	(2.4-19)	(1.6-7.6)	(4.0-13)	(1-13)	(3.0-11)
L./G.	avg[a]	19(21)	16(18)	11(22)	22(30)	18(22)	16(58)	13(18)	20(25)	20(28)	24(24)
c.	L.-M.	0.94	0.91	0.80	0.90	0.96	0.92	0.90	0.97	0.96	0.97
	L.-G.	0.92	0.98	0.87	0.96	0.94	0.88	0.86	0.98	0.88	0.98
	M.-G.	0.94	0.93	0.97	0.92	0.97	0.98	0.89	0.98	0.95	0.98
M.	avg	0.024	0.044	0.038	0.018	0.037	0.114	0.102	0.04	0.037	0.027
	cold	0.043	0.067	0.066	0.034	0.068	0.212	0.160	0.065	0.069	0.047
G.	avg	0.007	0.010	0.012	0.005	0.014	0.033	0.037	0.011	0.012	0.007
	cold	0.013	0.02	0.022	0.01	0.025	0.063	0.07	0.018	0.024	0.012

BQL below quantification limit, w/s is the ratio $\frac{winter}{summer}$, L/M is the ratio $\frac{levoglucosan}{mannosan}$, c. are the correlations, L., M. and G. are levoglucosan, mannosan and galactosan, respectively. cold is the cold season (January–March and October–December).

[a] weighed average ratio for the months January, February and December. Into brackets: January to May and September to December (September was omitted at Vienna sites and at BB).

[b] minimum and maximum values for pools in January, February and December (into brackets: January to May and September to December, September was omitted at Vienna sites and at BB).

Mannosan and galactosan annual averages (Table 9.3) were around a factor of 4–7 and 11–24 lower than the respective levoglucosan values. Levolgucosan/mannosan and levoglucosan/galactosan ratios might change between the seasons, due to different emission patterns of the three anhydrosugars from the different types of combustion occurring in different seasons. Thus, we investigated in more detail the seasonal variation of those compounds.

9.1.3 Anhydrosugars seasonal variation

At all sites, levoglucosan had a clear annual cycle with higher concentrations in the cold season and lower in the warm season (Figure 9.1). Winter average concentrations were around 6 to 8 times higher than summer ones in the three experimental regions. The winter/summer ratio in Vienna (6.1 to 8.2) was more pronounced in the urban fringe sites, and less important at the heavy traffic-impacted site. In Salzburg (ratios in the range 5.9–8.1) the same trend was observed, with a higher ratio at the rural site AN, an intermediate ratio at the urban site with residential characteristics LE and the lower ratio at RU, the site located nearby a traffic source. In Styria, winter/summer ratios were between 5.8 and 8.4, on the other hand, the difference was more accentuated in the city sites DB and GS (Table 9.3) and more moderate at the background site BB.

Both mannosan and galactosan had the same seasonal trend as levoglucosan. Mannosan concentrations were lower than levoglucosan ones (Figures 9.2 and 9.3). Averages for the cold season (January to March and October to December) ranged from 35 to 68, 69 to 212 and 46 to 69 ng/m^3 in the Vienna, Graz and Salzburg regions, respectively. Galactosan occurred in even lower levels, with cold season averages of 6–20 ng/m^3 (Vienna), 24–70 ng/m^3 (Graz) and 9–23 ng/m^3 (Salzburg). The values found in Austria are comparable to those reported for Ghent by Zdrahal *et al.* (2002) and Pashynska *et al.* (2002) [220, 126]. As for levoglucosan, concentration ranges were higher (about the double) in the Graz region. This is probably a consequence of the geophysical surroundings of the city, which are able to confer its atmosphere stagnant characteristics where the accumulation of particulate matter can be important. Though the seasonality is similar, at all sites except SCH and LOB the concentrations of mannosan and galactosan at the end of the year were clearly higher than at the beginning. Indeed, the concentration in December is about the double of that in January. For levoglucosan, this feature was only observed for the city of Salzburg. Probably, a change in the types of wood burnt (e.g. for availability reasons), and not an increase in the quantity of wood burnt was the reason for such observations [109].

The mannosan and galactosan concentrations from the warm season were frequently below the quantification limit. Therefore, those months were omitted in the following discussion.

9.1.4 Contribution of Levoglucosan-C to OC

The average contribution of Levoglucosan to the organic carbon (OC) load ranged between 1.3 % (RIN) and 1.6 % (SCH) in Vienna in 2004. Lower values were recorded in summer (less than 0.5 percent on average) and higher values during the cold season (winter and autumn, around 2–3%). In the regions of Styria and Salzburg, the contributions were higher (1.7–2.8% in Styria, 1.6–2.7% in Salzburg). Seasonally, the contribution of Levoglucosan to OC was also higher there: up to 5%, on average, in the cold season. Except for Styria, where this trend is not as clear, it can be noted that the contribution of levoglucosan to OC is higher at the background sites, lower at the traffic impacted sites and intermediate in the residential areas.

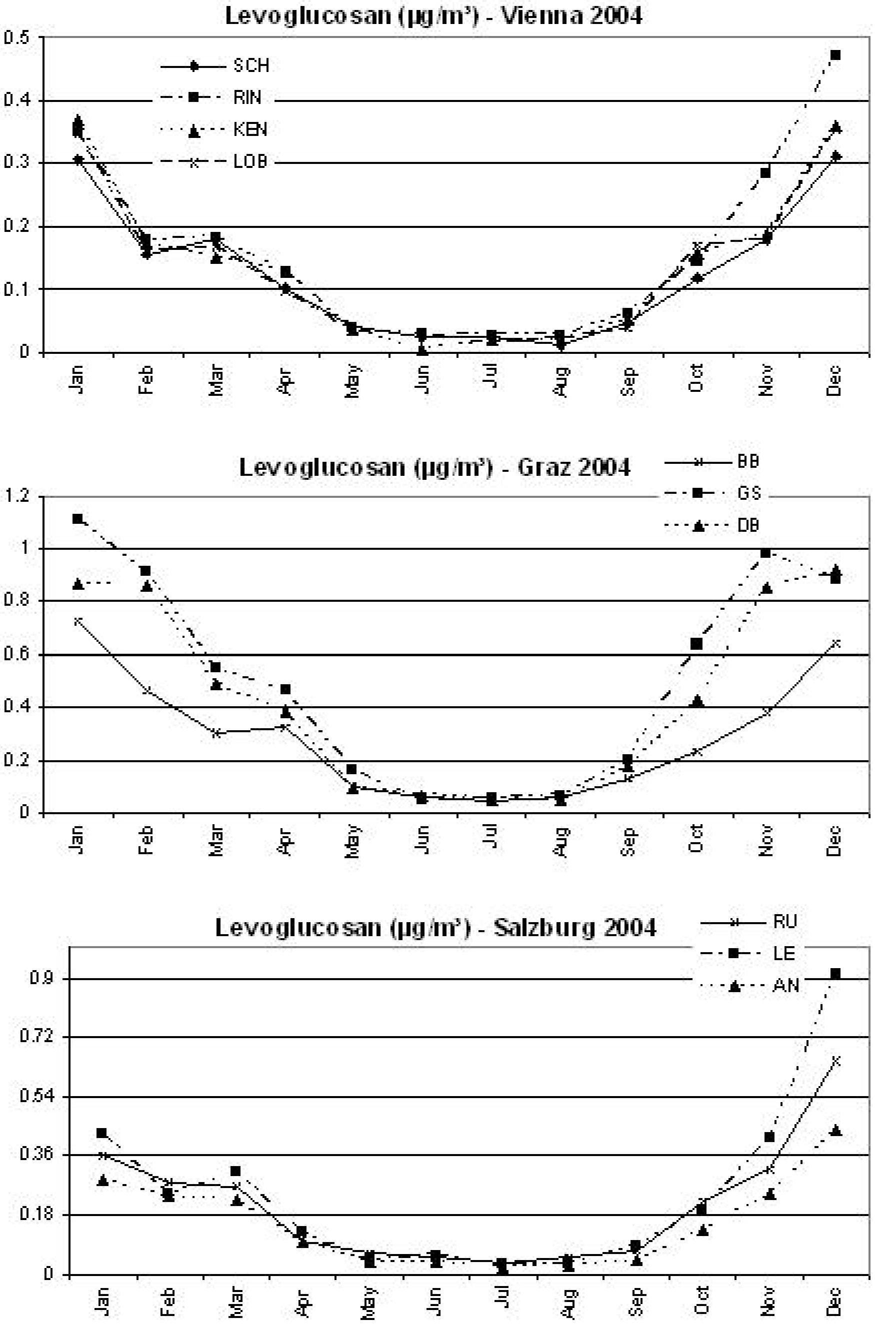


Figure 9.1: Levoglucosan monthly means for the AQUELLA campaigns

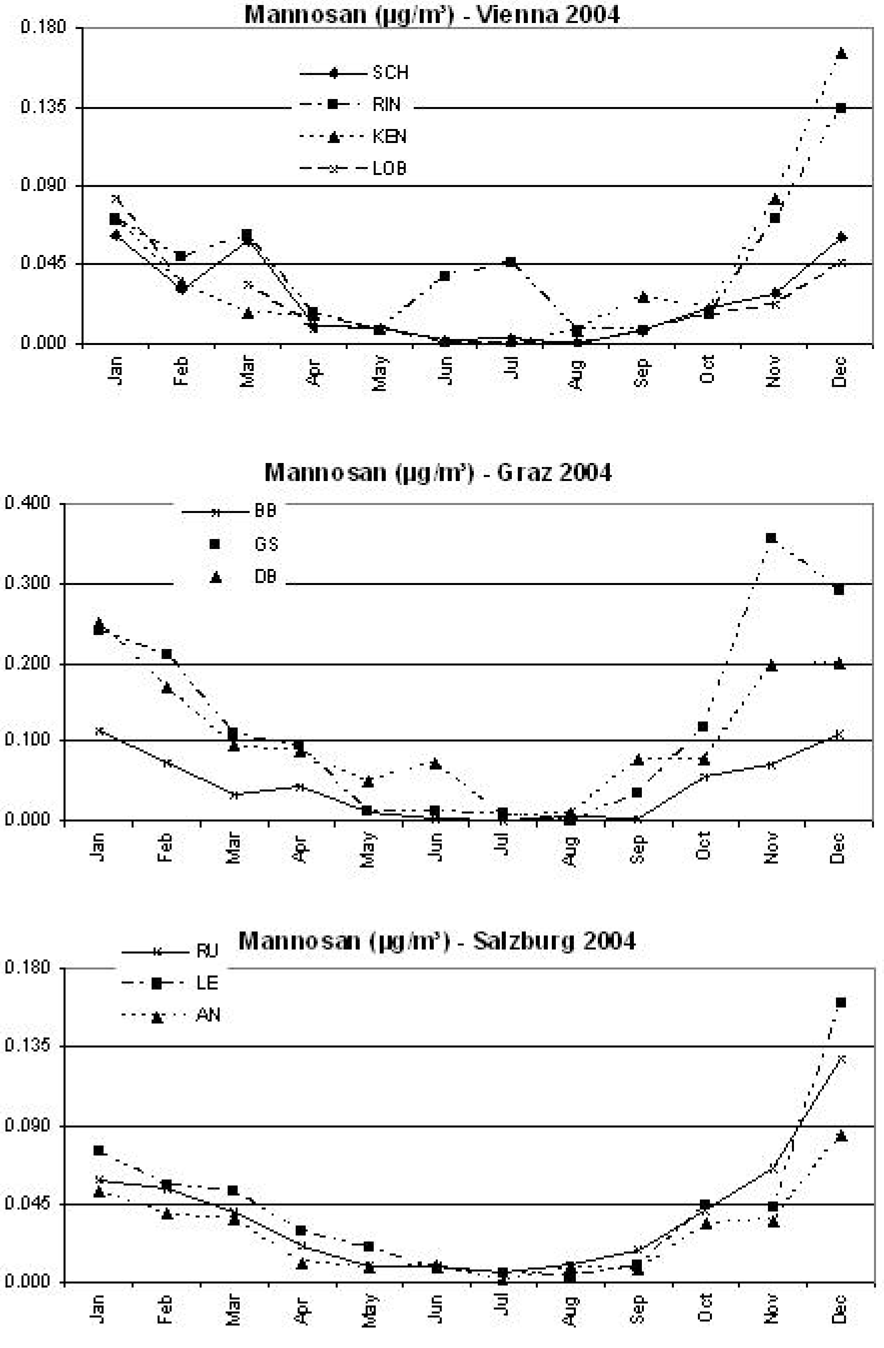


Figure 9.2: Mannosan monthly means for the AQUELLA campaigns

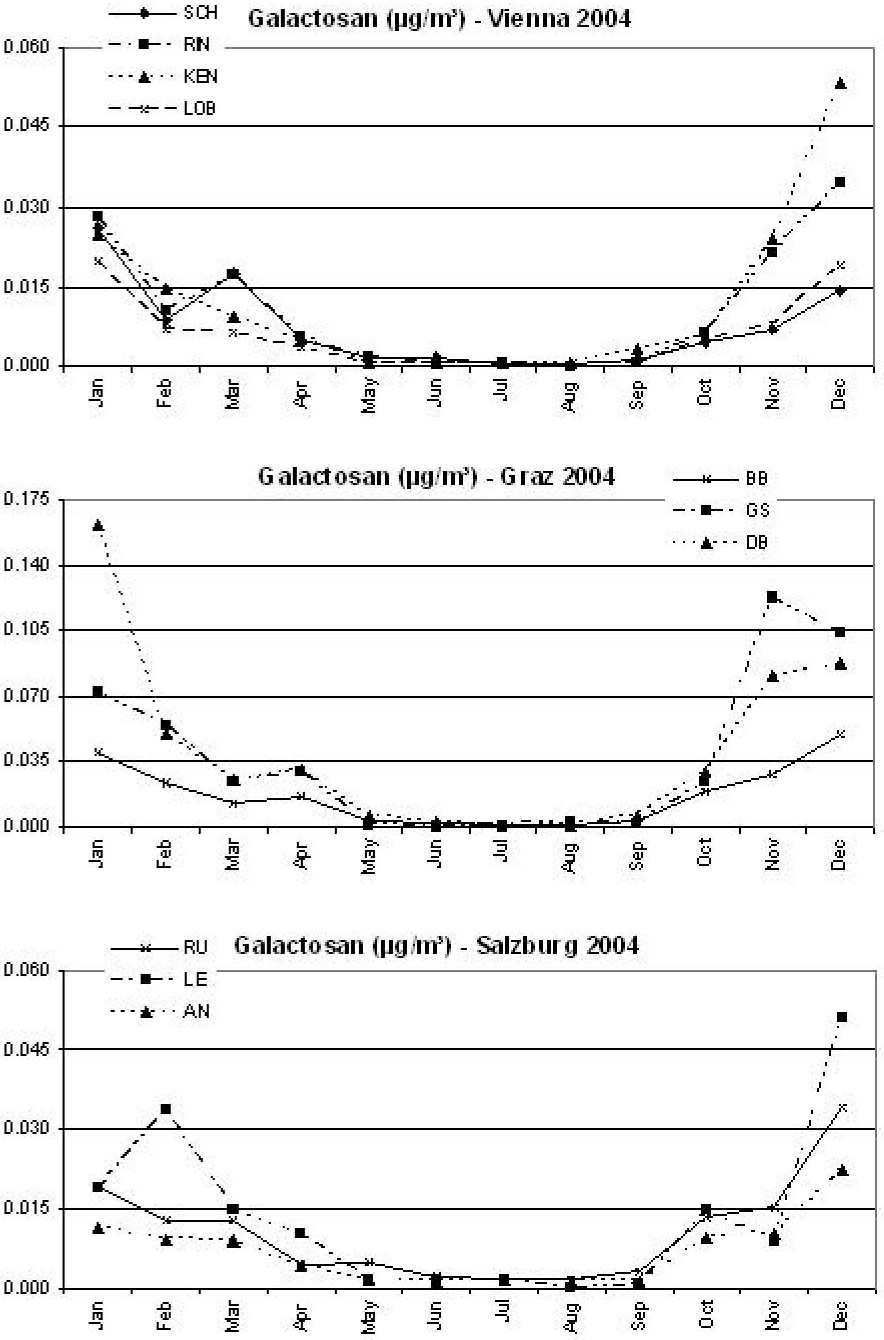


Figure 9.3: Galactosan monthly means for the AQUELLA campaigns

This reveals the contribution of other sources to organic carbon at the urban sites and not a higher input from wood smoke at the background sites (see the wood smoke PM load section 9.1.5).

9.1.5 Contribution of wood smoke to OC, OM and PM

Using the factors given by Schmidl *et al.* [109], it was possible to compute the relative contribution of wood smoke to the total OC, OM and PM load. The considered relationships were the following:

$$Biomass\ Smoke\ OC = Levoglucosan \times 6.1 \tag{9.1}$$

$$Biomass\ Smoke\ OM = Levoglucosan \times 9.1 \tag{9.2}$$

$$Biomass\ Smoke\ PM = Levoglucosan \times 10.7 \tag{9.3}$$

The relationship to convert ambient OC into OM used was [319]:

$$OM_{ambient} = OC_{ambient} \times 1.7 \tag{9.4}$$

Since this methodology is based on average values, it has some limitations. Indeed, in sites where the wood smoke impact is the strongest, it is possible that the average factors are not totally adequate and the calculated contribution to OC or OM may be beyond 100%. This was the case for one pool in LE and another one in GS. For calculations purposes, those values were set to 100%.

On a yearly average, wood smoke (WS) is a considerable source of organic carbon and organic matter in the ambient aerosol. About one fifth to one third of the annual OC and OM could be attributed to wood smoke (Table 9.4). In Vienna, WS contributed 18 to 22% to the yearly OC and OM, with differences between sites being small, but with higher contributions at the urban fringe sites. The differences between sites were not much more pronounced during the different seasons. At the other two regions, a gradient in the relative contribution of WS can be observed: higher relative contributions occurred at the background sites (BB and AN) and lower at the traffic impacted sites (DB and RU). The sites with densely populated residential characteristics (GS and LE) generally showed contributions close to those of the rural sites (GS and BB had similar figures). The relative contributions in Graz and Salzburg were higher than in Vienna: 19 to 38% of the annual particulate OC or OM load was found to originate in WS (30 to 70% in winter). At all sites, maximum values of the individual analysed pools ranged up to, or close to, 100%. For the residential and rural sites located in or around those two regions, WS was an overwhelming contributor to OM (40 to 62% in the cold season), clearly higher than for the urban-fringe sites in Vienna, where the difference between sites, as well as the individual values, were not as high (Table 9.4). Still, though the annual averages and the contributions at the traffic-impact site are very similar, a difference between the Salzburg and Graz regions can be found for the residential and rural sites, with higher contributions in Salzburg. It is interesting that, in winter, background sites have the highest relative biomass-OC contributions, while for Salzburg and Graz, where the background sites are further away from the city borders, in autumn the residential sites within the city show the higher relative biomass-C to OC contributions. This might be due to an increased use of supplementary wood stoves in addition to central heating.

Table 9.4: Contribution of levoglucosan and wood smoke to OC and OM.

		Vienna				Styria			Salzburg		
		SCH	RIN	KEN	LOB	BB	GS	DB	RU	LE	AN
L.	avg	1.61	1.31	1.29	1.52	2.68	2.78	1.71	1.61	2.38	2.74
-C	(min-max)	(0-3.63)	(0.29-4.03)	(0.10-3.34)	(0.20-4.78)	(0.5-7.4)	(0.8-8.4)	(0.4-5.0)	(0.3-4.2)	(0.3-10.7)	(0.4-7.6)
/OC	winter	2.68	2.28	2.34	2.88	4.40	3.04	2.80	2.50	4.48	5.13
(%)	spring	1.72	1.11	1.27	1.45	3.24	2.63	1.61	1.17	1.91	2.44
	summer	0.41	0.38	0.22	0.42	0.95	1.06	0.59	0.52	0.71	0.71
	autumn	1.68	1.49	1.33	1.65	2.64	3.80	2.03	2.04	3.41	2.80
	w/s	6.56	5.95	10.73	6.89	4.61	2.86	4.77	4.82	6.34	7.21
WS	avg	22.10	17.97	17.68	20.90	35.12	37.73^c	23.42	22.16	31.87	37.51
-OC	(min-max)	(0-49.9)	(4.0-55.8)	(1.4-45.9)	(2.7-65.7)	(6.2-100)	(10.4-100)	(4.8-69.3)	(3.4-57.2)	(3.9-100)	(5.7-100)
/OC	winter	36.78	31.27	32.19	39.53	58.90	41.65	38.42	34.39	57.86	70.16
(%)	spring	23.63	15.30	17.41	19.77	43.03	36.07	22.11	16.07	26.28	33.55
	summer	5.60	5.26	3.00	5.74	13.10	14.57^c	8.05	7.13	9.69	9.77
	autumn	23.03	20.51	18.27	22.67	35.98	51.28	27.66	27.97	46.90	38.43
	w/s	6.56	5.95	10.73	6.89	4.50	2.86^c	4.77	4.82	5.97	7.18
WS	avg	19.39	15.77	15.51	18.34	32.30	33.53^c	20.63	19.45	28.25	32.98
-OM	(min-max)	(0-43.7)	(3.5-49.0)	(1.2-40.3)	(2.4-57.7)	(5.4-89.6)	(9.1-100)	(4.2-60.8)	(3.0-50.2)	(3.5-100)	(5.0-91.6)
/OM	winter	32.28	31.10	32.02	34.69	53.00	40.16	36.98	33.10	56.04	61.84
(%)	spring	20.74	15.21	17.32	17.35	39.11	34.84	21.28	15.46	25.30	29.44
	summer	4.92	5.23	2.98	5.04	11.50	14.02^c	7.75	6.86	9.33	8.58
	autumn	20.21	20.40	18.17	19.90	31.88	49.81	26.84	26.92	45.14	33.73
	w/s	6.56	5.95	10.73	6.89	4.61	2.86^c	4.77	4.82	6.01	7.21

^{c}: GS no OC data for June

L.-C/OC is the contribution of Levoglucosan-C to OC (in %).

WS-OC/OC and WS-OM/OM are the contributions of wood smoke to OC and OM, respectively (in %).

On a yearly average basis, wood smoke contributed less to the PM load in Vienna (5.1–6.7%) than in the other regions (Graz: 8.9 to 13%; Salzburg: 7 to 12%) (Table 9.5). On absolute values, the concentration of wood smoke PM_{10} was the strongest in Graz (2.7 to 5.2 $\mu g/m^3$), followed by Salzburg (1.7–2.3 $\mu g/m^3$). The absolute values were the lowest in Vienna (1.3–1.7 $\mu g/m^3$). Absolute contributions of wood smoke were higher in winter and autumn and the relative contribution was on average around 4 times stronger in winter than in summer. In Vienna, the winter/summer difference in the relative contribution of wood smoke to the total PM load was slightly higher in the residential sites than in the traffic-impacted ones, in Salzburg it was clearly stronger and in Graz the ratios were fairly similar. The cold season relative contribution in Viennese residential sites (about 10%) was higher than in the traffic-impacted ones (about 8%). This tendency was also seen in the other regions, where the relative contribution of WS at background and residential areas was stronger than at traffic-impacted sites: LE and AN: around 19%, DB: 14%; GS and BB: around 20%, RU: 11%.

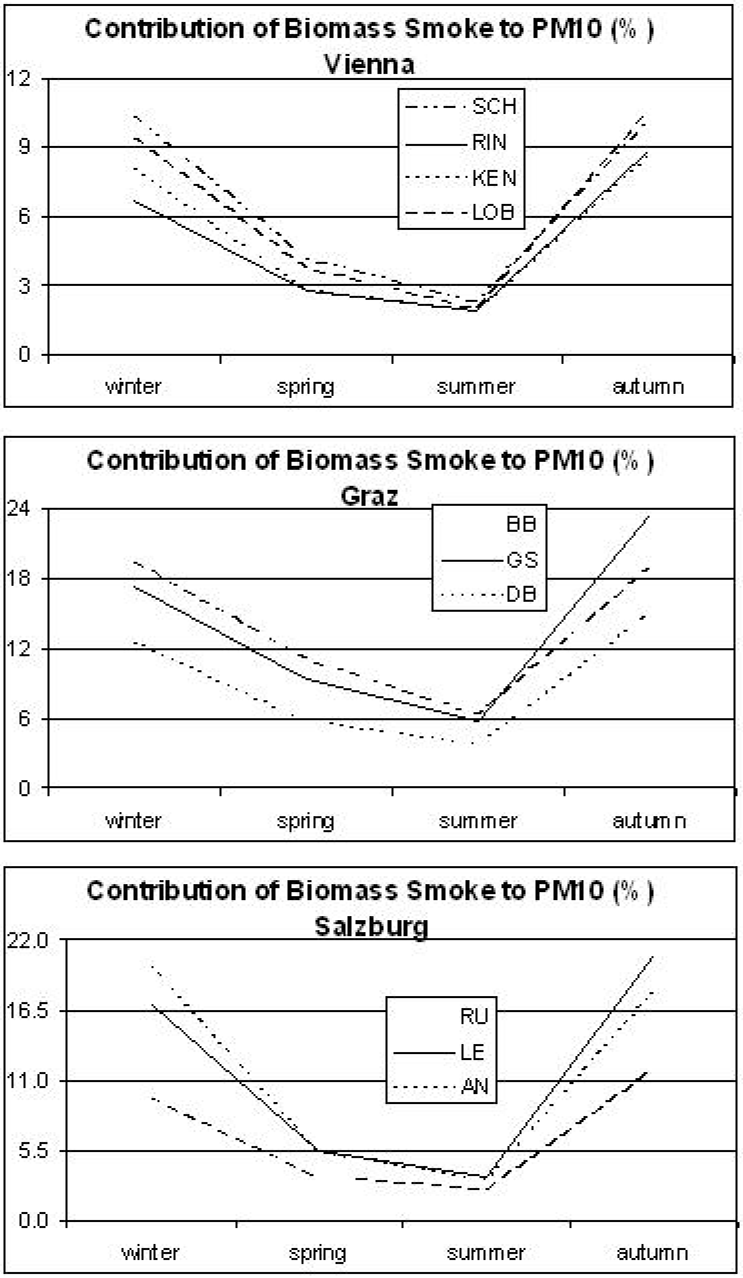


Figure 9.4: Contribution of wood smoke to PM_{10}

Table 9.5: Contribution of wood smoke to PM_{10}. Absolute concentration of PM_{10} from wood smoke.

		Vienna			Styria			Salzburg			
		SCH	RIN	KEN	LOB	BB	GS	DB	RU	LE	AN
WS	avg	1.3	1.7	1.5	1.3	2.7	5.2	4.4	2.3	2.2	1.7
(μg/m^3)	(min-max)	(0-7)	(0.22-8.92)	(12.62-0.12)	(0.16-6.91)	(0.5-14)	(0.5-24)	(0.4-21)	(0.3-11)	(0.2-13)	(0.2-8)
	winter	2.3	2.5	2.5	2.1	4.8	9.2	7.9	3.2	3.5	2.7
	spring	0.6	0.7	0.6	0.6	1.7	2.4	1.9	0.8	0.8	0.6
	summer	0.3	0.4	0.3	0.3	0.8	1.1	0.9	0.6	0.5	0.3
	autumn	2.1	3.2	2.5	2.5	3.9	8.7	7.3	4.3	5.7	2.9
	w/s	8.2	6.1	7.6	8.0	5.8	8.2	8.4	5.9	6.5	8.1
WS	avg (min-max)	6.7	5.1	5.4	6.2	13)	13	8.9	7	10	12
/PM_{10}	(min-max)	(0-41)	(0.8-23)	(0.5-32)	(0.6-38)	(1.7-59)	(1.3-100)	(1-42)	(0.9-36)	(0.6-73)	(1-100)
(%)	winter	10.3	6.7	8.0	9.3	19.3	17.2	12.4	9.5	16.8	19.9
	spring	4.2	2.8	2.9	3.7	11.1	9.3	5.7	3.4	5.5	5.3
	summer	2.3	1.9	1.9	2.0	6.3	5.6	3.7	2.3	3.6	3.0
	autumn	10.1	8.8	8.6	10.6	19.0	23.4	15.0	11.6	20.8	17.9
	w/s	4.6	3.5	4.3	4.7	3.1	3.1	3.4	4.1	4.7	6.6

Table 9.6 reports the concentration of WS and PM_{10} during exceedance periods and non-exceedance periods for the cold season (January to March and October to December). It can be seen that the increase in the concentrations is always higher for PM_{10} than for WS, except in DB, where the increase is equal. Thus, the relative contribution of WS to PM_{10} increases, at most, as much as the total PM_{10}. This is an indication that other sources, or meteorological effects, such as accumulation, are responsible for the exceedances.

9.1.6 Mannosan, galactosan and the differentiation between the soft and hardwood combustion contributions

At all sites, the correlation between the three anhydrosugars was high: all were above 0.8 and only 6 out of 30 below 0.9. (Table 9.3). Both mannosan and galactosan followed the same trend shown by levoglucosan, with lower concentrations at the background sites.

The average levoglucosan/mannosan ratios did not vary much when considering the period when wood burning is at its highest (January-February-December) or January-May / September (October) -December. However, the dispersion is much higher when considering the longer period (Table 9.3). The maximum ratio for individual sample pools (not considering June through August, and September for Vienna and BB) occurred at BB and GS (19) and the lowest at LE (1). The former is a bit higher than the typical value for hardwood combustion, while the latter is somewhat lower than the value for briquettes [109]. The levoglucosan/mannosan ratio (weighed average) for the months January, February and December was between 4.1 and 6.4. Following the findings by [109], this indicates that the use of biofuel is dominated by softwoods. In Austria, the main softwood sold for residential heating is spruce. While in Vienna and in Styria, the ratio was slightly higher at the background sites, in Salzburg, the difference was very small (Table 9.3). This lower ratio at the city centre sites might indicate the use of different biofuels. Indeed, briquettes from softwood have a levoglucosan/mannosan ratio of about 2.5 [109], lower than for softwoods. Due to availability reasons, it is possible that the share of wood in the biofuels mix is higher at the background sites than at the city centre.

Schmidl *et al.* [109] proposed the following equation to calculate the contribution of softwood burning to PM_{10} (in Austria, softwood burned for residential heating is mainly spruce) using the levoglucosan/mannosan ratio:

$$\%spruce = \frac{14.8 R_{\frac{Levo}{Mannno}}}{0.112} \tag{9.5}$$

Using the ratio levoglucosan/mannosan for the months January, February and December given in Table 9.3 and the equation above, the spruce contribution in the biofuel mix burned was found to be in the ranges 75–95%, 75–90% and 81–84% in Vienna, Styria and Salzburg, respectively. At the three regions, the background sites evidenced ratios at the lower end of the range, though this was a very minor difference in the case of AN (Salzburg). From Austrian selling statistics, one can find the information that the burning wood sold in Austria is a mix of soft and hardwoods (59% and 41% respectively). The discrepancy may arise from the fact, that the equation used was obtained for combustion in a ceramic stove, which is widely used in Austria but not the sole source of biomass emissions, and from a potential distortion of the statistics not accounting for private wood sources from forests and gardens. Thus, one may conclude that softwood will be the major wood type used in Austria, with a contribution between the numbers obtained from the two evaluations (e.g. 60-85% in the

Table 9.6: PM_{10} and wood smoke (WS) concentrations (μg m^{-3}) for exceedance and non-exceedance periods during the cold season.

		Exceedance	Non-exceedance	$\frac{Exceedance}{Non-exceedance}$
SCH	PM_{10}	60.9	22.8	2.7
	WS	*4.6*	*2.0*	*2.3*
RIN	PM_{10}	60.5	29.8	2.2
	WS	*4.5*	*2.1*	*2.1*
KEN	PM_{10}	66.6	27.6	2.4
	WS	*4.1*	*2.1*	*1.9*
LOB	PM_{10}	56.4	20.8	2.7
	WS	*5.5*	*2.1*	*2.6*
BB	PM_{10}	58.0	18.9	3.1
	WS	*7.1*	*4.1*	*1.7*
GS	PM_{10}	76.4	29.8	2.6
	WS	*12.4*	*6.1*	*2.0*
DB	PM_{10}	77.4	33.8	2.3
	WS	*12.1*	*4.4*	*2.3*
RU	PM_{10}	64.3	33.0	1.9
	WS	*5.4*	*3.3*	*1.6*
LE	PM_{10}	61.1	17.7	3.4
	WS	*8.3*	*3.7*	*2.2*
AN	PM_{10}	61.6	18.5	3.3
	WS	*3.7*	*2.8*	*1.3*

Table 9.7: Limits of detection (LOD) and number of sample pools below the LOD for cellulose during the AQUELLA campaigns.

Site	LOD (μg free cellulose cm^{-2}	LOD free cellulose m^3	n° of field blanks	n° of pools	Pools < LOD
SCH	0.160	0.033	25	47	5 (10.6%)
RIN	0.145	0.030	25	52	0
KEN	0.193	0.040	25	52	0
LOB	0.153	0.031	25	42	1 (2.4%)
BB	0.141	0.029	22	39	0
GS	0.201	0.041	15	44	3 (6.8%)
DB	0.179	0.037	23	44	0
RU	0.175	0.039	23	39	1 (2.6%)
LE	0.118	0.024	22	36	3 (8.3%)
AN	0.236	0.048	23	40	12 (30%)

mix). Further combustion tests with different types of stoves and wood types typical for Europe will be required, to evaluate with better accuracy the soft/hardwood contributions.

Galactosan concentrations happened to be low in relation to levoglucosan. The levoglucosan/galactosan ratios ranged between 6.4–26, 4.4–24 and 2.0–30 in Vienna, Styria and Salzburg, respectively, omitting the summer pools. As for the levoglucosan/mannosan ratio, it is not possible to observe a seasonal trend since many sample pools in Summer had mannosan or galactosan levels below the quantification limit.

9.2 Concentrations of cellulose, a plant debris proxy

9.2.1 Blank filters and detection limit

A detection limit (LOD) was calculated for each site from the blank filters analysis (228 field blank filters in total), which corresponds to three times the standard deviation of the average blank filter signal (0.0013 is the probability that a sample containing no cellulose gives a signal above the LOD). [323] LOD ranged from 0.029 to 0.048 μg m^{-3}. These LOD are higher than those reported by Snchez-Ochoa *et al.* (2007), though for that study, sampled volumes were considerably higher. The LOD reported by Puxbaum and Tenze-Kunit (2003) [135] were higher (0.05-0.11 μg m^{-3}), for lower sampled volumes. For calculation purposes, free cellulose values falling below the method detection limit were considered as one half of the site detection limit.

The factors to convert free cellulose into total cellulose and total cellulose into Plant Debris is based on Kunit and Puxbaum (1996) [49] and Puxbaum and Tenze-Kunit (2003) [135]: free cellulose makes up 72% of the total cellulose and total cellulose accounts for 50% of the Plant Debris. Snchez-Ochoa *et al.* (2007) [324], who used the same technique for a two-year continuous study in six European background sites, present an error discussion about these factors and estimate the total uncertainty on the Plant Debris values to be 37%. The factor to convert OC into OM is 1.7 [319].

9.2.2 Cellulose annual concentrations and seasonality

Cellulose concentrations were, at all sites, mostly above the detection limit (only 25 out of 435 pools below the LOD, Table 9.7). Total cellulose concentrations are reported for the ten sites studied in Table 9.8. Annual averages varied from 0.08 μg m^{-3} in AN to 0.23 μg m^{-3} in GS. The maximum concentration for individual pools occurred in GS (0.83 μg m^{-3}). Annual average concentrations were higher in Styria (0.13–0.23) than in Vienna (0.09–0.14) or Salzburg (0.08–0.13). This is probably due to an accumulation effect characteristic of that region: Graz lies in a basin with only a southerly opening where air circulation is somewhat hindered. Such a geomorphological surrounding allows the pollutants emitted to the atmosphere to accumulate. At the three regions, annual average concentrations, as well as seasonal concentrations, were lower at the rural/background sites (0.08–0.13 μg m^{-3}) and higher at the heavy-traffic impacted sites (0.13–0.23 μg m^{-3}). Sites with residential characteristics experienced intermediate concentrations which were closer to the concentrations at the heavy traffic-impacted sites than to the rural/background sites (0.11–0.2 μg m^{-3}). This indicates that the city is a possible source of atmospheric cellulose, likely through the milling of plant material by traffic. Other possible sources could be paper use, cotton clothes, grass cutting, or dry grass. The averages observed here are higher than those observed at six European background sites by Snchez-Ochoa *et al.* (2007) [324] , which were in the range 0.016–0.181 μg m^{-3}. These lower concentrations are due to two factors: the sites of that study were mostly equipped with $PM_{2.5}$ samplers and representative of remote areas. Values in Vienna were lower than observed by Kunit and Puxbaum (1996) [49] and Puxbaum and Tenze-Kunit (2003) [135] for total suspended particles (TSP) (0.11–0.94 μg m^{-3} in September-November and 0.374±0.115 μg m^{-3} as yearly average, respectively). Again, the difference between that study and the results presented here is consistent with the difference in the sampled particles' size.

Table 9.8: Cellulose concentrations (in μg m^{-3}) and contributions to OC for the AQUELLA campaigns.

		Vienna				Styria			Salzburg		
		SCH	RIN	KEN	LOB	DB	GS	BB	RU	LE	AN
Cell.	avg	0.09	0.14	0.13	0.09	0.13	0.2	0.23	0.13	0.11	0.08
	min	0	0.03	0.04	0.02	0.04	0	0.11	0.05	0.03	0.04
	max	0.55	0.56	0.35	0.2	0.54	0.83	0.72	0.44	0.18	0.13
	winter	0.126	0.143	0.128	0.075	0.116	0.276	0.320	0.125	0.087	0.054
	spring	0.079	0.133	0.137	0.088	0.159	0.231	0.232	0.119	0.135	0.072
	summer	0.085	0.150	0.139	0.107	0.141	0.134	0.174	0.102	0.099	0.101
	autumn	0.083	0.120	0.098	0.079	0.114	0.156	0.200	0.163	0.090	0.074
Cell.	avg	1.57	1.37	1.6	1.4	1.91	1.48	1.4	1.17	1.62	1.68
-C	min	0.03	0.18	0.2	0.17	0.22	0	0.23	0.38	0.25	0.36
%	max	7.1	5.49	3.66	3.37	4.96	3.44	2.66	2.24	2.53	3.65
of	winter	1.660	1.040	1.168	0.906	0.929	0.798	0.990	0.757	0.905	0.950
OC	spring	1.373	1.288	1.844	1.402	2.590	1.986	1.470	1.107	2.004	1.867
	summer	1.813	1.987	2.342	1.970	2.273	1.710	1.943	1.214	1.831	2.489
	autumn	1.435	1.172	1.042	1.210	1.505	1.366	1.126	1.644	1.558	1.378

Seasonal variations do not show a trend that is recognisable at all sites, neither one that is repeated in all of the sites of one region or of one kind (Table 9.8 and Figure 9.5). The correlation coefficients (R^2) of the monthly averages within a same region are low to moderate (Vienna: 0.12–0.69, Graz: 0.06–0.68, Salzburg: 0.002–0.023), further evidencing the lack of a common temporal variation.

9.2.3 Contribution of Cellulose-C to OC

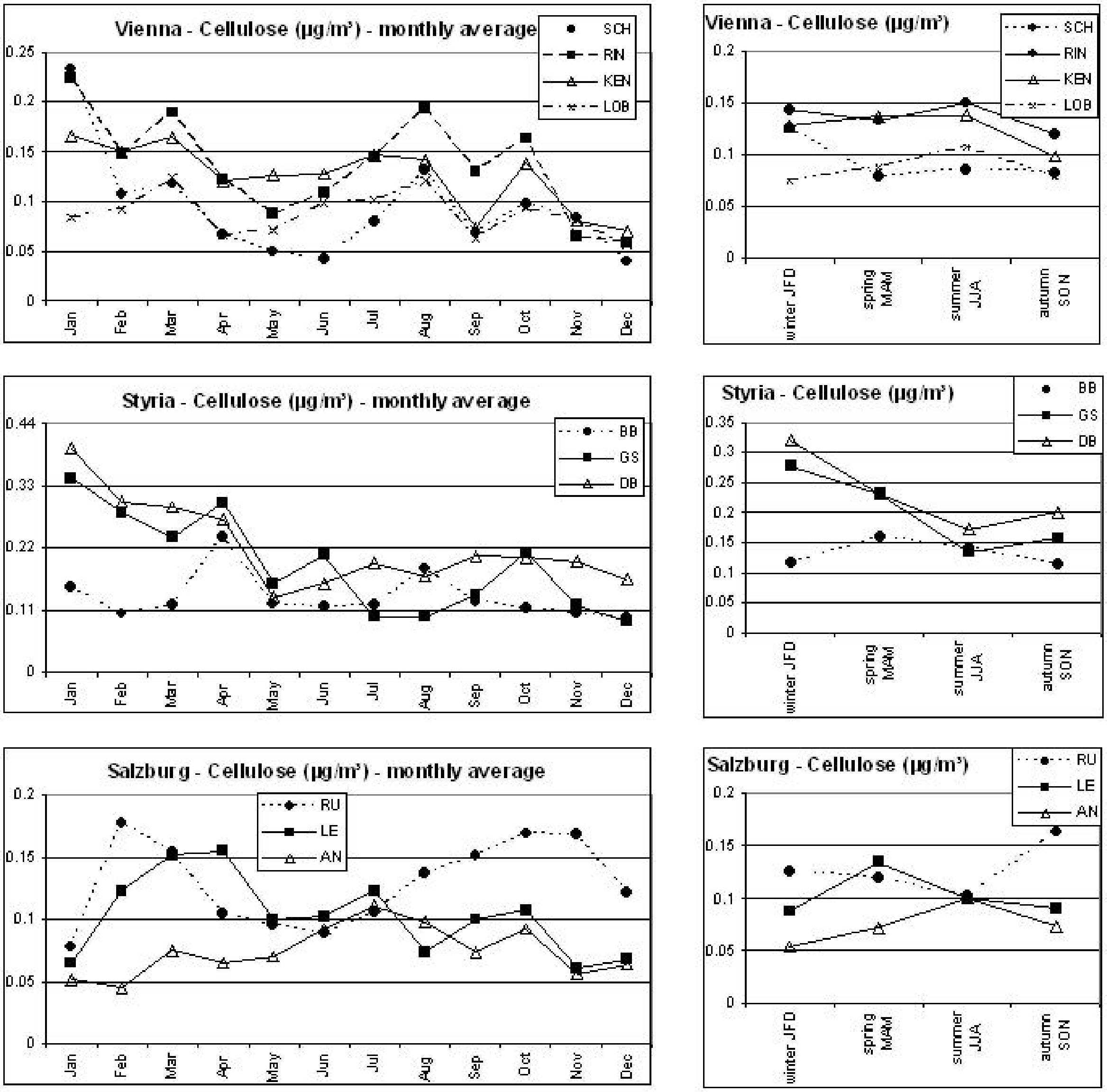
The annual average of the cellulose contribution to OC ranged from 1.17 to 1.91% (Table 9.8). This is in the same range of the contribution at the central European continental site K-puszta (1.6%), but lower than at mountain sites [324]. Unlike the cellulose concentrations, which were clearly higher in Graz, there is not a stressed difference between the regions in the cellulose-C contribution to OC (annual averages of 1.5, 1.6 and 1.5 in Vienna, Graz and Salzburg, respectively). This confirms that the higher cellulose concentrations in Graz are due to accumulation effects. Within a same region, though, higher contributions are reached at the background sites. This is clear for Graz and Salzburg (absolute differences in the annual average of cellulose-C contribution to OC between heavy traffic-impacted sites and background sites up to 0.51%) but not for Vienna (Table 9.8). Maximum values for the cellulose-C contribution to OC (individual pools) ranged up to 7%. At all sites, the contribution of Cellulose-C to OC was higher in the cold season (January-February and September till December) than in the warm season (March till August). The cold/warm ratio was in the range 0.6–0.9 in Vienna, 0.5–0.6 in Graz and 0.5–0.7 in Salzburg. Seasonal averages show a broad spring/summer maximum at all sites except SCH and RU (Table 9.8).

9.2.4 Plant Debris concentration and its contribution to OM and PM_{10}

Assuming that all the cellulose present in the PM_{10} aerosol has vegetative detritus as its origin, the concentration of plant debris PM_{10} can be calculated [49]. Plant debris annual average ranged from 0.18 to 0.45 μg m^{-3} (Table 9.9), with individual pools' maxima up to 1.65 μg m^{-3}, and its trends were the ones evidenced by cellulose concentrations (Table 9.8).

Organic matter (OM) was computed multiplying OC by 1.7. [319] The annual averages of the contributions of plant debris to OM were in the range 3.1–5.4% in Vienna, Styria and Salzburg. The seasonality of the contribution of plant debris to OM is the same as the one of cellulose-C to OC (Table 9.8 and Table 9.9). Such contributions are in the same range as those reported by Snchez-Ochoa *et al.* (2007) for European continental backround and mountain sites. Plant debris could account for a large fraction of OM: up to 18.8% for individual pools. In the two less populated cities, higher contributions occurred at the rural sites (close to 5%). In Vienna, however, that trend was not observed.

With concentrations up to 1.65 μg m^{-3} PD can indeed be an appreciable contributor to total PM_{10}. The yearly mean of plant debris contribution to PM_{10} at all 10 sites ranged from 0.89 to 1.77%. Annual averages were higher in Styria (1.2–1.8%) than in Vienna (1–1.3%) and Salzburg (0.89–1.33%). This range is not as large in Vienna as in the other regions, evidencing minor spatial variations. In the regions of Graz and Salzburg the rural sites clearly exhibited a higher average contributions than the sites more impacted by automotive traffic (Table 9.9). Sites with residential characteristics (GS and LE), had an average plant debris/PM_{10} ratio either close to the ratio at the rural site (LE) either close to the one of the traffic-impacted site (GS). The maximum value of an individual pool was 11% in SCH.


Vienna - Cellulose (µg/m³) - monthly average

Vienna - Cellulose (µg/m³)

Styria - Cellulose (µg/m³) - monthly average

Styria - Cellulose (µg/m³)

Salzburg - Cellulose (µg/m³) - monthly average

Salzburg - Cellulose (µg/m³)

Figure 9.5: Cellulose seasonal averages for the AQUELLA campaigns

The general seasonality of the contribution of plant debris to PM_{10} ratio was a broad spring-summer maximum (Figure 9.6). In Vienna, the seasonal differences were not as stressed as at the other regions.

Kotianová *et al.* (2008) [325] derived plant debris from C_{23}–C_{34} n-alkanes for Vienna and found a similar, though more pronounced (higher in summer, lower in winter), seasonality of the plant debris contribution to PM_{10}. The authors proposed that the differences between the two approaches probably resides in the fact that alkanes are mainly from plant wax which is on the surface of the leaves and thus are representative for surface abrasion products of leaves. Atmospheric cellulose requires a destruction process (weathering, grinding or similar) to allow that cellulose-containing parts smaller than 10 μm enter the atmosphere. This could also explain the spatial distribution of cellulose, with higher grinding occurring in the city due to automotive traffic.

Vegetative detritus (derived from leaves abrasion particulates chemical profiles using CMB) and plant debris (derived from cellulose) are conceptually different but overlap to some extent. In studies from Northern America, Schauer *et al.* (1996) [5] and Zheng *et al.* (2002) [83] found contributions of vegetative detritus to PM in ranges of the same order of magnitude (around 1%) as those presented here.

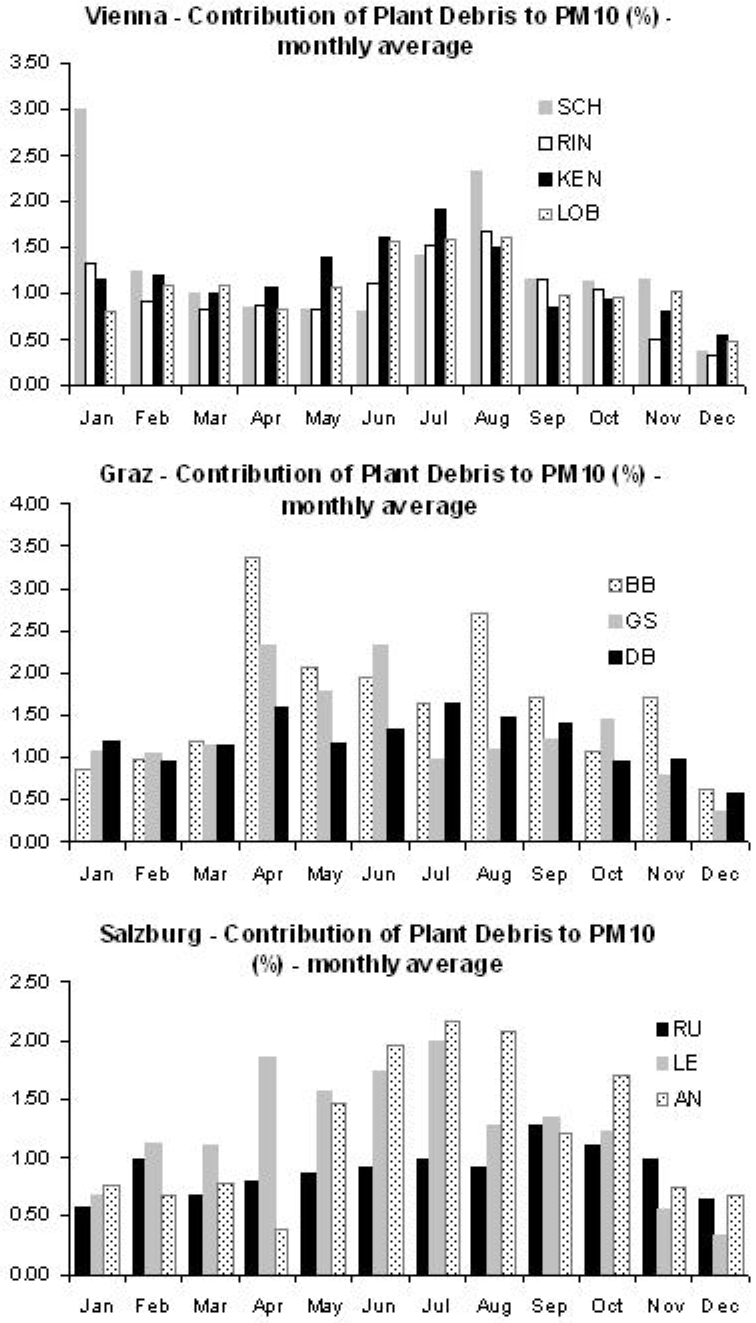


Figure 9.6: Plant debris contribution to PM_{10} (monthly averages)

Table 9.9: Plant debris concentrations (in μg m^{-3}) and contributions to OM and PM$_{10}$ for the AQUELLA campaigns.

		Vienna				Styria			Salzburg		
		SCH	RIN	KEN	LOB	DB	GS	BB	RU	LE	AN
PD	avg	0.18	0.27	0.25	0.18	0.27	0.39	0.45	0.26	0.21	0.15
	min	0.01	0.06	0.08	0.05	0.08	0	0.23	0.13	0.05	0.08
	max	1.1	1.13	0.7	0.4	1.08	1.65	1.44	0.87	0.35	0.27
PD	avg	4.15	3.63	4.24	3.71	5.06	3.92	3.70	3.09	4.28	4.44
%	min	0.09	0.49	0.54	0.44	0.59	0.1	0.6	1.01	0.66)	0.95
of	max	18.8	14.5	9.7	8.9	13.1	9.09	7.05	5.92	6.69	9.7
OM	winter	4.39	2.75	3.09	2.40	2.46	2.11	2.62	2.00	2.40	2.52
	spring	3.63	3.41	4.88	3.71	6.86	5.26	3.89	2.93	5.31	4.94
	summer	4.80	5.26	6.20	5.22	6.02	4.53	5.14	3.21	4.85	6.59
	autumn	3.80	3.10	2.76	3.20	3.99	3.62	2.98	4.35	4.13	3.65
PD	avg	1.26	1.01	1.16	1.11	1.75	1.35	1.24	0.89	1.32	1.32
%	min	0.02	0.1	0.16	0.1	0.19	0	0.27	0.29	0.2	0.17
of	max	10.97	5.65	4.9	4.19	8.56	6.13	3.88	2.87	4.07	6.2
PM$_{10}$	winter	1.519	0.849	0.962	0.789	0.870	0.945	1.003	0.730	0.778	0.837
	spring	0.887	0.842	1.154	0.990	2.191	1.745	1.295	0.782	1.510	1.096
	summer	1.527	1.445	1.674	1.588	2.143	1.461	1.485	0.947	1.692	2.067
	autumn	1.148	0.902	0.863	0.980	1.506	1.160	1.116	1.124	1.116	1.246

Part IV

Conclusions

Chapter 10

Conclusions

Regarding the contribution of biomass burning to the PM_{10} or $PM_{2.5}$ load at european background sites, the following conclusions can be made:

- Highest levels of levoglucosan in the biannual average were found at the low-level sites Aveiro and K-Puszta. Lowest concentrations were noted at the Atlantic background site Azores and the continental high-elevation site Sonnblick (3106 m a.s.l.). Average concentrations showed a clear elevational gradient for the continental sites (KPZ, SIL,PDD, SBO), with a ratio of around 40 for KPZ versus SBO.

- At the low-level sites AVE and KPZ, as well as at the elevated sites PDD and SIL, distinct seasonalities with winter maxima and summer minima were observed, while at the maritime background site, the winter/summer ratio was as low as 3, and summer and winter levels at the midtropospheric site SBO were relatively similar.

- Relative contributions of levoglucosan-C to OC (2-year averages) in the west-east transect ranged from around 0.7% at the high mountain site SBO to 3.2% at AVE. Relative contributions of levoglucosan-C to OC did not show a pronounced trend in terms of altitude. At all sites, the values were higher in winter than in summer. Also at the oceanic AZO site, the relative fraction of levoglucosan-C to OC was enhanced in winter (winter/summer ratio = 9).

- To derive a "wood smoke" contribution to organic matter, conversion factors from Fine *et al.* (2002) [88] and Schmidl *et al.* (2008) [109] and derived factors from field measurements were compared. For fires in small ovens the conversion factor CF for biomass smoke $OC = CF \times levoglucosan$ is around 5, while for fireplaces it is around 7–10, and for open wildfires it is > 10. A factor of 7.35 was here applied which bears an estimated uncertainty of ± 30% for all sites, except for AVE, where a factor of 6 was applied. A seasonal variation of the conversion factor is likely. Namely, during the cold season biomass smoke emissions are rather from domestic heating (ovens), while in the warm season fores fires, burning of agricultural and garden waste, and cooking may contribute to the biomass smoke emissions. As the extent of these activities is not clear in western and central Europe, a single factor was applied.

- The atmospheric concentration of biomass smoke (2-year averages) ranged from 0.05 μg m^{-3} at AZO to 4.3 μg m^{-3} at AVE. The highest monthly concentrations (up to 14 μg m^{-3}) were observed in winter at AVE, the second highest (9.5 μg m^{-3}) at KPZ. As for levoglucosan, "biomass smoke" concentrations decreased with altitude.

- Relative contributions of biomass smoke to organic matter (OM, 2-year averages) in the west-east transect ranged from around 9% at the high-elevation site SBO to 36% at the low-level site AVE. Relative contributions of biomass smoke to organic matter were similar at elevated sites and AZO (912%) and increased at KPZ and AVE (28 and 36%), sites affected by anthropogenic activities. Winter relative contributions were higher than summer levels at all sites. At the oceanic AZO sites, the relative winter enrichment versus summer levels (factor of 9) of the fraction of biomass smoke in OM may have originated from long-range transport or, additionally, from local emissions.

- Surprisingly high relative concentrations of biomass smoke in organic matter were observed at all sites in winter, ranging from 18% at AZO to 21–23% at the elevated sites, and from 47 to 68% at KPZ and AVE. Thus biomass smoke is the major constituent of the organic material in the wintry European aerosol background. Also during summer, biomass smoke contributed to OM in relative fractions of 1–5.5%.

- From the data it was derived that typical mid and west European levels of the biomass smoke contribution to organic matter are around 10–30% on an annual basis and around 20–50% during the cold season. In emission regions (e.g., communities with a high share of biomass based domestic heating) the contributions will be possibly even higher. From this follows that biomass smoke is the predominant organic aerosol constituent in wintertime mid and western Europe.

From the observation of polyols and primary sugars in european background aerosol samples, the followin concluding remarks were made:

- Saccharides concentrations were higher at KPZ, a low-altitude site where PM$_2$ was sampled. At the other sites were the fine fraction was sampled (PM$_{2.5}$: AZO, AVE and SBO), concentrations were lower than at the sites where PM$_{10}$ was sampled (PDD and SIL). What occurred at KPZ is surprising, because PBAPs were expected to occur more in the coarse fraction. This shows that PBAPs are a considerable contributor to the fine fraction, namely at continental sites. The four compounds had, generally, an annual cycle with higher concentrations in the warm season. This does not agree with the findings of Matthias-Maser *et al.* (2000) [44] who did not find any seasonal variation in PBAPs.

- Glucose has revealed to follow an annual cycle, with higher concentrations in the warm season and lower in the colder months. This cycle is probably linked with the ecosystem's aerosol production. However, such was not observed at Aveiro, at the Portuguese coast. At that site, higher winter glucose concentrations originated with the emissions due to biomass burning. Though showing a different annual pattern, KPZ also exhibits winter levels influenced by biomass burning, as, possibly, do AZO. The mountain sites PDD, SIL and SBO do not, though. This difference is most likely due to differences in ecosystem's aerosol production and dilution between those sites. Thus, continental sites show a large warm season biological contribution to glucose, while oceanic sites do not, and low level sites show a winter biomass burning contribution, whereas mountain sites do not. Except at AVE, the fructose concentration roughly followed the same annual pattern of the biogenic primary sources activity. Fructose levels support that the variations in the PBAPs (other than spores) contribution is more subject to the site's location (continental or maritime) and not to the size fraction.

- Relating glucose and levoglucosan, a molecular marker for the thermal degradtion of cellulosic products, emission factors ranging from 2.5×10^{-3}–$5.4\times10^{-3}\frac{ng\ Glucose}{ng\ wood\ burning\ PM_{2.5}}$ emitted at AVE and from $1.1 \times 10^{-3} - 7.7 \times 10^{-3}\frac{ng\ Glucose}{ng\ wood\ burning\ PM_{2.5}}$ emitted at KPZ were determined. For the other four sites, the methodology used was not applicable, either because its assumptions were inappropriate or because the biomass burned at those sites was not quantitatively significant and/or different in its emissions so that the methodology could not be applied.

- Polyols showed a wide warm season maximum at all sites except the remote site AZO (fairly low and constant concentrations throughout the campaign) and PDD (the maximum was not as broad). At the high level sites SIL and SBO this maximum was more localised in spring and summer, while at the low-altitude sites AVE and KPZ it was in summer and autumn.

- Inter-annual differences in the saccharides concentrations can be related to variations in the meteorological variables that control the biological activity and thus the release of some PBAPs. For example, relative humidity is important for the release of spores from some fungal species, while rainfall is necessary for the release of spores from other. Differences in the cycles of arabitol and mannitol are a possible indication of the diversity of fungal communities, of which they are markers. Glucose and fructose are also expected from the spores' contribution, but they may originate from other classes of PBAPs as well. The data shows that the evolution of the primary sugars' concentrations can be, to some extent, related to that of the polyols. However, this is not always the case. Most surprisingly, those differences occurred not only in sites where PM_{10} was sampled, but also in KPZ, where only the fine fraction was considered. It is not expected that PBAPs other than fungal spores or pollen fragments reach the aerosol fine fraction. Inter-annual differences in the glucose concentrations could be linked to the grass pollen's concentration at SIL and PDD.

About the input of wood burning to the austrian PM_{10}:

- Levoglucosan yearly averages ranged from 0.12 to 0.48 μg m^{-3}. The sites in Graz showed higher concentrations compared to the other regions, while background sites, in general, evidenced slightly lower concentrations than urban sites.

- Levoglucosan showed a pronounced seasonal cycle. Concentrations were 6 to 8 times higher higher during the colder months.

- Annual averaged levoglucosan-C contributions to OC were lower in Vienna (1.3 to 1.6%) and higher in Graz and Salzburg (1.6 to 2.8%). There was a strong seasonality of the contribution of levoglucosan to OC with ratios between winter and summer in the range of around 3–11.

- The yearly average contributions of WS to OC, OM and PM were in the ranges 18-38%, 16-34% and 5.1-13%, respectively. Values in the larger city, Vienna, were lower than in the regions of Graz and Salzburg. Contributions were generally lower at sites located closer to the city-center (traffic sources). Cold season (winter and autumn) average contributions to OM were very high: 24-30%, 30-44% and 28-52% in Vienna, Graz and Salzburg, respectively. Thus making wood smoke the main contributor to the organic aerosol in the cold season and a major contributor to PM. For the residential and rural sites, the contribution of wood smoke to OM was overwhelming (close to or above 50% in the less populated cities). The difference between the city-fringe sites and the city centre sites in Vienna were not as marked as in the other two regions.

- The relative contribution of wood burning to PM $_{10}$, in the cold season, does not increase during PM $_{10}$ exceedance episodes. This is an indication that other sources, or meteorological factors (such as accumulation of particulate matter in a given area), are responsible for the occurrence exceedances.
- Mannosan and galactosan had a similar seasonal cycle as levoglucosan, and the correlation between the compounds were quite high. Their concentrations, however, were much lower than for Levoglucosan.
- The ratios between levoglucosan and mannosan and between levoglucosan and galactosan showed a range of 4–6 and 11–22, respectively, in the periods where biomass burning is expected to be a strong source.
- The best estimate for the contribution of softwood in the mix of burned wood ranged between 60 and 85% for the three regions.

On cellulose, its contribution to the fine particulate load and that of plant debris in Austria:

- Cellulose concentrations ranged from below the detection limit up to 0.83 μg m^{-3}. Annual averages ranged from 0.08 to 0.23 μg m^{-3}. Concentrations in Graz were higher, this is possibly due to an accumulation effect.
- For each region, sites within the city have higher annual and seasonal cellulose concentrations than sites outside or at the city fringe. This indicates the city as a possible source of atmospheric cellulose, possibly due to grinding processes from traffic.
- No seasonal trend was identified for total cellulose neither at sites from a same region nor of a same type.
- Cellulose-C can contribute up to about 5% of OC (yearly average: 1.17–1.91%) and is thus a main constituent of OC.
- The cellulose-derived plant debris contributed about 1.4% to PM$_{10}$ as yearly average of all sites, with higher contributions in the warmer months. The contribution of plant debris to PM$_{10}$ was higher at the background sites.

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