Environmental Pollution 241 (2018) 841–851

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Comparison of $PM_{2.5}$ chemical composition and sources at a rural background site in Central Europe between 1993/1994/1995 and 2009/2010: Effect of legislative regulations and economic transformation on the air quality[☆]

Petra Pokorná [a,*], Jaroslav Schwarz [a], Radovan Krejci [b], Erik Swietlicki [c], Vladimír Havránek [d], Vladimír Ždímal [a]

[a] Department of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Rozvojová 1/135, 165 02 Prague 6, Czech Republic
[b] Department of Environmental Science and Analytical Chemistry, Stockholm University, Svante Arrhenius väg 16, S-106 91 Stockholm, Sweden
[c] Departement of Nuclear Physics, Lund University, Sölvegatan 14, S-223 62 Lund, Sweden
[d] Nuclear Physics Institute of the Czech Academy of Sciences, Řež at Prague, 250 68 Řež Czech Republic

ARTICLE INFO

Article history:
Received 21 March 2018
Received in revised form
25 May 2018
Accepted 4 June 2018
Available online 14 June 2018

Keywords:
Atmospheric aerosol
Trace elements
Ions
Source apportionment
Positive matrix factorization
Long-range transport
Concentrations trends

ABSTRACT

From December 1993 to January 1995 and from October 2009 to October 2010, a total of 320 and 365 daily samples of the $PM_{2.5}$ were collected at a rural background site (National Atmospheric Observatory Košetice) in Central Europe. The $PM_{2.5}$ samples were analyzed for 29 and 26 elements respectively by Particle-Induced X-ray Emission (PIXE) and water-soluble inorganic ions by Ion Chromatography (IC) in 2009/2010. The Positive Matrix Factorization (PMF) was applied to the chemical composition of $PM_{2.5}$ to determine its sources. The decreasing trends of almost all elements concentrations, especially the metals regulated by the EU Directive (2004/107/EC) are evident. The annual median ratios indicate a decrease in concentrations of the $PM_{2.5}$ elements. The slight increase of K concentrations and Spearman's rank correlation coefficient r_s 0.09 K/Se points to a rise in residential wood combustion. The S concentrations are nearly comparable (higher mean in 2009/2010, while the annual median ratio is under 1). The five major source types in the mid-1990s were ascribed to brown coal combustion, oil combustion, sea salt and dust – long-range transport, re-suspended dust and black coal combustion. The industrial combustion of brown and/or black coal (r_s 0.75 Se/As, r_s 0.57 Ga/Ge and r_s 0.20 As/Zn) and oil (r_s 0.72 V/Ni) of the regional origin dominated. In the 1990s, the potential source regions were the border area of Czech Republic, German and Poland (brown coal), the Moravia-Silesia region at the Czech-Polish border (black coal), and Slovakia, Austria, Hungary, and the Balkans (oil). In 2009/2010, the apportioned sources were sulfate, residential heating, nitrate, industry, re-suspended dust, and sea salt and dust – long-range transport. The secondary sulfate from coal combustion and residential biomass burning (r_s 0.96, K/K^+) of local origin dominated.

The declining trend of the elemental concentrations and change in the source pattern of the regional background PM2.5 in Central Europe between the mid-1990s and 2009/10 reflects the economic transformation and impact of stricter legislation in Central Europe.

1. Introduction

During the 1980s and 1990s, there was great progress in defining the main anthropogenic sources of trace metals in Europe (Pacyna, 1996; Olendrzynski et al., 1996; Pacyna and Pacyna, 1999). In the mid-1990s, the stationary fossil fuel combustion continued to be the major source of Cr, Hg, Mn, Sb, Se, Sn, and Tl with respect

---

[☆] This paper has been recommended for acceptance by Haidong Kan.

[*] Corresponding author. Department of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Rozvojová 2/135, 165 02 Prague 6, Czech Republic.

E-mail address: pokornap@icpf.cas.cz (P. Pokorná).

https://doi.org/10.1016/j.envpol.2018.06.015

to the coal combustion and the major source of Ni and V with respect to oil combustion. The combustion of leaded, low-leaded, and unleaded gasoline continues to be the major source of atmospheric Pb emissions. The third major source of trace metals is non-ferrous metal production, which is the largest source of atmospheric As, Cd, Cu, In, and Zn. The main improvement of the efficiency of emission control for fine particles and the change of the national fuel base has been observed in Europe during the 1980s (the period of comparison being the beginning of the 1980s and the mid-1990s) resulting in a decrease of emissions of trace metals (Pacyna and Pacyna, 2001).

In Central European post-communist countries, the distinct improvement was observed a decade later. In the Czech Republic the total annual emissions of the main monitored pollutants in 1994 were: particulate matter (PM), SO_2, NO_x, CO, VOC, NH_3 were 258, 1205, 378, 1036, 310, 91 (1000 $tyear^{-1}$). The declining trend of the all the monitored pollutants between 1994 and 2010 was evident; a decline by 75% of PM, 86% of SO_2, 37% of NO_x, 62% of CO, 51% of VOC, 26% of NH_3 (CHMI, 2011). The declining trend of emissions from the stationary and mobile sources was a result of the regulations, a gradual change of the fuel base (transfer from coal/oil to gas) by all categories of the stationary sources and the change of the vehicle fleet in particular of passenger cars.

There are few early studies from 1990s on PM and chemical composition conducted in Central Europe. PM_2 and elemental composition were measured at Bílý Kříž, a rural site in the North-eastern Czech Republic, by Swietlicki and Krejci (1996), while Borbély-Kiss et al. (1999) studied urban and rural sites in Hungary. Horvath et al. (1996) described PM for the urban area of Vienna and its surroundings, and two studies were performed by Maenhaut et al. (2005, 2008) on the fine and coarse fractions in Budapest and $PM_{2.5}$ and PM_{10} at K-Puzsta. In the study by Swietlicki and Krejci (1996) the East European aerosol was found to have a composition which differed from that of the West European aerosol, due to different industrial activities and air pollution control. The sampled fine fraction aerosol was clearly affected by the heavily industrialized region around the cities of Ostrava and Katowice close to the border between the Czech Republic and Poland. The influence of other large European source regions such as southern Ukraine, northern Italy, the SE Balkan peninsula, the Benelux countries and the "Black Triangle" in Germany, Poland and the Czech Republic was also apparent. The dominant anthropogenic source types affecting the aerosol composition at the Bílý Kříž station were ferrous and non-ferrous smelters together with oil and coal combustion, and the secondary sulfate source type. The soil dust and sea spray source types can be considered to be predominantly of natural origin. The study by Borbély-Kiss et al. (1999) has further investigated the existence and nature of the differences in air quality in Western and Eastern Europe caused by structural and technological differences in the energy sector and the industry of the regions. The clear influence of long-range transport from the "Black Triangle" was not proven due to the possible influence of the thermal power station situated 80 km NW from the rural sampling site. The sources affecting the aerosol composition at the urban site Debrecen and rural site nearby were **s**oil dust, motor vehicle/traffic, power generation/chemical industry, and coal/oil combustion.

In this work, the $PM_{2.5}$ chemical composition data from the first half of the 1990s, thus 5 years after the switch-over from centrally planned economy to market economy in Czech Republic, enable an assessment of the influence of legislative regulations and economic transformation on the air quality over the period of 15 years. The objective of this study is to compare the $PM_{2.5}$ chemical composition and sources at a rural background site in Central Europe between 1993/1994/1995 and 2009/2010.

2. Experimental

2.1. Sampling site and instrumentation

The sample campaigns were conducted at the National Atmospheric Observatory Košetice (N49°35′, E15°05′; 534 m ASL, Fig. SI1) administered by the Czech Hydrometeorological Institute (CHMI). The site is classified as a representative of the regional background in the Czech Republic. The observatory site is located 70 km south-east of the urban area of Prague, and the closest medium sized urban area lies 15 km to the south, with a population of 16 000. There are also several small settlements within a 3 km radius. One of the major national highways leads 6 km northwest-southeast of the site. The National Atmospheric Observatory Košetice is part of the EMEP, ACTRIS (formerly EUSAAR), and the GAW networks.

24 h samples of $PM_{2.5}$ were collected from 19th December 1993 to 25th January 1995 and from 15th October 2009 to 17th October 2010. During the earlier period, a 12-nozzle inertial impactor with an aerodynamic cut off $PM_{2.5}$ was used (Swietlicki and Krejci, 1996). During the later campaign 2009–2010, samples were collected using Leckel low-volume samplers equipped with $PM_{2.5}$ sampling inlets. The fine aerosol fraction for later elemental analysis by PIXE was collected on Nuclepore polycarbonate membrane filters (25 mm in diameter, 0.4 μm pore size) during both campaigns. In addition, fine aerosol fraction was also sampled on TEFLO filters (Pall, 47 mm in diameter, 3 μm pore size) during the 2009/2010 campaign for consecutive ion chromatography analysis. The TEFLO filters were weighed before and after sampling with microbalance SartoriusM5P under controlled conditions (RH: 30%–40%; temperature: 20 °C–25 °C). In order to assess the impact of unstable conditions, the control filters were regularly weighed during each weighing run and their weight changes were used to correct the measurements of the other filters. Field blanks were collected regularly, during which time filters were placed in the samplers and exposed to 10 s of sampling. This resulted in 20 field blanks from Nucleopore filters and 25 for the Teflon filters. These filters were then analyzed using the same method as the sample filters, and all data were corrected according to the blank filters.

2.2. Chemical analysis

The $PM_{2.5}$ samples collected in both periods were analyzed using the Particle Induced X-ray Emission (PIXE). The 1993/94/95 samples were analyzed with PIXE (JC88, Ma90) at the Department of Nuclear Physics in Lund, Sweden, using a proton beam energy of 2.55 MeV (Pelletron, NEC3UDH electrostatic tandem accelerator). Only the central part of the filters was irradiated, as defined by a 9 mm diameter collimator. A 340 m external Mylar X-ray absorber with a small hole was placed in front of the Si(Li)-detector in order to balance the intensities of the characteristic X-rays with low and high energies. A total charge of 40 C was collected for each sample at a beam current of about 110–130 nA. This resulted in an irradiation time of about 5 min for each filter. The X-ray spectra were evaluated using computer software HEX (Johansson, 1982). The accuracy and precision of the PIXE analysis was of order of 10–15%.

The 2009/2010 samples were analyzed with PIXE at the Nuclear Physics Institute in Řež, Czech Republic, using a proton beam of 2.2 MeV, beam diameter of 5 mm, and beam current of about 10 nA (3.5 MV Van de Graff accelerator). The PIXE spectra from two Si(Li) detectors were used. The measurements typically ranged from 800 to 1000 s, resulting in an average collected charge of 10 μC per analysis. A set of thin MICROMATTER™ filters were used to calibrate the PIXE and the PIXE-INP computer code (Havránek et al., 1994). The total relative uncertainty budget of PIXE was of an