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HEAVY METALS IDENTIFIED IN AIRBORNE PARTICLES DURING WEEKEND PERIODS IN BRUSSELS URBAN ENVIRONMENT

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Abstract

There has recently been growing interest in the study of atmospheric particulate matter, specifically towards improved understanding of the long-term transport and impact of different elements of the lithosphere on atmospheric pollution. Close to the ground level, a fairly thin layer of the lithosphere and atmosphere, on both sides of their interface, serves as the major platform for human life and activity. Both the lithosphere and the atmosphere are mutually responsible for sustaining their natural equilibrium.
Investigations related to the studies of atmospheric particulate matter are intended to provide information that is still required for the implementation and the eventual revision of European standard tolerance norms for environmental protection. To this aim, WHO (the World Health Organization) and the EU (European Union) Working Groups on airborne particles are requiring additional information in this field.
Airborne particles of heavy metals, especially in overdose, may harm population health in a long or a short term. Our objective in the present study is to describe and compare the presence of heavy metals in the Brussels atmosphere during three days periods including Saturdays, Sundays and Mondays and their possible effect on human health. The heavy metals were divided into three main groups for: "high dangerous elements" (Pb, Sb, Cd and As); "non dangerous and low dangerous elements" (Sn, Cu, Ti, Cs, Bi, Zr, W, Ag, V, Ni and Al) and "micro-elements" (Co, Zn, Mn, Mg and Cr).
This study has been carried out during the period extending from September 2002 up to October 2003.

Keywords: *pollution, human health, atmospheric airborne particles*

Rezumat

Metalele grele identificate în particulele în suspensie în mediul urban din Bruxelles în week-end-uri. În ultima perioadă, a existat o preocupare mai intensă pentru studiul particulelor atmosferice, mai ales pentru o cunoaştere mai aprofundată a transporturilor pe termen lung şi sub aspectul impactului diverselor elemente ale litosferei asupra poluării atmosferice. În apropierea nivelului suprafeței terestre, un strat destul de subțire al litosferei şi atmosferei, pe ambele laturi ale interfaței lor, servesc drept bază a activității şi vieții umane. Atât litosfera, cât şi atmosfera sunt reciproc responsabile pentru păstrarea echilibrului lor natural.
Investigațiile legate de studiul particulelor atmosferice sunt menite să furnizeze informații care să fie necesare pentru implementarea și eventuala revizuire a standardului european vizând normele de toleranță pentru protecția environmentală. În acest scop, OMS (Organizația Mondială a Sănătății) şi grupurile de lucru ale UE (Uniunii Europene) care se ocupă de particulele în suspensie solicită informații suplimentare în acest domeniu.
Particulele în suspensie ale metalelor grele, în special peste limita normală admisă, pot dăuna sănătății populației pe termen lung şi mediu. Obiectivul nostru în cadrul studiului de față este să descriem şi să comparăm prezența metalelor grele în atmosfera oraşului Bruxelles pe parcursul a trei zile, incluzând sâmbăta, duminica şi lunea, dar şi posibilele lor efecte asupra sănătății umane. Metalele grele au fost divizate în trei grupe mari: „elemente foarte periculoase" (Pb, Sb, Cd and As); „elemente puțin dăunătoare sau deloc dăunătoare" (Sn, Cu, Ti, Cs, Bi, Zr, W, Ag, V, Ni and Al) şi micro-elemente (Co, Zn, Mn, Mg and Cr).
Acest studiu a fost realizat pe parcursul unei perioade cuprinse între Septembrie, 2002 până în octombrie, 2003.

Cuvinte-cheie: *poluare, sănătatea umană, particule atmosferice în suspensie*

INTRODUCTION

Airborne particles, or particles in suspension, are the common name for all kinds of solid particles freely floating in the surrounding air. In contrast with the gaseous components in the air, these particles are not made of pure substances, but, they may be constituted of several components that may be slightly different chemically (atomic elements), physically (shape, color, size, reflectance) as well as from the standpoint of their origin (Florig, 1997).

Smaller particles penetrate deeper in the respiratory system. Larger particles can reach only the pharynx or/and the larynx. In contrast, they are found in the atmosphere as suspended particles that penetrate the living bodies via the respiratory systems or, more generally, via their gas exchanges with the environment. The fraction of smaller particles (the thoracic fraction) penetrates farther in the rib-cage, in the wind-pipe and in the whole network of smaller radius airways up to the pulmonary alveoli (Fergusson, 1990). The heavy metals tend to concentrate in the body and cause damage in the kidneys, lungs, brain and nervous system and in the body metabolism (Fergusson 1990).

When the 1999/30/CE European Commission directive came into effect, the PM10 fraction of airborne particles has been declared an essential parameter for evaluating the quality of air and its effects on human health. At that time, the PM2.5 fraction of airborne particles was not a mandatory parameter although its evaluation was strongly recommended. The more recent EU directive 2008/50/CE however clearly imposes air quality objectives to be met for PM2.5 in the near future.

The choice of the PM10 fraction as a health parameter can be defended as it includes both the PM2.5 fraction of thin particles (diameter < 2.5 μm) that penetrates deeply in the respiratory system and the larger particles (from 2.5 μm to 10 μm).

Heavy metals are defined as metals having specific gravity greater than $5 gr/cm^{-3}$. Heavy metals elements are frequently associated to harmful influence on the environment (Fergusson, 1990, Alloway, 1990). Among these elements, metals such as cobalt, chromium, molybdenum, iron, nickel, selenium, tin, vanadium and zinc, are consumed in very low amounts by living organisms for their metabolism. Other elements, however, may become toxic in higher concentrations. As for cadmium, mercury and lead, these elements have no metabolic function in the human body (Sawidis et al., 2004). The importance of heavy metals in the environmental conditions comes from their harmful effects on public health. These health effects are due to the carcinogenic and mutagenic properties of these metals when they are in overdose in the environment. Regarding the exposure time and concentration level, these effects and their intensity may be quite different.

Furthermore, when concentrated in industrial products such as paints, chemicals, glasses, batteries, cars, electronics, textile or engines, these chemical elements may reach the aquifers through water sewage systems, thereby leading to their consumption by living organisms (Rühling and Tyler, 2004).

In the present study, we limited our scope to the quantitative investigation concerning the presence of heavy metal elements in the airborne particles found in Brussels urban area. More precisely, we compared the amount of these elements during consecutive Saturdays, Sundays and Mondays, i.e. days of reduced activity, days of inactivity and days of normal activity. This study has been carried out during the period extending from September, 2002 up to October, 2003.

METHODS AND EXPERIMENT DESIGN

PM10 measurements in Brussels-Capital Region, using continuous monitoring, are more recent than the measurements for the gaseous pollutants. Established in 1996 with two PM10-systems (oscillating microbalance R&P TEOM 1400-Ab), the network now contains six PM10 monitors. These analyzers are installed in Molenbeek, Uccle, Haren, Berchem, Meudon Park and Woluwe. By 2005 all TEOM PM10 analyzers were equipped with FDMS systems. With the exception of the Woluwe site, PM2.5 analyzers of the same type are installed at all PM10 measuring sites. The PM2.5 sampler consists of a PM10 impact or connected to a PM2.5 cyclone.

At two of these stations, Uccle and Woluwe (IBGE-BIM) and also at the University of Brussels (ULB-Campus Plaine), additional 24-hour sampling (Airborne Particle Samplers) was carried out on filter membranes for the chemical and physical speciation of the airborne particles (Vanderstraeten et al., 2007). For the present research, a SEM (Philips Scanning Electron Microscope) was used for determining the composition of the particulates sampled on Saturdays, Sundays and Mondays. Because the SEM energy dispersive technique can focus on very small particles and resolve even trace amounts, we consider this determination to be reliable.

RESULTS AND DISCUSSIONS

The present investigation deals only with the percentage of the above-described heavy metals among all the elements found during the study period, extending from September, 2002 up to October, 2003.

The objective was to compare the variation of the heavy metal percentage in airborne particles in Brussels urban area between days of partial activity

- Saturdays, days of very low activity - Sundays and days of full activity - Mondays.

Heavy metals identified in airborne particles during weekend periods plus Mondays in Brussels Urban Environment (Fig. 1) were divided to three main groups according to their effect on human health: 'high dangerous', 'non dangerous' and 'low dangerous elements' and 'micro-elements' (Table 1).

When a concentration is higher on Monday than during the weekend (f.i. Pb, Cu and Zn), then traffic could be a main reason (in Brussels there is no large non ferrous industry) – this can be seen when looking at the differences between Uccle site (background) on one hand and Woluwe and ULB site on the other – this should be developed and discussed.

Table 1: Heavy metals in airborne particles as divided to three groups by their effect on human health

Category	Elements
High dangerous elements	Pb and Sb
Non dangerous and low dangerous elements	Sn, Cu, Ti, Cs, Bi, Zr, W, Ag, V, Ni and Al
Micro-elements	Co, Zn, Mn, Mg and Cr

The elements of the first group, Pb and Sb are toxic to human body and therefore are highly dangerous (no Cd and As were found in the particles of the airborne atmospheric samples). Within this first group, lead (Pb) is a poisonous metal that can damage nervous connections (especially at young children) and cause blood and brain disorders. Lead poisoning typically results from ingestion of food or water contaminated with lead; but may also occur after accidental ingestion of contaminated soil, dust, or lead-based paint. Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can cause nephropathy and colic-like abdominal pains. The effects of lead are the same whether it enters the body through breathing or swallowing (Needleman et al., 1990). Antimony (Sb-Stibium) and many of its compounds are toxic. Clinically, antimony poisoning is very similar to arsenic poisoning. In small doses, antimony causes headache, dizziness and depression. Larger doses cause violent and frequent vomiting, and will lead to death in a few days. The EU upper limit for tap water is 5 µg/L (Shotyk et al., 2006).

The second group contains: Sn, Cu, Ti, Cs, Bi, Zr, W, Ag, V, Ni and Al. These elements are biocompatible (non-toxic and they are not rejected by the body). Tin (Sn) plays no known natural biological role for humans. As tin itself is not toxic, most tin salts are (Blunden and Wallace, 2003). Copper (Cu) toxicity can occur from eating acidic food that has been cooked with copper cookware. Cirrhosis of the liver in children has been linked to boiling milk in copper cookware. A genetic defect is associated with this cirrhosis. Since copper is actively excreted by the normal body, chronic copper toxicosis in humans without a genetic defect in copper handling has not been demonstrated. However, large amounts (gram quantities) of copper salts taken in suicide attempts have produced acute copper toxicity in normal humans. Equivalent amounts of copper salts (30 mg/kg) are toxic in animals (Merck Manuals, 2005). Titanium (Ti) is used in a gamut of medical applications including surgical implements and implants, such as hip balls and sockets (joint replacement) that can stay in place for up to 20 years. Caesium (Cs) salts have been evaluated as antishock reagents to be used following the administration of arsenical drugs. Because of their effect on heart rhythms, however, they are less likely to be used than potassium or rubidium salts. They have also been used to treat epilepsy (Butterman et al., 2004). Bismuth (Bi) is not bio-accumulative. Its biological half-life for whole-body retention is 5 days but it can remain in the kidney for years in patients treated with bismuth compounds (Fowler, 1986). Short-term exposure to zirconium (Zr) powder can cause irritation, but only contact with the eyes requires medical attention. OSHA recommends a 5 mg/m^3 time weighted average limit and a 10 mg/m^3 short-term exposure limit (NIOHS, 2008). Tungsten (W) has not been found to be necessary or used in eukaryotes, but it is an essential nutrient for some bacteria (Lassner, 1999). Silver ions and silver compounds show a toxic effect on some bacteria, viruses, algae and fungi, but without the high toxicity to humans that are normally associated with these other metals (Chopra, 2007). Vanadium (V) plays a very limited role in biology. A vanadium-containing nitrogenase is used by some nitrogen-fixing micro-organisms (Schwarz and Milne, 1971). Nickel (Ni) plays important roles in the biology of microorganisms and plants. In fact urease (an enzyme which assists in the hydrolysis of urea) contains nickel. Exposure to nickel metal and soluble compounds should not exceed 0.05 mg/cm^3 in nickel equivalents per 40-hour work week. Nickel sulfide fume and dust is believed to be carcinogenic. Sensitized individuals may develop an allergy to nickel, affecting their skin, also known as dermatitis (Barceloux and Barceloux, 1999a; Sigel et al. 2008). Despite its natural abundance, aluminium (Al) has no known function in living cells and presents some toxic effects in elevated concentrations. In very high doses, aluminium can cause neurotoxicity, and is associated with altered function of the blood-brain barrier.

The third group includes Co, Zn, Mn, Mg and Cr. These elements are needed by human body and plant tissues in limited quantities (ppm or less) (Table 1). Cobalt (Co) is essential to all animals, including humans. It is a key constituent of cobalamin, also known as vitamin B_{12}. A deficiency of cobalt leads to pernicious anemia, a lethal disorder. Pernicious anemia is however very rare, because trace amounts of cobalt are available in most diets. The presence of 0.13 to 0.30 mg/kg of cobalt in soils markedly improves the health of grazing animals (Kobayashi and Shimizu, 1999). Zinc (Zn) is an essential trace element, necessary for plants, animals and microorganisms. Zinc is found in nearly 100 specific enzymes, serving as structural ions in transcription factors and being stored and transferred in metallothioneins. It is the second most abundant transition metal in organisms after iron and it is the only metal which appears in all enzyme classes. In proteins, Zn ions are often coordinated to the amino acid side chains of aspartic acid, glutamic acid, cysteine and histidine. There are 2-4 grams of zinc distributed throughout the human body. Most zinc is in the brain, muscle, bones, kidney, and liver, with the highest concentrations in the prostate and parts of the eye. Semen is particularly rich in zinc, which is a key factor in prostate gland function and reproductive organ growth (Berdanier et al., 2007). Nevertheless, although Zinc is an essential requirement for good health, the excess of zinc can be harmful. Excessive absorption of zinc suppresses copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish (Eisler, 1993). Manganese (Mg) is an essential trace nutrient in all forms of life. The classes of enzymes that have manganese cofactors are very broad and include oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases, lectins, and integrins. The best known manganese-containing polypeptides may be arginase (Emsley, 2001). The human body contains about 10 mg of manganese, which is stored mainly in the liver and kidneys. In the human brain, manganese is bound to manganese metalloproteins most notably glutamine synthetase in astrocytes (Takeda, 2003). Trivalent chromium (Cr^{3+}), even in trace, has an influence on the metabolism of sugar and lipid in humans. In the United States the dietary guidelines for daily chromium uptake were lowered from 50-200µg for an adult to 35µg (adult male) and to 25µg (adult female). Acute oral toxicity ranges between 1500 and 3300µg/kg (Barceloux and Barceloux, 1999b).

In figure 1, the measured percentage of the atomic weight of the heavy metals with respect to the total weight of the particles collected on Saturdays, Sundays and Mondays is given. Concerning the 'highly dangerous' group, Pb weight percentage in the environment has been decreasing between Saturdays and Sundays (variation of -0.38%). Ni and Al weight percentage in the environment increased between Saturdays to Sundays (variations of 0.42% and respectively, 0.45%). Pb, Cu and Al percentage increased between Sundays and Mondays (variations of 0.62%, 0.69% and respectively, 0.26%).

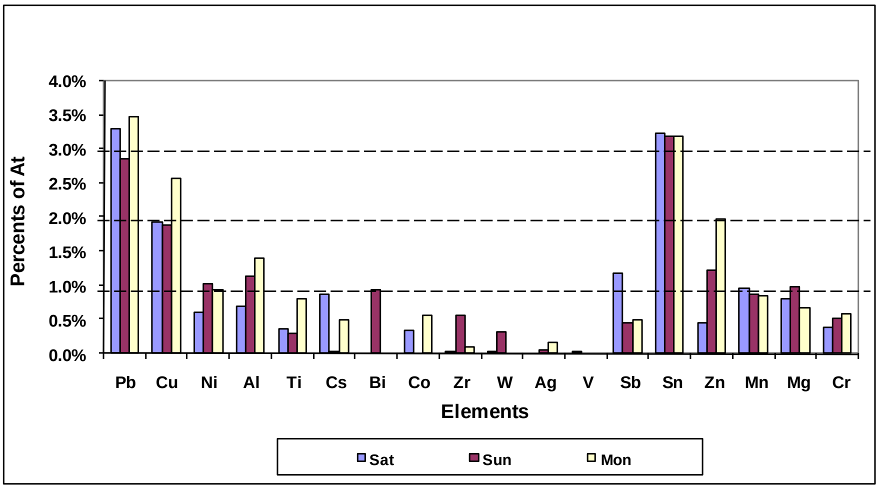

Fig. 1 The daily changes of the heavy metal elements identified in airborne particles during weekend periods in Brussels Urban Environment

As for the second 'dangerous' group: Ti, Cs, Co and Ag, concentrations increased between Sundays and Mondays (variations of 0.5%, 0.46%, 0.56% and respectively, 0.09%), while Bi, Zr and W peaked during Sundays. In the 'micro-elements' group, Zn showed high increase from Saturdays, Sundays to Mondays: the weight percentage of Zn has been 0.44%, 1.22% and respectively, 1.98%. The observed changes in the weight percentage of the heavy metals elements between the reduced working days (Saturdays), rest days (Sundays) and full working days (Mondays) might be explained by the different intensity of the industrial activities and transportation and the specific mechanism of the re-suspension of the airborne particles (Vanderstraeten et al., 2006).

'Heavy metals' is a contraversed term used to define high density metals. However, their toxicity is without any doubt and any atmospheric pollution in urban environment, and, in particular, in the region of Brussels, could lead to serious consequences on its inhabitants' health.

Henceforth, in future investigations, it would be necessary to further improve the understanding of the relations between atmospheric pollution by heavy metals, their sources and their correlated specific diseases.

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