

Chapter 1

Potentially Harmful Elements in the Atmosphere

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Abstract The atmosphere represents a complex system influenced by the chemical and physical processes that occur at the Earth surface. These processes include emissions, transport, lifetimes and fates of several anthropogenic and biogenic/geogenic chemicals emitted from a wide variety of sources. Among these chemicals, some are considered air pollutants, i.e. any substance present in ambient air and likely to have harmful effects on human health and/or the environment as a whole. Metals, and in general elements, are natural components of the earth's crust and constituents of all ecosystems. In the atmosphere, they are mainly related to particle phase but also they can be present in a liquid phase due to the dissolution of aerosol particles in the water drops. Whatever their origin, both natural and anthropogenic, most elements, and in particular heavy metals, are dangerous because they tend to bio-accumulate in the human body.

This chapter describes a general overview on elements and their sources and potential effects on human health in atmosphere. Furthermore, considering the increase of the interest on biological fraction of PM, a briefly description of bioaerosols will be made. Recently, the number of evidence that describes how this fraction may play a key role in the effects of PM on biological systems with negative impacts on human health and ecosystem functioning are increased.

Mathematical model applied to air pollution studies will be briefly described. Mathematical models (dispersion and transport model), that predict the concentration and the dispersion of primary and secondary pollutants in atmosphere, represent a fundamental tool in the atmospheric studies to develop health and/or environmental risk assessment and various control strategy actions. Moreover, some specific elements (Sb, Tl, V and Be) will be discussed investigating the effects on health, main sources application and reviewing the most recent studies.

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1 Introduction

In the last two centuries, the technological evolution accelerated sharply with the intensification of human activities after the Industrial Revolution. On one hand, scientific and technological knowledge increased in different areas, but on the other hand, several changes in atmospheric composition occurred, increasing interest on environmental issues. The idea of pollution is a paradox within the modern world, where the scientific and technological civilization promotes the improvement of human life quality and, on the contrary, contributes to endanger life on Earth.

Anthropogenic activities release several pollutants such as gases, aerosol and particulate matter. They are continuously emitted and the concentrations exceed those which would be naturally present in air. This leads to dangerous and harmful consequences for the living beings and also produce major threats to cultural heritage. To mitigate the underlying causes of this situation, a sustainable way must be conducted aiming to reduce the emissions from human activities (i.e.: transport emissions and industrial emissions) and to reach a compromise between industrial development and environmental well-being.

The atmosphere represents a complex system influenced by the chemical and physical processes that occur at the Earth surface. These processes include emissions, transport, lifetimes and fates of several anthropogenic and biogenic/geogenic chemicals emitted from a wide variety of sources. Among these, several substances may cause adverse effects on human health and environment as a function of chemical composition, reaction properties, emission, persistence in the environment and ability to be transported in long or short distances (Kampa and Castanas 2008). On this basis, atmospheric contamination represents a serious concern and may be invisible to humans as it begins to build and the concentrations of contaminants may be so gradual that it goes unnoticed (Farmer and Cook 2013). In addition, the chemical component is connected to the biological component. In effect, the atmospheric biological material commonly named “bioaerosol”, plays a role in air and cloud chemistry and meteorological dynamics and it’s frequently associated with allergic reaction and respiratory diseases with public health impact.

Air pollutant concentrations are strictly connected to the meteorological conditions (wind speed, humidity, temperature, solar radiation, height of the Planetary Boundary Layer, PBL) which influence both transport processes and formation processes. Under this point of view, air pollution description needs several information concerning the meteorological and geographical description of the study area and the application of chemical and physical aspects. Sampling all these variables and understanding the relationships among them could be really difficult from both logistic and economic point of view. Mathematical models represent the junction between these aspects and become fundamental tools in the atmospheric

studies to develop health and/or environmental risk assessment and various control strategy actions. A description of the air pollution modeling system will be briefly described in the Sect. 3.

Among the air pollutants, most of the harmful chemical species are PM-bound, i.e. they are mainly related to the particle phase. It is generally acknowledged that specific chemicals present in PM, such as metals or polycyclic aromatic hydrocarbons (PAHs) and their derivatives, determine to a large extent the toxic potency of PM. Particulate air pollution, contains organic compounds, hydrocarbons, acid aerosols and metals attached to a carbonaceous core (De Kok et al. 2006). The World Health Organization (WHO) and the International Agency for Research on Cancer (IARC) depicts as carcinogenics or harmful for human health several elements present in atmosphere. IARC includes As, Be, Cd, Cr and Ni in Group 1 (carcinogenic to humans) and Pb, Sb, Co and V in Group 2 (probably carcinogenic to humans) (IARC 2013). Furthermore, in the Air Quality Guidelines for Europe (WHO 2000), As, Cd, Cr, Pb, Mn, Hg, Ni, Pt and V were considered in the evaluation of risk to human health. Despite this, in the European Community, just few elements have been considered in the recently UE Directive 2008/50/CE and previous ones (As, Cd, Hg, Ni, Pb). In this view, in the Sect. 4, some elements have been selected and describe considering the gap existing with respect to other much more studied elements especially in the analysis of atmospheric particulate and the potential toxicity and carcinogenicity: (i) Beryllium and related compounds are known to be human carcinogens; (ii) Vanadium is classified as possible human carcinogen by IARC (2006); (iii) Antimony and its compounds are considered pollutants of priority interest due to their potential toxicity and carcinogenicity and (iv) Thallium and related compounds are of particular scientific interest and environmental concern due to their high acute toxicity on living organisms.

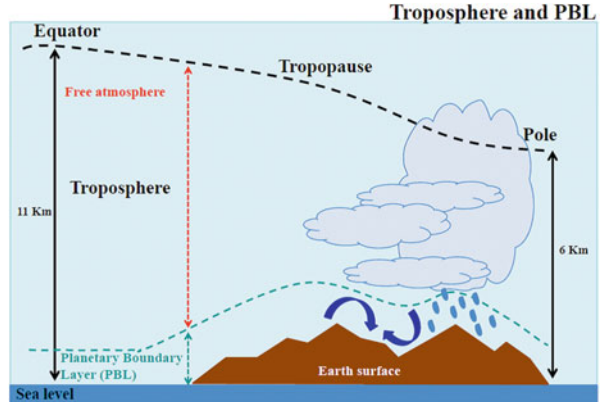
1.1 Planetary Boundary Layer (PBL) and Pollutants Dispersion

Human activities and natural sources release most of the pollutants in a thin atmospheric layer well distinguishable for its chemical and physical properties. This layer, called Planetary Boundary Layer (PBL), can be defined as the portion of the troposphere directly influenced by the Earth's surface and responds to the release of energy emanating from the surface with the time scales of 1 h (Stull 1988) (Fig. 1.1). This layer is particularly characterized by well developed mixing (turbulence) generated by frictional drag as the Atmosphere moves across the rough and rigid surface of the Earth, and by the 'bubbling-up' of the air parcels from the heated surface (Oke 1987).

The reasons of the interest in PBL studies can be summarized as (Stull 1988):

- its composition needs to be continuously monitored, as the man spends most of his life in the PBL and most of human activities taking place in it;

Fig. 1.1 Relationship between troposphere and planetary boundary layer



- most interest weather forecasts are that concerning the PBL;
- air pollutants emitted on the Earth surface can be trapped in the PBL;
- processes involving fog and smog formation occur on PBL and influence what happens in it;
- the most important energy source for the Earth's atmosphere is the solar radiation that is absorbed by the Earth and transmitted to the rest of the atmosphere by thermodynamic processes that characterize the PBL;
- about 50 % of the kinetic energy of the atmosphere is dissipated in the PBL through friction and turbulence;
- the evolution of some weather phenomena, i.e. storms and hurricanes, is related to the increase of humidity in the PBL;
- most of the aerosol sources are located on the Earth surface, therefore relevant aerosol concentrations can be detected within the PBL;
- internal stratification, height and others PBL features are important in atmospheric models since they are used as input or in validation processes.

As a consequence, several studies have been conducted on PBL.

The height of the PBL (i.e. the depth of surface-related influence) is not constant with time, it depends upon the strength of the surface-generated mixing. It varies in time and space from a few hundred meters to a few kilometers following a day-night cycles. By day, when the Earth's surface is heated by the Sun, there is an upward transfer of heat into the cooler Atmosphere. This vigorous thermal mixing (convection) enables the boundary layer depth to extend to about 1 to 2 km. Conversely by night, when the Earth's surface cools more rapidly than the Atmosphere, there is a downward transfer of heat. This tends to suppress mixing and the boundary layer depth may shrink to less than 100 m. Thus in the simple case we envisage a layer of influence which waxes in a rhythmic fashion in response to the daily solar cycle (Oke 1987). On these bases, the PBL can be compared to a heat engine that is able to use solar energy as fuel to propel the air masses (Sorbjan 1989). The changes on thickness occurring in the PBL are attributable to the combination of a number of factors related to the interaction between the Earth

surface and the layer of atmosphere overlying it. The influence of the Earth surface on the PBL is mainly determined from the following surface forcing, both natural and anthropogenic (Stull 1988):

- the aerodynamic drag (or air resistance) caused by viscous friction;
- the heat transfer to and from the soil, the evaporation and the evapotranspiration;
- the changes of the air flow induced by the surface roughness;
- the emissions of pollutants into the atmosphere, both from natural and anthropogenic sources, thermally inhomogeneous with respect to the surrounding environment.

As an obvious consequence PBL height and turbulence, and, consequently, pollutants dispersions, change in relation to the latitude considered, to the orography and to the land use of the local area. In particular, non-uniform terrain can produce advective effects causing changes in the thermal circulation systems considered. This peculiarity strongly affects the pollutants behavior that changes in relation to the latitude, climate and specific local meteorology.

As a result, the air pollution, mainly considered as particulate matter levels, is presented at the European level as often episodic situations. In northern Europe, thermal inversion conditions on the ground, stable atmosphere and low wind speed are the key factors leading to heavy pollution events. Moreover, even the local topography may affect, in some cases limiting the atmospheric circulation. In Northern and Central Europe, the resuspension of particles, for example from the road surface, is an important source of coarse particles. In South and Central Europe, stable atmosphere, low wind speed, meso-scale circulation patterns, topography and solar radiation are the most important factors that generate episodes of photochemical pollution, including the formation of ozone and new particles, which are commonly seen during the spring and summer (Valkama and Kukkonen 2004). Several authors have analyzed data on air quality with meteorological data relating them to interpret the levels of particulate matter and other pollutants in different European cities (e.g.: Querol et al. 2004; Kukkonen et al. 2005; Perrino et al. 2010) highlighting as the episodes of increased pollution are associated with high atmospheric pressures and events of thermal inversion.

Therefore, the episodes characterized by high levels of pollutants, especially particulate pollution, are in general primarily related to: (i) high traffic emissions, (ii) conditions of poor atmospheric dispersion at the local level (calm winds, thermal inversion), (iii) synoptic-scale climatic conditions that favor the long-distance transport of particles and (iv) natural sources of particles, in the coarse fraction, not easily controllable (sea-salt, wind dust) (Vardoulakis and Kassomenos 2008).

The concentration of any pollutant follows specific temporal cycles since the environmental phenomena and parameters that affect the dispersion of pollutants follow also cyclic behaviors (e.g.: the intensity of the solar radiation determines the variation in time of the photochemical pollutants). The variability of these factors influence above the average concentrations of pollutants in the short term (hourly or daily). These also can be caused by exceptional events that lead to high levels of

pollution. The medium to long term (seasonal or annual) only marginally affected by these cyclical fluctuations or exceptional events, and changes in pollutant levels on a seasonal or annual variations can depend only on prolonged or high and specific abnormalities (Perrino et al. 2010).

Accordingly, the air pollution measured at a given site is the result of a set of processes and characteristics that make up an appropriate setting to provide an aerosol with unique features and specifications. The knowledge of local sources is a starting point for characterizing different properties of the aerosol and its components but must also be considered those phenomena that occur at larger scales (regional and long-distance). These processes may involve arrivals of air masses rich in particulate and inorganic and organic component both of natural and anthropogenic origin, which may change the characteristics of the aerosol at local level (Salvador et al. 2007).

1.2 *Bioaerosol*

A new field of investigation in atmospheric science consists on the study of the relationship between elements and biological component. Microbic fraction is ubiquitous in atmosphere (Polymenakou 2012) and it is commonly named “bioaerosol”, as a mixture of viable and nonviable microorganisms (e.g. pollen, algae, bacteria, fungi, yeasts) as well as other types of biomass, including a wide range of antigenic compounds, dander, plant and insect debris, microbial toxins, and viruses (Lacey and West 2006; Peccia and Hernandez 2006) (Fig. 1.2). Among these, bacteria represent the most part of Earth’s biomass and they have been found in every environment, even the most extreme, surviving at heat, cold, radiation, pressure, salinity, acidity, and darkness (Polymenakou 2012). Biological material is mainly originated from natural sources like soil, vegetation, water, human activity like livestock, agriculture, and industrial process as fermentation. Despite the wide variety of microorganisms, taxonomic composition of atmospheric microbial community is still poorly described, because taxonomic studies of bacterial diversity are a new interest and the knowledge about the functional potential of air microbiota is not well developed.

The interest for the biogenic fraction of aerosol has increased because the exposure at biogenic material is frequently associated with allergic reaction and respiratory diseases. It is well know that bioaerosol can be associated with a wide range of adverse health effects with public health impact, including contagious infectious diseases, acute toxic effects, allergies, flu, pneumonia, tuberculosis, legionellosis, asthma, rhinitis, bronchitis, cancer (Douwes et al. 2003; Peccia and Hernandez 2006) lead to death in debilitated people and children (Kim and Kim 2007; Burger 1990; Peccia et al. 2008). Although bacteria represent the less part of bioaerosol and infrequently can induce acute diseases, they can produce endotoxines, and peptidoglycan that seems to play a role in the change of occurrence in asthma, noninfectious airway diseases such as allergies. In the developed

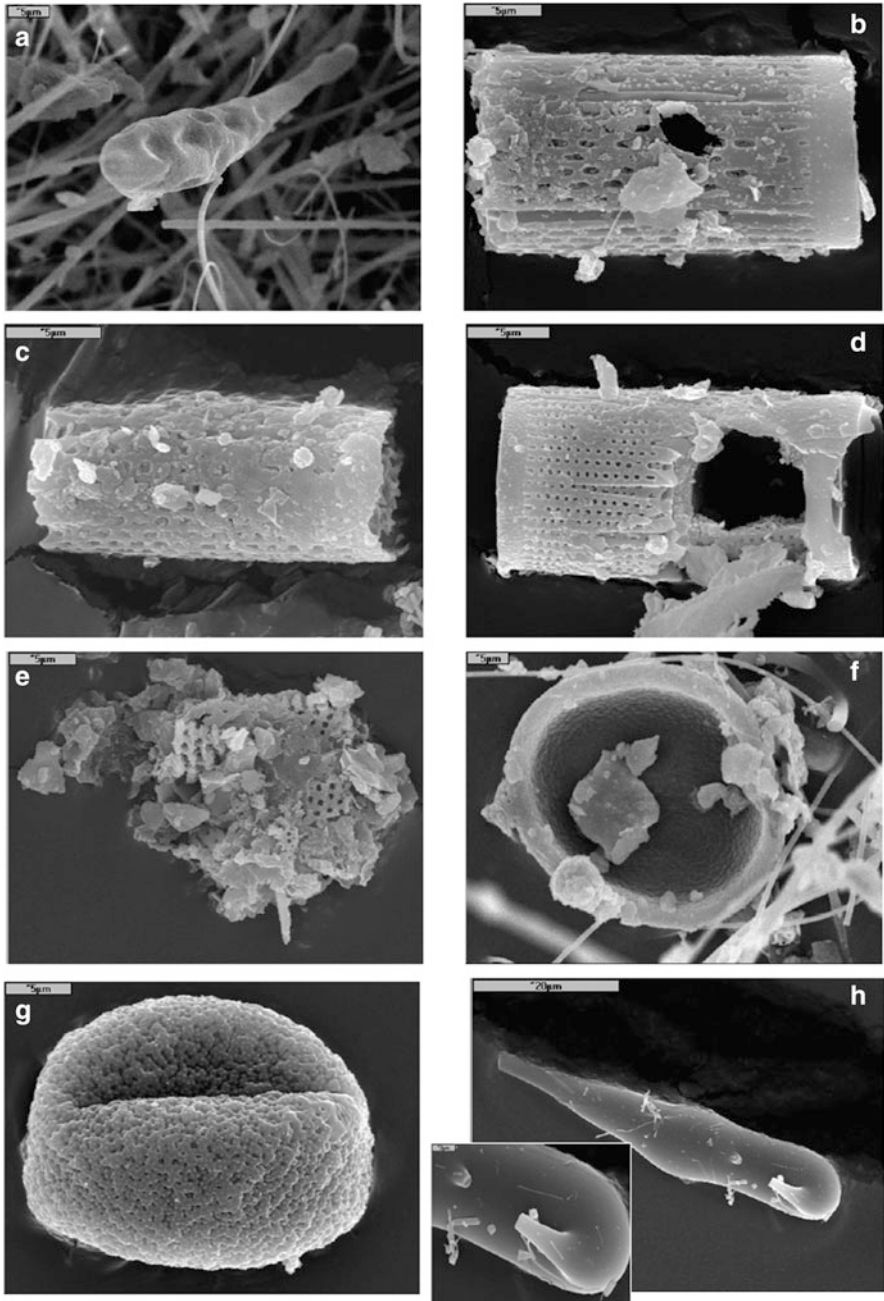


Fig. 1.2 SEM photographs of TSP and PMSEM photographs of TSP and PM 2.5, biogenic particulate matter or bioaerosols identified in dust filters from Tenerife (Canary Islands) during African dust intrusions. All samples from Las Cañadas (high mountain site), excepting **f** (Santa Cruz, coastal city). **(a)** Typically club-shaped Conidium of ascomycotan fungi (*Alternaria* sp., a cause of allergic fungal sinusitis). **(b–d)** Siliceous tests of freshwater diatoms (**(b, c)** *Aulacoseira*

world, allergies and asthma are a major cause of illness and disability, and the number of patient increase yearly.

In air, some studies report that bacteria, fungi and yeasts are viable in rainy drops, clouds and snow and have proposed that they play a role in air and cloud chemistry and meteorological dynamics (Amato et al. 2007a; Fuzzi et al. 1997; Deguillaume et al. 2008; Polymenakou 2012). Sattler (2001) collected bacteria from rain drop and demonstrated that bacteria, using carbon and nitrogen, are viable in rain droplet and can growth at low temperature. Moreover, bacteria are involved in chemical process in atmosphere, contributing to degradation of organic compounds (Ariya et al. 2002; Amato et al. 2007b) and transformation of dicarboxylic acids (Ariya et al. 2002).

When in air, bioaerosol can be transported by upper air currents over long distances across continents and they are find out in association with ambient particles, incorporated into water droplets of fog, clouds, and precipitation (Kuske 2006; Polymenakou 2012; Fuzzi et al 1997). Atmospheric bacteria can be deposited to earth surface via dry and wet deposition and they can generate adverse effect on ecosystem, human health or agriculture (Shinn et al. 2000).

Atmosphere represents a stressful environment for bacteria communities: low temperature are a limiting factor for cellular activity in the air even though studies have demonstrated that there is bacterial activity at subzero temperature. Another limiting factor is the presence in atmosphere of oxidants and solar radiation, although microbial cells can reduce the negative effects by the activity of specific enzymes (superoxidase or peroxydases). Bacteria are afforded to adopt several survival mechanisms: for instance at low temperature they can reduce cell size, and the thickness of capsular polysaccharide modifying their phospholipids composition. The damage due to solar radiation are prevented by the production of a wide range of pigments able to absorb from UV-B to red wavelengths, avoiding DNA damage (Polymenakou 2012).

In spite of chemical composition and the biogenic portion of atmospheric aerosol are the focus of many studies, the relationship between chemical composition and biological fraction has been poorly investigated and at today appear not clear. A recently published study (Bertolini et al. 2013) conducted in Milan, depicts that the bacteria communities were dominated by *Actinobacteridae*, *Clostridiales*, *Sphingobacteriales* and few *proteobacterial orders* (*Burkholderiales*, *Rhizobiales*, *Sphingomonadales* and *Pseudomonadales*). A higher abundance of *Actinobacteridae*, which are typical soil-inhabiting bacteria, has been detected in samples collected on cold days. The variation in community composition observed within seasons was comparable to that observed between seasons, thus suggesting

Fig. 1.2 (continued) *granulata*; (d) *A. islandica*), heavily eroded and worn due to the transport process. (e) Conglomerate of diatom test remains (presumably *Aulacoseira* spp.) with platy clay particles. (f) undetermined pollen grain, cross-section, containing mineral particles (Santa Cruz). (g) pollen grain, undetermined species. (h) fragmentary spicule-like particle (inset: magnification), origin (either abiotic or biological) and composition uncertain (From Delgado et al. 2010)

that airborne bacterial communities show large temporal variability, even between consecutive days. The structure of airborne bacterial communities therefore suggests that soil and plants are the sources which contribute most to the airborne communities of Milan atmosphere, but the structure of the bacterial community seems to depend mainly on the source of bacteria that predominates in a given period of time. In addition, the results indicate that different bacterial communities could be found in different PM fractions, thus suggesting that a detailed investigation of the structure, temporal variability and potential sources of bacterial communities associated to PM of different sizes may disclose further insights into the ecology of bioaerosols (Bertolini et al. 2013).

2 Elements in Atmosphere

On average the atmosphere is mainly composed by a mixture of gases represented by nitrogen (which occupies 78 % of the volume of the dry air), oxygen (21 %), and other gases present in minor amounts, such as argon, neon, helium, xenon and hydrogen (Table 1.1). These gases present constant concentration in time and within the PBL. In addition, several substances can be detected in the atmosphere, in gaseous, solid or liquid phase, emitted from natural and anthropogenic sources and some of these are considered air or atmospheric pollutants (e.g.: greenhouse gases, chlorofluorocarbons (CFC), carbon compounds, carbon monoxide (CO) and hydrocarbons).

Air pollutant can be defined as any substance present in ambient air and likely to have harmful effects on human health and/or the environment as a whole (European Community 2008). Primary pollutants or components are defined as those emitted directly into the air, e.g., SO₂, NO_x, CO, Pb, organics and combustion-generated particulate matter (PM). Once in the atmosphere, they are subjected to dispersion and transport and simultaneously to chemical-physical reaction forming secondary pollutants in gaseous or particulate phase. Both primary and secondary components are removed from the atmosphere via wet or dry deposition and can impact a variety of receptors, for example, humans, animals, aquatic ecosystem, forest and agricultural crops, and materials. Briefly, air pollutants can be grouped in four categories: (i) gaseous pollutants; (ii) persistent organic pollutants; (iii) heavy metals and (iv) particulate matter. Heavy metals, include basic metals elements such as lead, mercury, cadmium, silver, nickel, vanadium, chromium and manganese (Kampa and Castanas 2008) and the main emission sources are combustion of fuels in stationary sources for As, Cd, Cr, and Ni (more than a half of the total anthropogenic emissions) and combustion of gasoline for lead (Pacyna et al. 2007).

Metals, and in general elements, are natural components of the earth's crust and constituents of all ecosystems. In atmosphere, they are mainly related to particle phase but also they can be present inside a liquid phase due to the dissolution of aerosol particles in the water drops. They cannot be degraded or destroyed, and can be transported by air, and enter water and human food supply (Kampa and Castanas

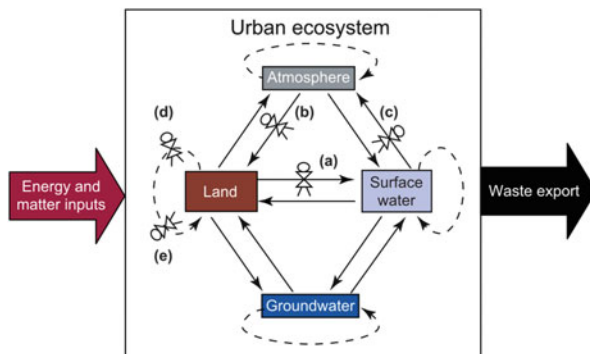
Table 1.1 Chemical composition of the atmosphere

Constituent	Fractional concentration by volume
Nitrogen (N ₂)	78.08 %
Oxygen (O ₂)	20.95 %
Water vapor (H ₂ O)	0–4 %
Argon (Ar)	0.93 %
Carbon dioxide (CO ₂)	0.04 %
Neon (Ne)	18 mg L ⁻¹
Helium (He)	5 mg L ⁻¹
Methane (CH ₄)	1.7 mg L ⁻¹
Hydrogen (H ₂)	0.5 mg L ⁻¹
Ozone (O ₃)	0.4 mg L ⁻¹
Nitrous oxide (N ₂ O)	0.3 mg L ⁻¹

2008), moving between atmosphere, hydrosphere, lithosphere, and biosphere. The dispersion and distribution of metals are highly dependent on the size of the particles and on the surface properties of the substrate on which the metals are deposited. Figure 1.2 represents fluxes and transfers of elements between the major environmental pools in a urban environment. The represented conceptual model of urban biogeochemical cycles, proposed by Kaye et al. (2006), includes major elemental pools (boxes), transformations of materials within those pools (dotted arrows), fluxes among pools (solid arrows), and controls on these fluxes (bowties). The urban ecosystem can be ‘black boxed’ such that only inputs and outputs to the entire system are measured (the largest box in Fig. 1.3), or internal components (land, atmosphere and hydrosphere) of the system can be studied. Humans control five dominant drivers of biogeochemical cycling: (i) hydrology (humans build impervious surfaces and drainage networks that alter aqueous flow paths and elemental transport) (Fig. 1.3a); (ii) atmospheric chemistry (elevated CO₂, NO_x, ozone, organic aerosols and metals in urban atmospheres interact to alter plant growth and ecosystem carbon and nitrogen cycling) (Fig. 1.3b); (iii) climate (urban heat islands and irrigation alter evaporation, transpiration and probably other biogeochemical process rates) (Fig. 1.3c); (iv) nutrients (food and fertilizer cycling affect plant growth and interact with human-dominated hydrology and atmospheric chemistry) (Fig. 1.3d); and (v) vegetation and land-use (humans impose a variable distribution of land use types within and around cities, and within each land-use type, they exert strong control over plant composition and, thus, ecosystem function) (Fig. 1.3e) (Kaye et al. 2006).

Elements deposited on land in an urban setting can be readily relocated and dispersed by wind, rain, and surface runoff (Swaine 2000; Callender and Rice 2000). Therefore, metal compounds are also increasingly introduced in the environment and could finally accumulate in a/biotic systems. In addition, acidification (e.g. upon acid rain fall) may increase their bioavailability and possibly raise their toxic potential (Florea and Büsselberg 2006). Most elements, and in particular heavy metals, are dangerous because they tend to bio-accumulate in the human body. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical’s concentration in the

Fig. 1.3 Conceptual model of urban biogeochemical cycles (From Kaye et al. 2006)



environment. Compounds accumulate in organisms any time they are taken in and stored faster than they are broken down (metabolized) or excreted (Kampa and Castanas 2008).

2.1 Overview on Main Emission Sources

The atmosphere concentrations of PM and related elements are mainly a function of the emission sources. Natural emissions derive from different kind of processes acting on crustal minerals (e.g. erosion, surface winds and volcanic eruptions), as well as from natural burning and from the oceans. On a global scale, the contribution of resuspended surface dust represents about 50 % of natural emissions of Cr, Mn, V and more than 20 % of Cu, Mo, Ni, Pb, Sb and Zn. Similar, volcanic eruption release about 20 % of Cd, Hg, As, Cr, Cu, Ni, Pb and Sb. The marine aerosol, generated by the action of wind and waves, may contribute to approximately 10 % of the emissions of trace metals. The combustion of biomass can contribute to emissions of Cu, Pb and Zn (Grgić 2008).

The main anthropogenic sources are linked to high temperature combustion processes, biomass burning, fossil fuel combustion, incinerator and industrial activities. Anthropogenic processes release metals in vapour phase that can form new particles by condensation or gas-to-particle conversion processes. Fossil fuels combustion represents the most important anthropogenic sources of Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V (Moreno et al. 2006; Grgić 2008) and contributes to the emissions of Cu, Mn and Zn. As, Cd, Cu, Ni and Zn primarily derived from steelworks (Moreno et al. 2006), coal combustion (Lin et al. 2005; Lim et al. 2010) and zinc metallurgy (Querol et al. 2007). V and Ni are linked to coal and oil combustion (Almeida et al. 2005; Elminir 2005; Hueglin et al. 2005; Moreno et al. 2007).

Vehicular traffic emits a wide range on elements deriving from exhaust gas of gasoline and diesel vehicles (Fe, Ba, Br, Pb, Cu, Zn, Cd) (Sternbeck et al. 2002; Moreno et al. 2006), tyre wear abrasion (Zn), lubricant (Sb) and fillers (Ba, Ca)

(Thorpe and Harrison 2008), while Mn and Pb are related to the erosion of the road surface (Amato et al. 2009). PM₁₀ metal emissions were dominated by crustal elements Si, Fe, Ca, Na, Mg, Al, and K, and elements associated with tailpipe emissions and brake and tire wear, including Cu, Zn, Sb, Ba, Pb, and S. Although the sum of Cu, Zn, Sb, Ba and Pb did not exceed 1 % of PM₁₀ mass in tunnel studies, they may be important for health effects and can provide some indications of the sources of particulate matter emissions, such as brake wear (Lough et al. 2005). Moreover, in the last decades, the introduction of the use of catalytic converters has contributed to the emission of platinum group elements (Pt, Pd, Rh) (PGEs).

2.2 *Particulate Matter and Trace Elements: Health Effect*

As describe above, elements in atmosphere are mainly related to particle phase but also their can be present inside a liquid phase due to the dissolution of aerosol particles in the water drops. Briefly, elemental fraction represents one of the components of the atmospheric aerosol (commonly identified as Particulate Matter), defined as complex mixture of particles both on liquid and solid phase, dispersed in a gaseous medium. Particulate matter plays a central role in atmospheric processes affecting human health (Pope et al. 2009); visibility (Bäumer et al. 2008), air quality and climate change (IPCC 2007). It also influences ecosystems and cultural heritage, being involved in acid deposition (Larssen et al. 2006; Nava et al. 2010).

The chemical composition of atmospheric aerosol in a given area depends on PM sources, physical and chemical processes of transformation, and processes of transport and mixing caused by atmospheric motions. The large surface area of the finer fraction favors the adsorption of heavy metals, ammonium ions, sulfates, nitrates and numerous organic compounds such as polycyclic aromatic hydrocarbons (PAHs).

On these bases, the pollution from particulate matter is an important environmental risk factor for both human health, for the disorders generated by it, and the possible effects on climate and ecosystems (e.g.: acidification, eutrophication, effects on the radiative balance, corrosion and degradation of materials) (Lazaridis et al. 1999). Recently there is a growing interest of the scientific community for the levels of pollution from particulate air pollution, due to the strong correlation between morbidity, mortality and concentration of inhalable and respirable particles (PM₁₀ and PM_{2.5}), highlighted from numerous epidemiological studies (Dockery and Pope 1996; Brunekreef et al. 1997; Englert 2004; Oberdoster et al. 2005). The association between the levels of concentration of the fine particles and the increase in risk has already been demonstrated, while the biological mechanisms that determine the health effects are still partially obscure. Elevated levels of particle in air have been associated with decreased lung function, increased respiratory symptoms such as cough, shortness of breath, wheezing and

asthma attacks, as well as chronic obstructive pulmonary disease, cardiovascular diseases and lung cancer.

Factors which may influence the toxicity of airborne particulate matter can be summarized as: (i) bulk chemical composition; (ii) trace element content; (iii) strong acid content; (iv) sulfate content; and (v) particle size distribution (Harrison and Yin 2000). The size of airborne particles is significant, as this determines in which parts of the respiratory tract the particles are deposited, as well as how rapidly and the manner in which they are cleared. Small airborne pollutant particles have small inertia and therefore are poorly impacted before entering the alveoli region of the lung; while in the alveoli, the probability of deposition is very high due to their high diffusion coefficient. A general trend of increasing element concentration with decreasing aerodynamic diameter was observed for elements V, Mn, Ni, Cu, Zn, Se, and Cd, indicating they were predominately concentrated in the nanoparticle size range. Other elements including Fe, Sr, Mo, Sn, Sb, Ba, and Pb were predominately concentrated in the fine-size range. Increased concentration of elements in the nano and fine particle size range is significant due to their ability to penetrate into the deepest alveolar area of the lungs. Moreover, particle size had an important effect on element bioaccessibility for the studied urban PM samples showing a general trend of increasing element bioaccessibility with decreasing particle size (Niu et al. 2010).

The particle composition may determine in what way the respiratory tract reacts, or the body responds. Some particles can act as carriers of adsorbed chemicals or gases which can act as triggers for various health effects (Morawska and Zhang 2002 and references therein). Cardiovascular effects have been mostly ascribed to particulate components (Bhatnagar 2006; Brook 2008; Araujo and Nel 2009). Various mechanisms have been proposed to explain how inhalation of ambient particulate could result in systemic cardiovascular effects such as: (1) activation of pulmonary receptors resulting in autonomic nervous system imbalance and the development of dysrhythmias; (2) induction of pulmonary and systemic inflammation; (3) access of particles or their chemical constituents to the systemic circulation (Araujo 2011).

Many elements, such as V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb are widely distributed in PM and, therefore, are suspected to be an important source of PM toxicity. Elemental PM Components have been reported to produce and release inflammatory mediators by respiratory tract epithelial cells and/or to catalyze oxidative stress resulting in potential tissue injury. Toxicological studies have suggested that it is the soluble trace element content instead of the total element content of PM that has more direct links to harmful. The production of radicals by soluble elements and their mediated Fenton chemical reaction is the primary pathway to generating oxidants, where particle size plays an important role in element bioaccessibility and, therefore, finally in bioavailability and toxicity (Niu et al. 2010 and references therein).

Trace elements found in association with fine particles and of toxicological concern include As, Cd, Cr, Hg, Mn, Ni, Pb, and V, exposure to which in occupational environments has been suspected of causing sinusitis, asthma and chronic

bronchitis, pneumonia, lung hemorrhage, lung cancer, and brain hemorrhage (Charlesworth et al. 2011 and references therein). Furthermore, trace elements are important because of their dual role in the health of plants, animals and humans, namely, their essentiality and their potential to be harmful. Consideration must be given to essentiality, non-essentiality and toxicity that depend on concentrations, the form of the element speciation, pH and oxidation–reduction conditions and other factors. For essential trace elements, there is an optimal range of concentration for healthy growth of organisms, varying for different plants, animals and humans. Concentrations less than the lower end of this range would give deficiency, while those above the upper end of the range could lead to harmful effects (Swaine 2000). A human health concern is usually associated with excessive exposures to metals that cause toxic effects to biological organisms, herein referred to as trace metals of environmental concern. These trace metals may include non-essential ones, such as Cd and Pb that can be toxic even at trace levels, and biologically essential elements, such as Cu and Zn, which might cause toxic effects at elevated concentrations. Other indirect consequences of trace metal contamination of the urban environment include the subsequent migration of the pollutants to receiving bodies of water via urban runoff, resulting in the trace metal enrichment of sediments (Wong et al. 2006).

Physicochemical properties of metal compounds govern uptake, intracellular distribution and binding of these in the organism. Interactions with proteins (e.g.: with zinc finger structures) appear to be more relevant for metal carcinogenicity than binding to DNA. In general, metal genotoxicity is caused by indirect mechanisms. In spite of diverse physico-chemical properties of metal compounds, three predominant mechanisms emerge: (1) interference with cellular redox regulation and induction of oxidative stress, which may cause oxidative DNA damage or trigger signaling cascades leading to stimulation of cell growth; (2) inhibition of major DNA repair systems resulting in genomic instability and accumulation of critical mutations; (3) deregulation of cell proliferation by induction of signalling pathways or inactivation of growth controls such as tumour suppressor genes. In addition, specific metal compounds exhibit unique mechanisms such as interruption of cell–cell adhesion by cadmium, direct DNA binding of trivalent chromium, and interaction of vanadate with phosphate binding sites of protein phosphatases (Beyersmann and Hartwig 2008).

Exposure to heavy metals is potentially harmful especially for those metal-compounds, which do not have any physiological role in the metabolism of cells. The ingestion of metals via food or water could modify the metabolism of other essential elements such as Zn, Cu, Fe and Se. Furthermore, most metals are capable of forming covalent bonds with carbon, resulting in metal-organic compounds. Transformation (by methylation or alkylation) influences their mobility, accumulation as well as their toxicity (e.g. Pb, Zn, Cu, Cd, As, Sb, Cr, Ca, Na, Au, Cl, Br). Prolonged exposure to metals and metal compounds could result in dysregulation of cellular pathways causing subsequent toxicity. Metals and metal compounds interfere with functions of the central nervous system (CNS), the haematopoietic

system, liver and kidneys. Recently, more attention and concern is given to metal compounds that have toxic effects at low levels of exposure.

3 Modelling Air Pollution

A mathematical model is a description of a system using mathematical concepts and language. The process of developing a mathematical model is termed mathematical modelling. A model may help to explain a system and to study the effects of different components, and to make predictions about behaviour. The model use equations to represent the interconnections in a system with several approaches that have lead to the creation of different model types: dynamical systems, statistical models, differential equations, etc. Models represent an important tools in environmental research giving a complementary instrument useful in data interpretation and are of great importance in natural science giving a complementary instrument useful in scenarios representation and data interpretation (Ford 2009).

Air pollution description needs several information concerning the meteorological and geographical description of the study area, the emission sources and the application of chemical and physical aspects involved on pollutant interactions. In this view, air quality is a complex phenomena and the use of modelling represent a fundamental tool for both research and applied objectives (e.g.: policies, action plans, risk assessment).

In order to modelling air pollution a modelling system must be implemented. A model system is composed of sub models that are necessary to create the input for the chemical model (Fig. 1.4).

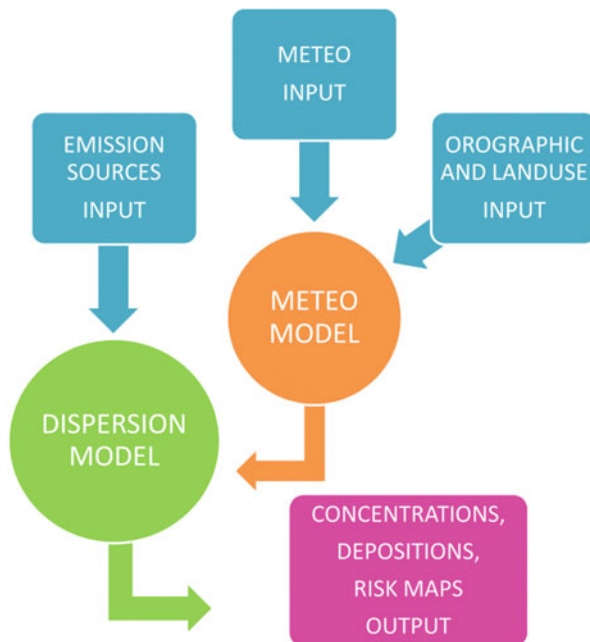
The main steps to create a model input are: (i) the creation of an appropriate emission inventory; (ii) the simulation of the meteorological fields and (iii) the simulation of the dispersion and transport. Very important are also the characterization of the topographical and land use coefficients that characterize the study domain as well as the geometric representation of the emission sources (as point, line and area source).

3.1 Air Pollution Modelling System

3.1.1 Emission Inventory and Emission Modelling

An *emissions inventory* is a database that lists, by source, the amount of air pollutants discharged into the atmosphere of a community during a given time period (EPA 2011). The development of a complete emission inventory is an important step in an air quality management process. Emission inventories are used to help determine significant sources of air pollutants, to establish emission trends over time, target regulatory actions, and to estimate air quality through

Fig. 1.4 A flow diagram of a typical modelling system used to simulate air pollutants dispersion



computer dispersion modeling. An emission inventory includes estimates of the emissions from various pollution sources in a specific geographical area. A complete inventory typically contains all regulated pollutants. Different methods for calculating the emissions inventories are available, and the choice of method depends on the availability of data, time, staff and funding.

The methods may include, but are not limited to: continuous monitoring to measure actual emissions; extrapolating the results from short-term source emissions tests and combining published emission factors with known activity levels. An emission factor may be used to estimate emissions when actual emission data is not available. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category.

In Europe, the third edition of the emission inventory guidebook (prepared by the United Nations European Environment Agency Task Force on Emissions Inventories and Projections) (EMEP 2009) provides a comprehensive guide to state-of-the-art atmospheric emissions inventory methodology to support reporting under the UNECE Convention on Long-Range Transboundary Air Pollution and the EU directive on national emission ceilings. In the U.S., the EPA Clearinghouse for Inventories & Emission Factors contains information on emissions inventories, emissions factors, software and tools used for emissions inventories, and emissions modeling (EPA 2011).

In the context of air quality modeling, *emission modeling* is the process by which emissions estimates are prepared for use in an air quality model. In general terms,

the emissions model is the suite of tools that are used to estimate and spatially and temporally allocate emissions for use in deterministic and statistical air quality models (Sarma 2008). Yet, the emissions estimates, that result from the emissions modeling process, are the critical link in the air quality modeling process. The emissions estimates model is a computerized system that utilizes data to estimate emissions from a specific source. The emissions modeling system is a computerized framework under which emissions estimates models operate.

3.1.2 Meteorological Models

Modeling air quality requires an accurate modeling of all the factors that control the concentrations of these chemical species, including the movement of these airborne species from one location to another. Hence, accurate air quality modeling is predicted by accurate meteorological modeling. The phrase meteorological modeling (or atmospheric modeling or numerical weather prediction, NWP) refers to any numerical representation of the atmosphere and its processes. A numerical representation is based on dynamical, thermodynamical, physical and chemical properties of the atmospheric system. Even though atmospheric modeling started out examining just the atmospheric processes, it is commonly understood that the atmospheric motions depend on the properties of the earth surface as well as the dynamics of the oceans. Therefore, it is appropriate to extend the definition of meteorological modeling to include the effects of the surface of the earth and the oceans (Sarma 2008). Meteorological models are developed and used for two main purposes: (i) to understand and forecast local, regional, or global meteorological phenomena and (ii) to provide the meteorological input required to run air pollution models. Numerical meteorological models can be divided in two groups: (i) diagnostic models, i.e., models that are based on interpolation/extrapolation of available measurements and contain no time-tendency terms and (ii) prognostic models, i.e., models that perform space-time integration of the conservation equations of mass, heat, motion, water, and if necessary other substances, such as gases and aerosols.

3.1.3 Diffusion and Transport Model

Air quality models use mathematical and numerical techniques to simulate the physical and chemical processes that affect air pollutants as they disperse and react in the atmosphere. Based on inputs of meteorological data and source information like emission rates and stack height, these models are designed to characterize primary pollutants that are emitted directly into the atmosphere and, in some cases, secondary pollutants that are formed as a result of complex chemical reactions within the atmosphere. These models are important to the air quality management system because they are widely used by agencies tasked with controlling air pollution to both identify source contributions to air quality problems and assist

in the design of effective strategies to reduce harmful air pollutants. For example, air quality models can be used during the permitting process to verify that a new source will not exceed ambient air quality standards or, if necessary, determine appropriate additional control requirements. In addition, air quality models can also be used to predict future pollutant concentrations from multiple sources after the implementation of a new regulatory program, in order to estimate the effectiveness of the program in reducing harmful exposures to humans and the environment.

The most commonly used air quality models include the following:

- Dispersion Modeling – These models are typically used in the permitting process to estimate the concentration of pollutants at specified ground-level receptors surrounding an emissions source (e.g.: Lagrangian models).
- Photochemical Modeling – These models are typically used in regulatory or policy assessments to simulate the impacts from all sources by estimating pollutant concentrations and deposition of both inert and chemically reactive pollutants over large spatial scales (e.g.: Eulerian models).
- Receptor Modeling – These models are observational techniques which use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations.

EPA (2011) suggests specific models for each type but several models are developed in the entire world. Differences on modeling output are highlighted in Fig. 1.5.

Models are typically applied to study impacts of individual sources, multiple-source industrial facilities, metropolitan areas, or larger regional areas up to sub-continental scale. The spatial scales range from up to few kilometers (for large industrial point sources), to hundred kilometers (for individual urban areas), to few thousand kilometers (for larger regional areas). When applying models to regional-scale domains, the spatial scale of important atmospheric phenomena that ultimately contributes to regional air quality problems must be accurately analyzed.

Nested grid capabilities, an important feature of contemporary regional models, allow them to resolve important phenomena and concentration gradients in areas of the domain where significant sources are present. The time scales of concern are related to ambient air quality standards, which have averaging times ranging from 1 h to 1 year.

3.2 Chemical Transport Model for Particulate Matter (PM)

A particular subject in air quality modelling is the simulation of PM (Particulate Matter) transport and chemical reaction. Particulate matter constitutes a multi-component system of material in solid or liquid state that could enter in the air by natural or anthropogenic causes. A crucial issue in understanding and managing atmospheric PM is the ability to link emissions of primary PM and precursors of

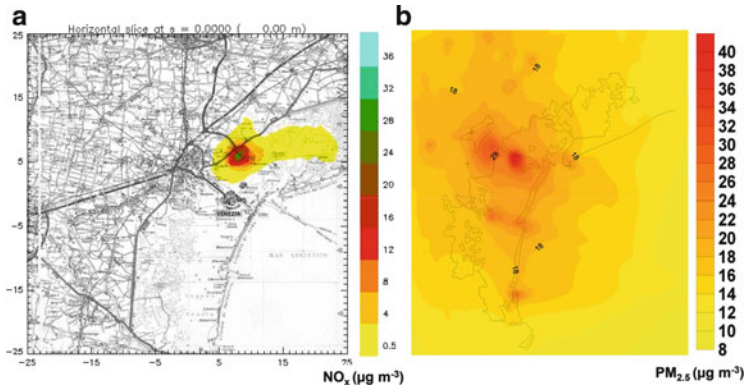


Fig. 1.5 An example of a Lagrangian dispersion simulation of an aircraft emission (a) (Pecorari 2010) and of an Eulerian $PM_{2.5}$ dispersion simulation (b) (Pecorari et al. 2013)

secondary PM quantitatively to ambient PM concentrations and other physiologically and optically important properties. Air quality models used to study PM distribution are generally called *Chemical-Transport Models* (CTMs). For PM they are an important quantitative tool with which to address this relationship. CTMs consist of mathematical representations of the relevant physical and chemical atmospheric processes, which are solved using numerical algorithms to obtain pollutant concentrations as a function of space and time for a given set of pollutant emissions and meteorological conditions (e.g.: Peters et al. 1995; Seinfeld and Pandis 2006; Jacobson 1999; NARSTO 2000; Russell and Dennis 2000). CTMs are prognostic models that, given the emission rates of selected pollutants and their precursors and prevailing meteorological conditions, predict the atmospheric concentrations of those pollutants based on a combination of fundamental and empirical representations of the relevant physicochemical atmospheric processes. Although most current CTMs tend to treat the same major physicochemical processes, there are significant differences among CTMs in their characterization of PM chemical composition and size distribution. Air-quality models that neglect atmospheric chemistry are often termed dispersion models, and such models are limited to the treatment of chemically inert species. An air quality modeling system is the set of emission, meteorological, and air-quality models needed to simulate air quality. In addition to PM, CTMs have been developed for other pollutants, including photochemical oxidants and chemicals deposition (wet and dry). As a general rule, all of the atmospheric processes relevant to photochemical oxidants and chemicals deposition are also relevant to PM, but some processes relevant to PM (for example, size-dependent droplet chemistry) are usually neglected in CTMs for photochemical oxidants or chemicals deposition. Consequently, PM CTMs are normally more complex than CTMs developed for other air pollutants, and they are often able to predict these other pollutants as well as PM. For this reason, they may also be referred to as “one atmosphere”, “multi-pollutant”, or “unified” air quality models (Seigneur and Moran 2004).

4 Selected Target Elements

4.1 *Beryllium (Be)*

4.1.1 Health

The primary route of human exposure to Beryllium and related compounds is through inhalation of dusts and fumes although it may be present in drinking water and food. As reported by the U.S. Department of Health and Human Services (HHS 2011), Beryllium and related compounds are known to be human carcinogens. Indeed several epidemiological studies indicate an increased risk of lung cancer in occupational groups exposed to this element or beryllium compounds. Workers more exposed to this metal are: beryllium miners, beryllium alloy makers and fabricators, phosphorus manufacturers, ceramics workers, missile technicians, nuclear reactor workers, electric and electronic equipment workers, and jewelers. Moreover, Beryllium metal and several beryllium compounds such as beryllium-aluminum alloy, beryllium sulfate and beryllium oxide cause lung tumors in rats, transgenic mice and rhesus monkeys by either inhalation or intratracheal instillation (HHS 2011).

The bioavailability (related to its solubility) of this element is strongly pH dependent. At pH of about 7, beryllium is poorly soluble but with decreasing pH, it becomes more soluble (Bohdalkova et al. 2012).

4.1.2 General Usage

The abundance of beryllium in the ecosystems and in the Earth's crust is low (Ryan 2002). Due to its peculiar properties (such as the lightness and a high melting point) Beryllium and related compounds are very useful for different applications in industry, computer science, telecommunications and aerospace (HHS 2011). Moreover Beryllium is useful in the production of nuclear weapons and in sealed neutron sources due to its small neutron cross-section.

According to the Agency for Toxic Substances and Disease Registry (ATSDR), 9.5 metric tons of beryllium and beryllium compounds is released annually to the atmosphere: the 54 % is from natural sources (windblown dust and volcanic particles) and the 81 % of the anthropogenic beryllium coming from electric utilities (ATSDR 2002). However, the open-pit coal mining and the coal combustion in power plants are the main regional sources of atmospheric pollution of this element. Furthermore the metallurgical plants could be also important point sources of this pollution (Aneja et al. 2012; Bohdalkova et al. 2012).

4.1.3 Results of Some Recent Studies

The majority of studies concerning the Be in the atmosphere are related to the isotope ^7Be that arise as a result of the spallation processes of light atmospheric elements in the upper atmosphere and is a relatively short-lived ($T_{1/2} = 53.3$ day) (Vecchi and Valli 1997; Papastefanou and Loannidou 1996 and references therein). The production rate of this isotope is maximum in the stratosphere, at about 20 km, and decreases exponentially with decreasing altitude but a significant quantities is still formed in the upper troposphere.

^7Be participates in the formation and growth of the accumulation mode aerosols (0.07 to 2 μm aerodynamic diameter). The size of particles which contain this isotope increases when there is high concentration of other pollutants, when the relative humidity increases and with large residence time of ^7Be in the atmosphere. Its removal occurs when aerosol is collected on droplets during condensation of moisture in the lower parts of the troposphere and by wet precipitation (dry fallout plays only a minor role) (Conaway et al. 2013). Due to these features and to its relative simplicity in measurement using high-resolution gamma-ray spectrometry, ^7Be is a powerful and commonly used tracer to study the nature of large scale atmospheric circulation and tropospheric aerosol scavenging processes (wet and dry deposition and trapping by above ground vegetation).

For example, Conaway et al. (2013) have investigated the temporal and spatial variability of ^7Be accumulation in atmospheric deposition at sites near northern Monterey Bay on the central California coast. They found values of activities and deposition fluxes comparable to those of other coastal locations with comparable latitude and Mediterranean-type climate (annual ^7Be atmospheric deposition was approximately $1,900 \text{ Bq m}^{-2} \text{ yr}^{-1}$, with most deposition via rainwater (>95 %) and less via dry deposition). Further, Vallés et al. (2009) identified similar seasonal variations of ^7Be and ^{210}Pb concentrations by characterizing the radioactivity of airborne particulate matter sampled in the Barcelona area from 2001 to 2005: the maximum values were recorded during the summer months and dry periods supporting that washout of atmospheric aerosols by rainfall carries these radionuclides. These results were not completely in agreement with those of Hernandez et al. (2005) that characterized the atmospheric particulate of Tenerife Island for a comparable sampling period. Indeed they found a linear correlation between ^7Be and ^{210}Pb but concentration lower than expected for a continental site at the same latitude and altitude and the maximum values were not detected during summer season. Subsequently, Hernandez et al. (2008) focused on the study of the time variation of ^7Be concentration to better characterize the long range transport of North African and oceanic aerosols. This research confirms that the downward transport from the mid-troposphere is a key mechanism for the increase of these radionuclide concentrations in the lower atmosphere. Moreover, this paper suggests that the flow of re-suspended particles in the aerosol transport zone can enhance the scavenging effect of ^7Be and then its atmospheric particulate concentration.

As regard the air concentration of Beryllium (not only the isotope ^7Be), Pandey et al. (1998) showed that this element is associate with Cadmium, Chromium, Nickel and Vanadium in the atmospheric particulate of Bhilai (an urbanized and industrialized city of India) suggesting that the most likely sources are: non-ferrous metallurgical operations, diesel exhaust and residual oil combustion.

Although Beryllium has been historically machined, handled and stored in facilities at Lawrence Livermore National Laboratory since the 1950s, the atmospheric concentrations of this element over three decades were comparable to those found elsewhere in the natural environment (Sutton et al. 2012). Indeed, the atmospheric concentrations show a typical seasonal periodicity characterized by high levels in late summer and early fall (related to elevated temperatures, wind speed, and lower precipitation), and lower ones in the winter (related to lower temperatures, wind speed, and greater precipitation). Moreover the mean annual concentrations decrement revealed at the National Laboratory since 1990 correspond to the national decrease in PM_{10} since the implementation of the EPA's 1990 Clean-Air-Act. On these bases, the laboratory operations have had a negligible impact on the Be content of airborne particulate near the monitored area and so, the detected beryllium mainly comes from soil resuspension and previous coal fired power station burden.

Lately, Bohdalkova et al. (2012) measured soluble and insoluble Be concentrations in rime and snow (these two matrices contribute to the scavenging of pollutants from the atmosphere (Brewer et al. 1983)) of mountains remote from residential and industrial areas of the Czech Republic (Europe). They revealed that on average about 34 % of total Be deposition occurred in soluble form (bioavailable) and that soluble concentrations in rime were 7 times higher compared to snow (6.1 vs. 0.9 ng L^{-1}) because the larger overall surface of water droplets in rime more efficiently scavenges pollutants from the atmosphere.

4.2 Vanadium (V)

4.2.1 Health

The environmental exposure to Vanadium and related compounds occurs via inhalation or through consumption of contaminated foods (IARC 2006). In Ress et al. (2003) was highlighted a spectrum of non-neoplastic lesions in rats and mice exposed to V_2O_5 by whole-body inhalation for 2 years and a clear evidence of carcinogenicity in male and female mice and some evidence of carcinogenicity in male rats. As concerns the human, the reactive oxygen species induced by Vanadium have been reported to trigger or potentiate cell apoptosis (evolutionary conserved homeostatic process involved in distinct physiological processes including organ and tissue morphogenesis, development and senescence), and to induce lipid peroxidation and oxidative DNA damage (Franco et al. 2009 and references therein). Specifically, the results of the research of Ehrlich et al. (2008) suggest that

the workers from a V_2O_5 factory are at increased risk for cancer and other diseases that are related to DNA instability due to the inhalation of this compound. Indeed this metal oxide is classified as possible human carcinogen by IARC (2006).

4.2.2 General Usage

According to IARC (2006), Vanadium is found in several minerals (prevailing in phosphate rock and iron ores) and in fossil fuels (oil, coal, shale) with an average concentration in the earth's crust of 150 mg kg^{-1} . In ores V is mainly in pentoxide form and sometimes as sodium or ammonium vanadates, in crude oil and residual fuel oil the most common oxidation state of Vanadium is +4. Only a few Vanadium compound are of commercial significance and the Vanadium pentoxide (V_2O_5) is the dominant one. This is a poor soluble compound of atmospheric particulate matter prevailing emitted by oil – coal burning and metallurgical plants (Ress et al. 2003). It is used in the production of metal alloys, electronic material, lithium batteries, high-pressure lamps, glass, paint, ceramics, in petrochemistry, for the enameling, for the synthesis of chemicals compounds as an oxidation catalyst in heterogeneous and homogeneous catalytic processes, as a corrosion inhibitor and in the photographic field (IARC 2006; Ehrlich et al. 2008 and references therein).

4.2.3 Results of Some Recent Studies

The main atmospheric natural source of V is the continental dust, followed by the sea spray salt and the volcanic emission. The anthropogenic ones are the activities related to the production-consumption of materials abovementioned. Specifically, the largest contributors are metallurgical works, coal and residual oil burning. During the combustion, V is mainly released as vanadium pentoxide or may be associate with sulfate in form of fly ash particulate. The common atmospheric concentration of this element is of the order of ng m^{-3} although in unpopulated areas such as Antarctica it was found at pg m^{-3} and near large metallurgical plant at $\mu\text{g m}^{-3}$ (IARC 2006 and references therein).

Usually, this element is used as a tracer to identify the heavy oil combustion sources (Wang et al. 2006; Moreno et al. 2010; Fernzandez Espinosa et al. 2002; Lupu and Maenhaut 2002; Mazzei et al. 2008; Hedberg et al. 2005; Jang et al. 2007; Rajšić et al. 2008) or coke combustion (Alastuey et al. 2007). However, most studies carried out in urban and suburban environments identified this element clustered with a mixture of more general anthropogenic tracers of industry or traffic sources (Viana et al. 2008; Sternbeck et al. 2002; Amato et al. 2010). Moreover, Hao et al. (2007) shown that V in the TSP of Qingdao (China) is mainly derived from soil with a minor contribution from ship emissions. Specifically, this element was characterized by a strong seasonal variation with the lowest mean value in fall, the highest in winter, a significant increase of concentration during the Asian dust

episodes and statistical analysis highlighted a significant correlation with Fe, Ti, Mn, and Ni.

Fernandez Espinosa et al. (2001) shown that Vanadium is prevailing concentrated in fine fraction ($<0.61 \mu\text{m}$) of atmospheric particulate of Seville at the end of twentieth-century. Similar size distribution was found for nickel, lead and cadmium suggesting as a potential source the combustion process. As regard the chemical speciation of Vanadium in fine fraction, about 50 % of this element is present in the “soluble and exchangeable fraction” (the most easily available to human body through breathing), about 25 % in the “carbonates, oxides and reducible fraction” (also bioavailable through the lung), and about 13 % in the “bound to organic matter, oxidable and sulphidic fractions” (Fernandez Espinosa et al. 2002). Moreover, a significant correlation between Ni and V in the chemical fraction of metal bound to organic matter or sulphidic metal was found, confirming that these metals have a strong relationship with the combustion of fuels used in the industrial activities of the city.

Also Okuda et al. (2007), by studying the TSP and $\text{PM}_{2.5}$ of Yokohama (Tokyo metropolitan area) found that almost all the Vanadium was contained in fine fraction. Moreover, they showed that this element was relatively high water-soluble and good correlated with Ni. According to Jang et al. (2007), the authors identify as a major source the heavy oil combustion. Furthermore, Moreno et al. (2010) showed that sometimes anomalous high values of V/Ni ratio (>4) can detect the influence of near high-V petcoke and fuel oil combustion sources. Indeed, in urban background PM the use of this ratio is limited due to the substantial contribution of other source. Finally, also Cheng et al. (2011) and Vecchi et al. (2008) found significant concentrations of V in PM_1 .

Moreno et al. (2008a) used Vanadium and some Lanthanide elements as geochemical markers in PM_{10} and $\text{PM}_{2.5}$ to better characterize the emission contributions of natural and anthropogenic sources in several cities of Spain (Moreno et al. 2008a, 2010) and Mexico City Moreno et al. (2008b). Specifically, atmospheric particles derived from fuel oil and petcoke combustion in power stations exhibit very low La/V ratios (<0.1) because the fly ash is enriched in V, the mineral PM derived from uncontaminated crustal materials or coal combustion are characterized by $\text{La/V} = 0.2\text{--}0.3$ and emissions from oil refineries using zeolitic fluid catalytic converters can be enriched in La to such an extent that the La/V value is above the normal crustal ratios. Another useful tool to improve the abovementioned source characterization is the three-component Ce-La-V or Ni-La-V plot where the sample are placed as a function of the concentration of three elements (Moreno et al. 2008b, 2010).

Finally, Sella et al. (2006), by characterizing the total suspended particulate (TSP) sampled in two site of a coastal region of Rio de Janeiro (Brazil), found that the atmospheric concentration of Vanadium was of ng m^{-3} order and increased by approaching to the ocean (unlike the other elements studied) especially during upwelling events. The authors suggested that the sea spray is an important source of V in particular during upwelling events when the presence of some marine tunicate, that bio-accumulate this element, is high.

4.3 Antimony (Sb)

Although, there are several reviews that characterize the Sb in different areas and the relative interest in the environmental field is growing in the last decade, a gap exists with respect to other much more studied elements especially in the analysis of atmospheric particulate. Between the various reviews is interest to mention Franco et al. (2009) and De Boeck et al. (2003) where the toxicity and carcinogenicity of this element is defined; He et al. (2012) where the Antimony pollution in several samples of soils, sediments, waters, plants and atmospheric particulate collected in China are characterized; and Smichowski (2008) where the research carried out on the determination of Sb and its predominant chemical species in atmospheric aerosols are summarized and discussed.

4.3.1 Health

United States Environmental Protection Agency and the European Union consider Antimony and its compounds as pollutants of priority interest due to their potential toxicity and carcinogenicity (He et al. 2012 and references therein). Indeed, due to its chemical similarity with As (same periodic group and oxidation states) it is plausible that the DNA damage induced by Sb follows similar pathways as those for arsenic. Moreover, Sb exposure induce apoptosis whose deregulation also participate in the etiology of several human diseases (e.g. neurodegenerative and autoimmune disorders) (Franco et al. 2009 and references therein). Specifically: elemental Sb is more toxic than its salts, inorganic species are more toxic than the organic ones, Sb(III) species are more toxic than Sb(V) compounds (Smichowski 2008 and references therein), Sb(III) and Sb(V) compounds are generally negative in non-mammalian genotoxicity tests instead they are generally positive and negative in vitro in mammalian test systems, respectively. Generally, population is rarely exposed to antimony but in case of occupational exposure, inhalation and skin contact are the main routes. Due to the frequent co-exposure to arsenic the human carcinogenicity is difficult to evaluate. Finally, antimony potassium tartrate (APT) has been used worldwide as an anti-shistosomal (anti-helminthic agent) drug until the 1990s and the pentavalent antimony compounds such as sodium stibogluconate have replaced the more toxic trivalent compounds for the treatment of leishmaniasis (De Boeck et al. 2003 and references therein).

4.3.2 General Usage

Sb and its compounds has been used since the Early Bronze Age in medicine, veterinary and cosmetics. In modern times, they are used in the manufacture of alloys, pigments, paints, ceramics, glass, glazing for pottery and tiles, colouring matter for paper and cloth, pharmaceutical preparations, ammunitions, fireworks,

bearings, tires, brake linings cable covering, as opacifying agent for enamels, as a flame retardant in rubber, plastics, pigments, adhesives, textiles, and paper (Sb_2O_3), as catalyst in the manufacture of polyethylene terephthalate, as component of brake linings (Sb_2O_3) (He et al. 2012; De Boeck et al. 2003; Smichowski 2008 and references therein).

Due to the natural dispersion process and its broad use in human activities, Antimony is ubiquitous throughout the environment. The main natural source of this element is the atmospheric volcanic emission, followed by the rock weathering and soil runoff (Smichowski 2008 and references therein). About the anthropogenic ones, in addition to those strictly related to the production and the use of the abovementioned objects, relevant sources of Sb are: the electronic waste, the non-ferrous metals refining, the smelting processes, the incineration of waste and sewage sludge, the fossil fuel combustion (especially coal of which China is one of the major production and consumers centres in the world) and the Sb mining (the majority of the world's reserves are located in China, the others are in Bolivia, Russia, South Africa and Tajikistan). It is therefore evident that China plays an important role in global anthropogenic Sb emissions. Indeed, severe environmental contamination have been reported in many areas (He et al. 2012 and references therein).

4.3.3 Results of Some Recent Studies

Generally, in unpolluted environments of China, Sb was detected in concentration of the order of ng m^{-3} but in mining areas and in fly ashes from waste incinerators elevated concentrations were found (mg m^{-3} order). At the beginning of the twenty-first century, in Beijing (where the main sources of Sb was the brake abrasion and the coal combustion) the mean concentration in total suspended particulate was of the order of $\mu\text{m m}^{-3}$ (He et al. 2012 and references therein). Conversely, in $\text{PM}_{2.5}$ of Palermo (Sicily, Italy) sampled from November 2006 to February 2008 the mean concentration was of ng m^{-3} order, although this element was characterized by an elevated Enrichment Factors (calculated by dividing the relative abundances in atmospheric particulate by the relative average abundances in local soils – $\text{EF} > 1,000$). Moreover, a close linear relationships between this element, Cu and $\text{PM}_{2.5}$ and between the respective enrichment factors were observed. Due to these findings, the authors suggested that Sb is probably originated from brake wear debris (Dongarrà et al. 2010).

By characterizing the elemental composition of atmospheric particulate sampled inside and outside an elementary school in Flagstaff (AZ – USA), Majestic et al. (2012) showed that Sb mass in PM_1 was significantly higher indoor (86 times greater than outdoor) with an air concentration of 17 ng m^{-3} . Because indoor Sb concentration was higher in the submicron fraction compared with the supermicron one and due to the lack of significant correlations with other elements in the PM_1 where Cu:Sb ratio is 0.08 (Cu:Sb ratio of crustal origin = 125, traffic = 2.3–10.1, fly ash ~ 20) they suggested as indoor source the

re-suspension of flame retardants embedded in the carpeting characterized by a Cu:Sb ratio of 0.18.

Little is known about the chemical speciation of this element and its reaction in the atmosphere; it is supposed that Sb is oxidized to Sb_2O_3 by reaction with atmospheric oxidants (Smichowski 2008 and references therein). Varrica et al. (2013) defined the speciation of Sb in several samples of brake linings, brake pad wear residues, road dust, PM_{10} and $\text{PM}_{2.5}$ (of Palermo – Italy) by combining several techniques including Synchrotron Radiation X-ray Absorption Spectroscopy (SR-XAS). They found that these samples were composed by an admixture of Sb(III) and Sb(V) oxide in different relative abundances. Specifically, brake linings contain Sb(III) oxide (Sb_2O_3) and stibnite (Sb_2S_3) Stibnite was also detected in some samples of atmospheric particulate. Moreover, they suggested that Sb_2S_3 during the brake abrasion process is easily decomposed forming more stable Sb mixed oxide compounds.

Similar results were found by Marconi et al. (2011) that quantified the Sb(III) and Sb(V) species concentrations in some samples of PM from brakes, road dust and atmospheric particulate by ion chromatography – inductively coupled plasma – mass spectrometry (IC-ICP-MS). They found that Sb(III) is predominant in brake pads while Sb(V) is the dominant form in dust from brake linings and in road dust. In most samples of atmospheric particulate both species were detected with ratio (Sb(III)/Sb(V)) that ranged from 0 to 1.5. Moreover, they showed that total Sb concentration was characterized by a bimodal pattern with the peaks centred at 0.65–1.6 and 4.4–10 μm .

4.4 *Thallium (Tl)*

4.4.1 Health

Due to their high acute toxicity on living organisms, Thallium and related compounds are of particular scientific interest and environmental concern. Nevertheless, this element has been less studied compared to other toxic elements mostly due to the poorer sensitivity of classical analytical methods. Tl is characterized by a relatively high solubility of all its forms and in natural waters it occurs almost exclusively as monovalent cation. Due to this it can be easily transported through aqueous routes and transferred from soils to crops, by entering the food chain (Peter and Viraraghavan 2005 and reference therein).

The main routes of absorption of this element are through the skin, the mucous membrane and by nutrition (mostly by assimilating home-grown fruits and green vegetables contaminated). Subsequently it is widely distributed throughout the body and accumulates in bones, in renal medulla and, in the central nervous system. Significant inhalations of thallium occur mostly during mining, ore processing and product application of this element or in the workplace where Tl-rich dusts are

handled or produced such as those originated from the roasting of pyrite (Peter and Viraraghavan 2005 and reference therein).

An elevated exposure by inhalation can produce several nervous system effects such as numbness of fingers and toes. In Peter and Viraraghavan (2005) and Kazantzis (2000) there are a long list of effects related to acute and chronic exposure to Thallium, among those it is worth remember tiredness, fatigue, headache, insomnia, vomiting, diarrheal, temporary hair loss, and effects on the nervous system, lungs, heart, liver, and kidneys.

4.4.2 General Usage

Thallium is a natural widely spread constituent of the earth crust where is found in trace amounts (average concentrations in the continental and oceanic crust are 991 0.49 ppm and 0.013 ppm, respectively), (Delvalls et al. 1999). It is mainly present in the sulphide ores of zinc, copper, lead and also in coal indeed Thallium was detected in base-metal mining effluents.

As described in the review of Peter and Viraraghavan (2005) and in Kazantzis (2000), Thallium and related compounds were used in medicinal purpose in the treatment of ringworm of the scalp, venereal diseases, syphilis, tuberculosis and malaria. Moreover they were used in many areas such as in the manufacture of insecticides, poison for rodents, imitation jewellery, low-temperature thermometers, ceramic semiconductor materials, special glass, laser equipment, crystals, alloys, optical systems, electronic devices, radioactivity detectors, infrared spectrometers, fireworks (thallium nitrate), pigments (thallium chromate) and dyes, impregnation of wood and leather against fungi and bacteria. Although the steady increase in use of Tl in these industrial sectors favoured the mobilization and the dispersion of this element, the main anthropogenic atmospheric source are the coal burning power plant (in particular those using brown coal or coal from the Jurassic 1006 period), (Kazantzis 2000), the brick work and cement plants, the ore processing and the ferrous and non-ferrous smelting operations (Cheam et al. 1995; Kazantzis 2000). The efficiency of retention of Tl-rich particles by electrostatic precipitators or other emission control facilities is limited because Tl-compounds are characterized by high temperatures of volatilization (Peter and Viraraghavan 2005 and references therein).

4.4.3 Results of Some Recent Studies

In the review of Juda-Rezler and Kowalczyk (2013) that discuss the parameters affecting the size distribution and the chemical composition of fly ash particles emitted from the combustion of hard coal pulverized in boilers, it is claimed that Thallium is volatile inside the boiler but subsequently a fair amount of this condenses on fly ash particles in electrostatic precipitators (Meij and Winkel

2007). The behavior of this element during the combustion and the relative enrichment factors are similar to those of As, Cd, Ge, Mo, Pb, Sb and Zn.

Kazantzis (2000) reported that higher concentration of Thallium are recognized in finer particles fraction. Indeed, in Hagler et al. (2007) concentrations of the order of magnitude of some ng m^{-3} and very high enrichment factors were observed for Thallium (and Zn, Br, Sn, As, S, Pb, Se) in $\text{PM}_{2.5}$ of Hong Kong suggesting anthropogenic origin linked to the coal burning.

Santacatalina et al. (2012) by characterizing the chemical composition of PM_{10} in the southeast of Spain (arid region with a great number of cement, ceramic and related industries) before and during the last economic crisis highlighted a significant decrease of several atmospheric pollutants in concordance with the reduction of industrial production. Specifically, during the crisis they have shown a reduction of the components that have as their main sources the soil-related industries and the crustal material re-suspension such as CO_3^{2-} , Ca, Sr, Tl and Pb. According to Querol et al. (2007), Sanchez de la Campa et al. (2010), Conesa et al. (2008) and Gutiérrez-Cañas et al. (2009) that used Thallium as a fingerprint for ceramic emissions and also as a semi-volatile metal escaping as dust from the clinker exit line depuration systems (Conesa et al. 2008; Gutiérrez-Cañas et al. 2009), Santacatalina et al. (2012) ascribed the Tl reduction to the decrease in the construction sector affecting the ceramic and cement industry. Moreover, by studying the relation between Vanadium and Thallium concentrations, they identified that the crisis has led to a larger decrease in ceramic production (bricks and tiles) than in clinker production because in that period the correlation between two element and the ratio V/Tl were higher.

The oxidation states of Thallium are Tl(III) that is characterized by strong oxidizing properties and is slowly converted to Tl(I) that generally form most stable compounds. Furthermore, the monovalent ion are dominant one in most natural environments (Peter and Viraraghavan 2005 and references therein). Zhu et al. (2001) by studying $\text{PM}_{2.5}$ collected in Salt Lake City (USA) by time of-flight secondary-ion mass spectrometry (TOF-SIMS) found that some particles contain ions of thallium such as Tl_2O^+ , Tl_2O^{2+} , Tl_2O^{3+} , Tl_3O^+ , indicating the oxide nature of this element.

Finally, Pappas et al. (2006, 2007) by analyzing the content of Tl, Cd, and Pb in different types of cigarettes found that Thallium was present in concentration of the order of magnitude of some ng cigarette^{-1} . Specifically their data show that the levels of all three metals in smoke particulate were proportional to their tar delivery category (full flavor > light > ultralight) and that the respective concentrations were far greater for counterfeit than the authentic brands (in some cases by an order of magnitude), even after the normalization by the nicotine concentration.

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