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Mercury in atmospheric aerosols: A preliminary case study for the city of Krakow, Poland

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ABSTRACT

The level of contamination by mercury associated with airborne particulate matter in Krakow was determined. Samples of PM10 were collected on quartz filters using low-volume samplers. The total particulate mercury (TPM) concentrations in collected samples were determined by mercury analyser MA-3000 (Nippon Instruments Corporation). The reported results include also data on the carbonaceous aerosol and inorganic ions concentrations during the reported sampling campaign. The average concentration of the Total Particulate Mercury (TPM) in Krakow (Poland) was 0.22 $ng \cdot m^{-3}$ (during the period from 22 February to 2 March) and 0.49 $ng \cdot m^{-3}$ (on 3 March). A marked correlation between TPM and elemental carbon (EC) as well as with Cl^- was found. No significant association of the TPM with NO_3^- and SO_4^{2-} could be shown. The dry deposition flux of mercury was calculated as an average over the sampling period and was 47.3 $ng \cdot m^{-2} \cdot d^{-1}$.

1. Introduction

During recent years, significant progress has been made regarding the knowledge on the mercury concentration level, its sources of emission and transport mechanisms in the environment. The Minamata Convention on Mercury (http://www.mercuryconvention.org/) is a global treaty to protect human health and the environment from the adverse effects of mercury. The major highlights of the Minamata Convention on Mercury include a ban on new mercury mines, control measures on air emissions, and the international regulation of the informal sector for artisanal and small-scale gold mining. The Convention draws the attention to a global and ubiquitous metal that, while naturally occurring, has broad uses in everyday objects and is released into the atmosphere, soil and water from a variety of sources. Controlling the anthropogenic releases of mercury throughout its lifecycle has been a key factor in shaping the obligations under the convention. Moreover, a system for mercury observations, called the Global Mercury Observation System, has been developed. The system includes, e.g., free tropospheric mercury measurements. This will then provide high-quality data for the validation and application of regional- and global-scale atmospheric models, to give a firm basis for a future policy of development and implementation.

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Atmospheric mercury occurs in the environment in three forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (Hg^{II}) compounds (GOM), and mercury associated with particulate matter (known also as total particulate mercury [TPM]). All three forms of the atmospheric mercury are released by anthropogenic sources, mainly combustion processes, as well as by a variety of natural sources and processes [1,2].

Total particulate mercury usually contributes a few percent of the total mercury in the atmosphere. On average, the TPM fraction contributes to the total mercury mass with around 2% in rural areas and ca. 6% in urbanized areas [3]. The dry and wet deposition of TPM by rain and washout and oxidation of Hg^0 into Hg^{II} in particulate phase are the main processes of the self-purification of the atmosphere with mercury [4]. The lifetime of TPM in the air ranges from several hours to several days, depending on the lifetime of ambient particles [5]. The rate of particle deposition depends on their aerodynamic diameter and ranges between 0,1 and 1 $cm \cdot s^{-1}$ [6]. Coarse particles are removed near the source of emission, whereas fine particles are transported over longer distances [7,8]. The particle-bound mercury is either directly emitted or formed due to adsorption of the gaseous mercury (mainly Hg^{II}, and Hg^0) onto existing particles. The processes of dissolution of the Hg compounds in the wet aerosol particles and inclusion of contained mercury minerals into the structure of particles might also occur [9,10]. Therefore, it has been suggested that atmospheric particulate matter has catalytic properties for mercury oxidation and reduction reactions [11].

Table 1 comprises the updated inventory emissions of mercury to air developed by the team of the United Nations Environmental Programme (UNEP). In accordance with the new inventory, more than 85% of these emissions originate from coal combustion for power generation and industrial processes [12].

The authors of the report for the United Nations Environmental Programme point out the sectors for which emissions of mercury are currently not quantified: biofuel production and combustion, vinyl-chloride monomer production, secondary metals and production of ferroalloys, oil and gas extraction, transport and processing other than refinery emissions, industrial and hazardous waste incineration and disposal, sewage sludge incineration, preparation of dental amalgam fillings and disposal of removed fillings containing mercury [12]. The sum of emission from 'by-product' sectors, and the conservative emission estimates from intentional use of mercury in products and artisanal mining, and emission associated with cremations result in a global anthropogenic mercury emission equal to 1960 tonnes for the reference year 2010.

Multiple studies on the negative impact of ambient particulate matter were conducted [13–18]. Major components represent several percent of the total mass of the PM, whereas trace elements usually represent less than 1% of the PM [19]. Sulphate, nitrate and ammonium ions originate predominantly from gaseous precursors: sulphur dioxide, nitrogen oxides and ammonia, respectively. Thus, they are considered as secondary aerosols. Their ambient concentrations are not necessarily proportional to the quantity of gas emissions, since the formation pathways and the gas/particle equilibrium may be controlled by factors other than the concentration of the precursor gas [17,20–25].

Table 1
Emission of mercury from various sectors (tonnes per year) [12].

Sector	Emission (range) [t]	%
By-product or unintentional emissions		
Fossil fuel burning		
Coal burning (all uses)	474 (304–678)	24
Oil and natural gas burning	9.9 (4.5–16.3)	1
Mining, smelting, and production of metals		
Primary production of ferrous metals	45.5 (20.5–241)	2
Primary production of non-ferrous metals (Al, Cu, Pb, Zn)	193 (82–660)	10
Large-scale gold production	97.3 (0.7–247)	5
Mine production of mercury	11.7 (6.9–17.8)	<1
Cement production	173 (65.5–646)	9
Oil refining	16 (7.3–26.4)	1
Contaminated sites	82.5 (70–95)	4
Intentional uses		
Artisanal and small-scale gold mining	727 (410–1040)	37
Chlor-alkali industry	28.4 (10.2–54.7)	1
Consumer product waste	95.6 (23.7–330)	5
Cremation (dental amalgam)	3.6 (0.9–11.9)	<1
Grand total	1960 (1010–4070)	100

Carbonaceous particles (organic carbon [OC], elemental carbon [EC] and carbonate carbon [CC]) account for up to 50% of the total mass of the PM10. Elemental carbon is emitted into the atmosphere, as a primary aerosol, mainly during incomplete combustion of fossil fuels (traffic, industry, domestic heating, and refuse burning) and biomass, and is therefore treated as a direct indicator of urban pollution and traffic intensity [26,27]. Moreover, elemental carbon is considered to act as a carrier of mercury as both EC and Hg have an origin in coal combustion [11]. Organic carbon can be present in both primary and secondary aerosols. Primary OC is formed during combustion processes, including unleaded gasoline combustion, biomass burning and agricultural activity, as well as emitted from natural sources (plant debris, pollen or fungi). Furthermore OC is formed during oxidation and gas-to-particle conversion of volatile organic compounds (VOC) emitted by anthropogenic or natural processes [28–30].

The goal of this study was to determine the total particulate mercury concentration in the urban area of Krakow, Poland, in the winter of 2011. Moreover, the study presents data for organic and elemental carbon as well as of inorganic ion concentrations in PM10 measured during the sampling campaign and discusses the relations between the measured parameters.

The authors of the paper do not assess the level of pollution of Krakow, indicating particulate mercury as a tracer for air pollution in the city. They are aware that TPM contributes only a few percent of the total mercury balance in the atmosphere. But in association with augmented concentrations of PM10 in Krakow (which is a really