Chapter 4
Atmosphere

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The atmosphere is the receiver of many by-products of our society, such us products of combustion of fossil fuels and industrial manufacturing. The studies on chemical pathways of trace atmospheric species are often complexes since the life cycles of such species are linked to an elaborate system of chemical and physical processes. As a result, it is possible that a perturbation in the concentration of one species leads to significant changes in quantity and lifetimes of other trace species; the feedback could also amplify or damp the original perturbation. Trace species can exhibit an enormous range of spatial and temporal variability, depending on their lifetime in the atmosphere. Relatively long-lived species are usually uniformly distributed: in this case strategically located sampling sites around the globe could be adequate to characterize their spatial distribution and temporal trend. As species lifetimes become shorter, their spatial and temporal distributions become more variable.

The Earth's atmosphere is composed primarily of the gases N_2 (78 %), O_2 (21 %) and Ar (1 %); their abundance is controlled by the biosphere over geologic timescales, through uptake and release from crustal material and degassing of the interior. The later most abundant constituent of the atmosphere is water vapour; it is found mainly in the lower layer (troposphere) and its concentration is highly variable, reaching 3 % of concentration. The remaining gaseous constituents (trace gases) represent less than 1 % of the atmosphere. Trace gases play a crucial role in the Earth's radioactive equilibrium and in the chemical properties of the atmosphere. Besides gases, the atmosphere, whether in urban or remote areas, contains significant concentrations of "particulate matter" or aerosol. By "particulate matter" we refer to any substance, except pure water, that exists as a liquid or solid in the atmosphere under normal conditions and is of microscopic or

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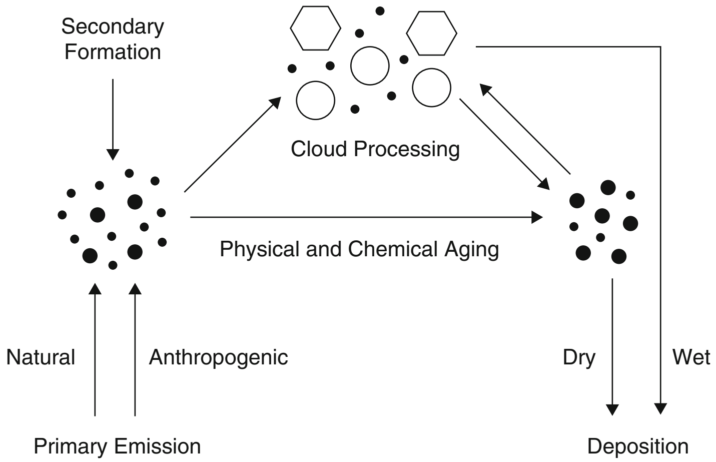

Fig. 4.1 Atmospheric cycling of aerosol (reproduced from reference$^{(2)}$ with permission from John Wiley and Sons)

submicroscopic size larger than molecular dimensions.[1] Among atmospheric constituents, particulate matter is unique in its complexity. Atmospheric particles affect a great variety of processes such as solar radiation scattering, visibility, climate and health effects. Moreover the atmospheric particles play an important role in the transport of chemical compounds both at local and remote scales. Atmospheric particles are classified by their size, shape and composition. They can be the result of primary emission that means they are directly emitted from sources or can be produced in the atmosphere by physical processes or chemical reactions (secondary formation, Fig. 4.1). The properties of such particles can be modulated by atmospheric processes, like condensation, evaporation and coagulation. Particles can persist in the environment from minutes to weeks after their release or formation, and can travel meters to thousands of kilometres; the typical removing mechanisms are wet or dry deposition.

There are three distinct modes into which airborne particles can typically be divided, based on their size, that are the following:

1. Transient nuclei mode: These particles are typically less than ca. 100 nm in diameter; they are formed by the condensation of less volatile materials and subsequently grow by condensation processes. Their formation can occur both in hot combustion gases and within the atmosphere itself from chemical reactions of gases.
2. Accumulation mode: Particles in the transient nuclei mode can grow both by condensation of low-volatility materials and through coagulation, reaching the state of "accumulation mode" that consists of particles between ca. 100 nm and 2 μm in diameter. The accumulation mode is so called because particle removal mechanisms are the less efficient in this regime, causing particle to be accumulated.

3. Coarse particle mode: The coarse particles are usually formed by mechanical action at high temperatures, crustal erosion, road dust resuspension and sea salts, being the fine fraction of a mixture of primary and secondary aerosol, principally emitted from anthropogenic sources (combustion, high-temperature industrial activities, automotive traffic, etc.).

Therefore, detailed information on the aerosol mass distribution and on its chemical composition is essential to identify their sources as well as to assess the environmental and health risks.[3]

Estimations of global emissions, as reported by many authors, have shown that natural and anthropogenic sources can contribute to the principal dimensional classes (coarse, fine and ultrafine)[4,5] of atmospheric particulate matter (PM). About 10–20 % of the aerosols can be characterized as anthropogenic on a global scale,[1] but these values may drastically change due to local scenarios, human activities and the prevailing particle cut-off.

A condition of "air pollution" may be defined as a situation in which substances that result from anthropogenic activities are present at concentrations sufficiently high above their normal ambient levels to produce a measurable effect on humans, animals, vegetation or materials.[1]

4.1 Gaseous Constituents

4.1.1 Sulfur Oxides

Sulfur oxides in the atmosphere are usually present as sulfurous anhydride or sulfur dioxide (SO_2) and sulfuric anhydride or sulfur trioxide (SO_3). Sulfur dioxide is a colourless, irritating, non-flammable, very soluble gas. It is one of the most aggressive and dangerous pollutants; it derives from the oxidation of sulfur during combustion processes. Health effects of sulfur oxides are prevalently linked to respiratory system pathologies, but in high concentration they can cause asphyxiation.

The most used analytical technique for SO_2 monitoring is based on fluorescence. Excitation of sulfur dioxide molecules by ultraviolet radiation (UV) in the 190–230 nm region gives an emitting fluorescent radiation, whose wavelength and intensity are directly proportional to the concentration of sulfur dioxide. The main interfering compound is represented by polycyclic aromatic hydrocarbons: to eliminate their effect, the analyzers are equipped with a permeation device which selectively removes hydrocarbon molecules from the gas sample.[6]

4.1.2 Nitrogen Oxides

The most important nitrogen oxides, from an environmental point of view, are the so-called NO_x that indicates the sum of nitrous oxide or nitrogen monoxide

Table 4.1 Typical analytical techniques used to analyze gaseous components of atmosphere

Compound	Analytical method
Sulfur oxides	Fluorescence
Nitrogen oxides	Chemiluminescence
Ozone	Spectrophotometry

(NO) and nitric oxide or nitrogen dioxide (NO_2). NO is produced during high-temperature combustion processes and comes principally from motor vehicle exhaust and stationary sources. NO_2 derives from the oxidation of NO in the atmosphere and represents an intermediate in the production of several secondary pollutants as ozone. Nitrogen dioxide is highly oxidant and toxic: it can irritate the lungs and lower resistance to respiratory infections.

Nitrogen oxides are usually analyzed by a chemiluminescence technique. In this method a gas-phase reaction between nitrogen monoxide and ozone produces excited NO_2 molecules (NO_2*). Excited molecules emit light, as they return to the ground state: the intensity of the emission peak at 1,200 nm is linearly proportional to the concentration of nitrogen monoxide (NO). The chemiluminescent reaction occurs only between NO and ozone; therefore it is necessary to convert nitrogen dioxide (NO_2) to nitric oxide (NO). For this purpose, the analyzer contains a molybdenum converter, heated at 315 °C: the sample gas flow intercepts a switching valve, that periodically deviates it to the converter before entering the reaction chamber. In these conditions, the analyzer measures the concentration of NO_x, as the sum of NO and NO_2. NO_2 concentration is obtained by the difference between NO_x and NO concentrations.[7]

4.1.3 *Ozone*

Ozone is a toxic gas, consisting of unstable molecules formed by three oxygen atoms (O_3); these molecules are easily broken releasing molecular oxygen (O_2) and an extremely reactive oxygen atom ($O_3 \rightarrow O_2 + O$). Because of these properties, ozone is an energetic oxidant, able to react both with organic and inorganic materials. Ozone is present for more than 90 % in the stratosphere (10–50 km of altitude) where it is produced by the solar ultraviolet radiation action. In the stratosphere it protects us against UV radiation generated by the sun. As a result of the atmospheric circulation it can be transported to a small extent also in the lower atmosphere (troposphere), but it can also be produced as result of photochemical reactions from primary pollutants. Health effects of excessive exposure to ozone involve mainly the respiratory tract.

Ozone (O_3) is often analyzed by a spectrophotometric method. The sample is irradiated by UV light that is partially adsorbed by ozone. The decrease of light intensity is registered by the detector and the ozone concentration is calculated following the Lambert-Beer law. Since that calculus requires a reference state, the analyzer is equipped with a device that removes O_3, giving the reference and a valve that permits the analyzer to shift from the measure and the reference mode. In Table 4.1 a summary of the typical analytical techniques used to analyze gas in atmosphere is reported.[8]

4.2 Atmospheric Aerosol

The principal chemical components of particulate matter (PM) are the following: sulfate, nitrate, ammonium, mineral dust, sea salt, organic compounds and black or elemental carbon; an example of the relative contribution of PM components is represented in Fig. 4.2.

- Sulfate—a secondary component, usually originated from atmospheric oxidation of SO_2.
- Nitrate—product from the neutralization of nitric acid vapour by ammonia in the form of ammonium nitrate (NH_4NO_3) or by the displacement of hydrogen chloride from sodium chloride by nitric acid vapour, forming sodium nitrate ($NaNO_3$).
- Ammonium—usually present in the form of ammonium sulfate ($(NH_4)_2SO_4$) or nitrate (NH_4NO_3).
- Sodium and chloride—typical of coastal area, these components are coming from sea salt.
- Elemental carbon—originated during high-temperature combustion of fossil and biomass fuels.
- Organic carbon—carbon present in the form of organic compounds: could be either primary, originated from traffic or industrial processes, or secondary, resulting from the oxidation of volatile organic compounds.
- Mineral components—the coarse fraction is rich in aluminium, silicon, iron and calcium.
- Water may also be present within water-soluble components, such as ammonium sulfate, ammonium nitrate and sodium chloride. These chemicals are able to take up water from the atmosphere at high relative humidity, thereby turning from crystalline solids into liquid droplets.

In addition to the main components, many minor chemicals are present in aerosol particles. Their concentration can be very low, but they have physical and chemical characteristics that lead up to a great interest about their detection:

- Trace metals—lead, cadmium, mercury, nickel, chromium and zinc.
- Trace organic compounds—although the total mass of organic compounds can constitute an important fraction of the whole mass of particles, the contribute of each individual organic compound can be very small.[9]

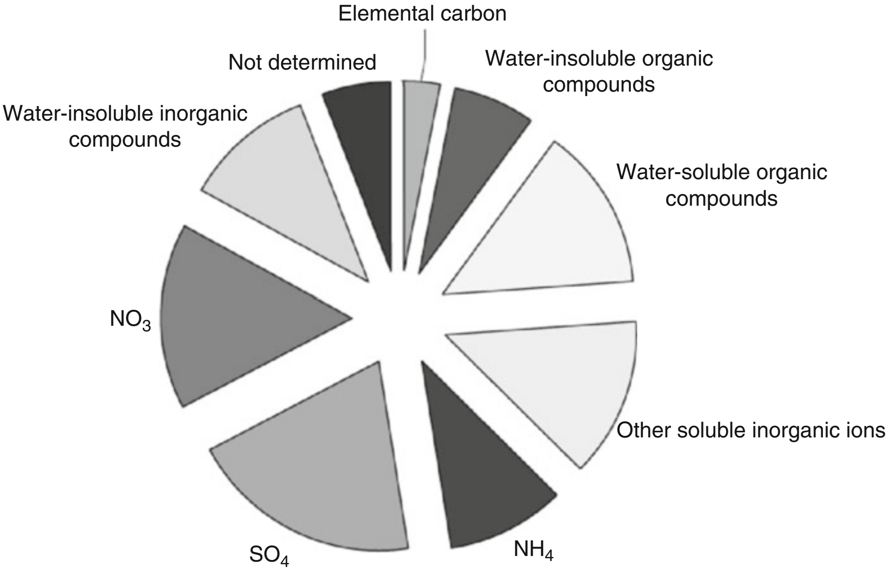

Fig. 4.2 Chemical balance on element constituents of aerosol mass in Italy (reproduced from (10) with permission from Elsevier)

4.3 Inorganic Aerosol

In the last few years much attention has been given to the evaluation of the elemental content of airborne particulate matter due to their detrimental effects on human health. Many epidemiological studies have revealed that the degree of adverse respiratory effects depends on the physical and chemical properties of atmospheric aerosol.[11–13] The particulate matter with an aerodynamic diameter <10 μm (PM_{10}) constitutes the inhalable fraction of aerosol, while the particulate matter with an aerodynamic diameter <2.5 μm ($PM_{2.5}$) could have more serious toxic effects as it constitutes the breathable fraction of the aerosol. Under this framework, European Commission (EC) legislation requires that member states monitor the PM_{10} and the lead concentration in atmosphere.[14] Furthermore the EC has recently proposed the monitoring of other toxic elements such as arsenic, cadmium and nickel in atmospheric particulate.[15]

Major and trace elements in particulate matter can be classified as natural (Na, Mg, K, Ca, Si, Al, Mn, etc.) or anthropogenic (V, Cr, Mn, Ni, Cu, Zn, Cd, Pb, etc.). The principal anthropogenic emission sources are attributed to fossil fuels: Cr, Mn and Sb are good markers for this source as they are present in coal, while V, Ni and Pb are emitted by fuel oil combustion. Industrial processes and non-ferrous mineral extraction are important sources for Cd, Zn, Cu and Hg, while elements like Ni, Zn, Pb and Cu are emitted during industrial processing of iron, cast iron and steel.

Since the atmospheric particulate samples are often constituted of minute quantities of dust (fractions of milligrams) collected onto large cellulose filters, total sample digestion is widely used for trace element analysis. Various methods using microwave-assisted digestion with different acid mixtures and different heating programs are described in the literature.[16–19] Yet in the total digestion of aerosol samples, elements contained in the cellulose material as impurities, as well as the large amounts of chemicals required, could give high blank levels and matrix effects during analysis. Therefore a careful quality control and optimization of the analytical procedure are crucial. Improvements in analytical techniques, together with the increase in awareness of ultraclean procedures, have drawn on reliable information about trace element concentrations in the different size ranges of airborne particles. No matter how much air is drawn through a filter and despite occasionally high particle loadings in the atmosphere, the amount of sample available for chemical analysis is small.

Several analytical techniques can be used to quantify metals in the aerosol. X-ray fluorescence (XRF) and proton-induced X-ray emission (PIXE) spectroscopy quantify the concentrations of elements with atomic numbers ranging from 11 (sodium) to 92 (uranium). In addition to providing a large number of chemical concentrations, neither XRF nor PIXE requires sample preparation or extensive operator time after they are loaded into the analyzer. Filters remain intact after analysis and can be used for additional analyses by other methods. Inductively coupled plasma (ICP) and instrumental neutron activation analysis (INAA) are as commonly applied to aerosol samples as XRF and PIXE. ICP requires destroying the filter, and INAA wads up the filter and makes it radioactive. These analyses are useful in certain applications owing to lower detection limits for some species used in source apportionment studies. Atomic absorption spectrophotometry (AAS) is useful for few elements, but it requires a too great dilution of the sample to be an effective technique when many different elements are to be measured. Ionic species, that are soluble in water, are important constituents of secondary aerosol, and can often be used to distinguish among pollution sources, as in the case of soluble potassium for wood smoke. Several simple ions, such as sodium, magnesium, potassium and calcium, are best quantified by ICP-optical emission spectrometry (ICP-OES). Generally lower elemental limits of detections are obtained using a microwave digestion procedure associated with an inductively coupled plasma mass spectrometry (ICP-MS) determination.

Polyatomic ions, such as sulfate, nitrate, ammonium and phosphate, must be quantified by other methods such as ion chromatography (IC). Ion analysis methods require filters to be extracted in deionized distilled water and then filtered to remove the insoluble residue. The extraction volume needs to be as small as possible, lest the solution become too dilute to detect the desired constituents (Table 4.2).

Table 4.2 Typical analytical techniques used to analyze inorganic components of atmosphere

Analytical method	Characteristics
X-ray fluorescence (HRF)	No sample preparation
Proton-induced X-ray emission (PIXE)	Non-destructive
Inductive coupled plasma (ICP)	Destructive
	Low detection limit
Instrumental neutron activation analysis (INAA)	Makes the filter radioactive
	Low detection limit
Atomic adsorption spectroscopy (AAS)	Useful only for few elements
Inductive coupled plasma-optical emission spectrometry (ICP-OES)	Useful for simple ions (Na, Mg, K, Ca)
Inductive coupled plasma-mass spectrometry (ICP-MS)	Low detection limit

4.4 Organic Aerosol

In the lower atmosphere the main components of PM are the following: highly water-soluble inorganic salts, insoluble mineral dust and carbonaceous material, including soluble and insoluble organic compounds and elemental carbon. A complete characterization of the organic fraction of PM is extremely difficult because of the high variability of physical properties and reactivity associated to both natural and anthropogenic particles. The best knowledge on the effects of organic compounds on climate and health can be achieved by the study of the distribution, lifetime and removal mechanisms. As atmospheric organic compounds are present in both the gaseous and condensed phases, the investigation of the gas-particle partitioning of such compounds becomes crucial.[20]

The most studied organic compounds in the aerosol are the persistent organic compounds (POPs) as polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs).

If compared with other environmental compartments, the atmospheric burden of POPs is relatively small, but air is considered the most important vehicle for their global redistribution. POPs can persist in the environment for a long time; they are affected by long-range transport and their presence has been discovered in remote environments such as Arctic[21,22] and Antarctica.[23–25]

Gas chromatography-mass spectrometry (GC-MS) is the most common analytical technique used to identify and quantify organic compounds in atmospheric aerosol. The usefulness of GC resides in the very wide range of compounds that can be separated on a single column and on the easy online coupling to mass spectrometry (generally electron-impact quadrupole). This method has been precious in revealing that PM contains a very large number of different organic compounds.

Because of the convenience of GC methods, liquid chromatography (LC) has seldom been used for the study of organic aerosols. LC methods employ a very wide

Table 4.3 Typical analytical techniques used to analyze organic components of atmosphere

Compound	Analytical method
POPs	GC-MS
MAs	GC-MS after derivatization
	HPLC-MS and other detectors

range of different kinds of columns and solvents with different compositions, while using GC methods a single column and a change in temperature can give a good separation of compounds. On the other hand GC-MS appears capable of accounting for only about 25 % of organic compounds in several locations; so LC-MS should be considered a good alternative for those compounds that cannot be identified by GC methods, like water-soluble organic compounds (WSOCs) in the aerosol.[20]

Recently a lot of studies are focusing on biomass burning evaluation in aerosol. Important WSOCs from biomass burning are the monosaccharide anhydrides (MAs), and the most important tracer compound among them is levoglucosan (1,6-anhydro-β-D-glucopyranose) with small amounts of galactosan (1,6-anhydro-β-D-galactopyranose) and mannosan (1,6-anhydro-β-D-mannopyranose). Even though the MAs and, in particular, the levoglucosan content in organic aerosols have been the topic of many studies, a diversity between the methodologies for the chemical analysis has been observed.

Various chromatographic techniques have been used for MA analysis including gas chromatography-mass spectrometry (GC-MS) after derivatization and high-performance liquid chromatography (HPLC) by various detectors,[26–28] among which high-resolution mass spectrometry was included (Table 4.3).[29] Schkolnik and Rudich,[30] in a review on detection and quantification in atmospheric aerosols, report that GC with mass spectrometer as detector is the most commonly used method for levoglucosan quantification, despite requiring long preparation time and dry conditions. Recently alternative methods using HPLC with mass spectrometric detection have been proposed, and great efforts have been directed toward simple, fast, precise, accurate and possibly direct analytical methods. Engling et al.[31] report a high-performance anion-exchange chromatography method with pulsed amperometric detection for the determination of anhydrosugars in smoke aerosol that requires minimal sample preparation. Dixon and Baltzell[26] investigating HPLC with aerosol charge detection for the analysis of the main MAs in atmospheric aerosols reported for levoglucosan a limit of detection (LOD) lower than the lowest LODs listed by Garcia et al.[32] using electrophoretic microchip with pulsed amperometric detection (CE-PAD) and by Schkolnik et al.[30] using ion-exclusion HPLC and spectroscopic detection but higher than electrospray ionization (ESI-MS) and high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD). A recent work determined phenolic compounds (PCLCs) in atmospheric aerosols at trace levels using liquid chromatography electrospray ionization tandem mass spectrometry (HPLC/(-)ESI-MS/MS).[33]

4.5 Conclusions

The atmosphere is a very complex mixture of chemicals. Some of them, both in gaseous and in particulate phase, can affect environment, climate and human health, so the development of newer and more specific techniques that permit to quantify pollutants in a fast and accurate way is very important. Among the gaseous constituents of atmosphere, sulfur oxides, nitrogen oxides and ozone are the most commonly monitored: for these chemicals European Regulations established spectrophotometric, luminescence and chemiluminescence techniques, respectively, because of their velocity and convenience. For monitoring purpose electrochemical sensors are likewise used; in addition to an accurate and rapid determination, the miniaturization of the sensors gives the possibility to obtain portable devices, very useful for in situ determinations. Despite the atmosphere is mainly composed by gases, it is very important to consider also the particulate matter in the environmental and health risk assessment. The predominant chemical components of PM are sulfate, nitrate, ammonium, sea salt, mineral dust and organic and elemental carbon; minor chemicals are trace metals and trace organic compounds. Different analytical techniques can be employed to investigate the inorganic part of aerosol: metals are historically analyzed by electrochemical stripping analysis using anodic stripping voltammetry (ASV) that gives simplicity, inexpensive, portability and accurate determination to the metal detection (see Chap. 10 vol 1 and Chap. 5 vol 2). Depending on the purpose of the analysis metals can be alternatively determined with X-ray fluorescence (XRF), proton-induced X-ray emission (PIXE) spectroscopy, inductive coupled plasma (ICP), instrumental neutron activation analysis (INAA) or atomic absorption spectroscopy (AAS). Several simple ions are best quantified by ICP-OES (optical emission spectrometry) or ICP-MS (mass spectrometry), while polyatomic ions must be analyzed by ion chromatography (IC). The most studied organic chemicals in aerosol are the persistent organic compounds (POPs), usually identified by gas chromatography-mass spectrometry (GC-MS). Immunosensors for the quantification of POPs have also been developed (see Chap. 13). Liquid chromatography (LC) can be useful for the determination of water-soluble organic compounds (WSOCs), including the monosaccharide anhydrides (MAs), which are biomass-burning markers in atmosphere. To quantify MAs several techniques have been improved: GC-MS after derivatization and high-performance liquid chromatography (HPLC) coupled with various detectors.

References

1. Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn. Wiley, New York
2. Poschl U (2005) Atmospheric aerosols: composition, transformation, climate and health effects. Angew Chem Int Ed 44:7520–7540

3. Harrison RM, Shi JP, Xi S et al (2000) Measurement of number, mass and size distribution of particles in the atmosphere. Philos Trans R Soc Lond A 358(1775):2567–2580
4. Chung SH, Seinfeld JH (2002) Global distribution and climate forcing of carbonaceous aerosols. J Geophys Res 107:509–512
5. Liao H, Seinfeld JH, Adams PJ et al (2004) Global radiative forcing of coupled tropospheric ozone and aerosols in a unified general circulation model. J Geophys Res 109, D16207
6. EN-14212 (2012) Ambient air—standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence. European Regulations
7. EN-14211 (2012) Ambient air—standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence. European Regulations
8. EN-14625 (2012) Ambient air - Standard method for the measurement of the concentration of ozone by ultraviolet photometry. European Regulations
9. Colbeck I (2008) Environmental chemistry of aerosols. Blackwell, London
10. Zappoli S, Andracchio A, Fuzzi S et al (1999) Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. Atmos Environ 33(17):2733–2743
11. Englert N (2004) Fine particles and human health: a review of epidemiological studies. Toxicol Lett 149:235–242
12. Pope CA III (1996) Adverse health effects of air pollutants in a nonsmoking population. Toxicology 111:149–155
13. Schwartz J, Dockery DW, Neas LM (1996) Is daily mortality associated specifically with fine particles? J Air Waste Manag Assoc 46:927–939
14. EC (European Commission) (1998) No. 57/98, 98/C360/04. Official Journal of European Communications C360/99, 23 Nov 1998
15. EC (European Commission) (2003) Commission of the European Communities, COM(2003) 423 final, 16 July 2003
16. Karanasiou AA, Thomaidis NS, Eleftheriadis K et al (2005) Comparative study of pretreatment methods for the determination of metals in atmospheric aerosol by electrothermal atomic absorption spectrometry. Talanta 65:1196–1202
17. Yang KX, Swami K, Husain L (2002) Determination of trace metals in atmospheric aerosols with a heavy matrix of cellulose by microwave digestion-inductively coupled plasma mass spectroscopy. Spectrochim Acta B 57:73–84
18. Pekney NJ, Davidson CI (2005) Determination of trace elements in ambient aerosol samples. Anal Chim Acta 540:269–277
19. Fernández Álvarez F, Ternero Rodríguez M, Fernández Espinosa AJ et al (2004) Physical speciation of arsenic, mercury, lead, cadmium and nickel in inhalable atmospheric particles. Anal Chim Acta 524:33–40
20. Jacobson MC, Hansson H-C, Noone KJ et al (2000) Organic atmospheric aerosols: review and state of the science. Rev Geophys 38(2):267–294
21. Hung H, Blanchard P, Halsall CJ et al (2005) Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: results from a decade of monitoring. Sci Total Environ 32(1–3):119–144
22. Polkowska Z, Cichala-Kamrowska K, Ruman M (2011) Organic pollution in surface waters from the Fuglebekken Basin in Svalbard, Norwegian Arctic. Sensors 11(9):8910–8929
23. Dickhut RM, Cincinelli A, Cochran M et al (2012) Aerosol-mediated transport and deposition of brominated diphenyl ethers to Antarctica. Environ Sci Technol 46(6):3135–3140
24. Klanova J, Matykiewiczova N, Macka Z et al (2008) Persistent organic pollutants in soils and sediments from James Ross Island, Antarctica. Environ Pollut 152(2):416–423
25. Negri A, Burns K, Boyle S et al (2006) Contamination in sediments, bivalves and sponges of McMurdo Sound, Antarctica. Environ Pollut 143(3):456–467

26. Dixon RW, Baltzell G (2006) Determination of levoglucosan in atmospheric aerosols using high performance liquid chromatography with aerosol charge detection. J Chromatogr A 1109:214–221
27. Palma P, Cappiello A, De Simoni E et al (2004) Identification of levoglucosan and related stereoisomers in fog water as a biomass combustion tracer by ESI-MS/MS. Ann Chim-Rome 94:911–919
28. Cappiello A, De Simoni E, Fiorucci C et al (2003) Molecular characterization of the water-soluble organic compounds in fog water by ESIMS/MS. Environ Sci Technol 37:1229–1240
29. Dye C, Yttri KE (2005) Determination of monosaccharide anhydrides in atmospheric aerosols by use of high-performance liquid chromatography combined with high-resolution mass spectrometry. Anal Chem 77:1853–1858
30. Schkolnik G, Rudich Y (2006) Detection and quantification of levoglucosan in atmospheric aerosols: a review. Anal Bioanal Chem 385(1):26–33
31. Engling G, Carrico CM, Kreidenweis SM et al (2006) Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection. Atmos Environ 40:S299–S311
32. Garcia CD, Engling G, Herckes P et al (2005) Determination of levoglucosan from smoke samples using microchip capillary electrophoresis with pulsed amperometric detection. Environ Sci Technol 39:618–623
33. Zangrando R, Barbaro E, Zennaro P et al (2013) Molecular markers of biomass burning in arctic aerosols. Environ Sci Technol 47(15):8565–8574