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Chemical composition of submicron and fine particulate matter collected in Krakow, Poland. Consequences for the APARIC project

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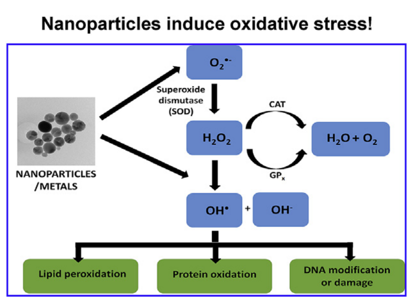
HIGHLIGHTS

- Krakow is a highly polluted city with serious environmental health problems.
- Patients in Krakow suffer from respiratory track, cardiovascular and immunological diseases.
- The composition of PM1 and PM2.5 fractions collected in Krakow was determined.
- A large fraction of submicron PM was found that could have important health consequences.

GRAPHICAL ABSTRACT



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ABSTRACT

Submicron particulate matter containing particles with an aerodynamic diameter ≤1 μm (PM1) are not monitored continuously by Environmental Protection Agencies around the World and are seldom studied. Numerous studies have indicated that people exposed to ultrafine (≤100 nm), submicron and fine particulate matter containing particles with an aerodynamic diameter ≤2.5 μm (PM2.5), can suffer from respiratory track diseases, cardiovascular, immunological or heart diseases and others. Inorganic pollutants containing redox active transition metals and small gaseous molecules, are involved in the generation of reactive oxygen and reactive nitrogen species. Inhalation of this kind of particles can affect immune-toxicity. Environmental pollution may aggravate the course of autoimmune diseases, in particular influence the mechanisms of the autoimmune system. Important factors that influence the toxicity of particulate matter, are particle size distribution, composition and concentration. This report deals with the composition of PM1 and PM2.5 fractions collected in Krakow, Poland. In spring 2015, the mean concentrations of PM1 and PM2.5 were 19 ± 14 and 27 ± 19 $\mu g/m^3$, respectively. The PM2.5 fraction contained approximately 70 ± 17% of submicron particulate matter. In spring 2016, the mean concentrations of PM1 and PM2.5 were 12 ± 5 and 22 ± 12 $\mu g/m^3$, respectively. The PM2.5 fraction contained approximately 60 ± 15% of submicron particulate matter. The concentrations of the elements Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr and Pb in both fractions were determined by X-ray fluorescence spectrometry. Most of the analyzed metals had higher concentrations in the fine fraction than in the submicron one. Concentrations of V and As were below the detection limit in both fractions, whereas concentrations of Mn and Ca were below the detection limits in the PM1 fraction. The results are

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discussed in terms of the consequences they may have on the APARIC project presently underway in Krakow.

1. Introduction

The results from this study form an important part of an interdisciplinary project on 'Air Pollution versus Autoimmunity: Role of multiphase aqueous Inorganic Chemistry' (APARIC) supported by the National Science Center of Poland. Based on the expertise of the project participants in chemistry, pre-clinical and clinical immunology, a multilevel, interdisciplinary approach is adopted. Experiments are carried out using chemical and cellular models, animal models of selected autoimmune disorders and clinical material.

The general aim of the project is to identify the relationship between transition metal containing particulate matter (TMCPM), as components of air pollution, and the course of autoimmune diseases by following a comprehensive approach, i.e. involving biomolecules, cells, tissue and living organisms. The project is performed at three levels: *Chemistry* – with the main task of screening a wide spectrum of TMCPM in regard to their reactivity towards biological systems and the selection of candidates for further study in relevance to their fundamental physicochemical properties; *Pre-clinical Immunology* – with the main task of *in vitro* testing of the influence of selected compositions on the function of immune/inflammatory cells relevant to autoimmunity, as well as mechanistic assessment of the influence of selected compositions on the course and molecular determinants of severity in selected *animal models* of autoimmune disorders; *Clinical Immunology* – with the main task to estimate the influence of selected compositions on the immune functions of cells isolated from donors with autoimmune disorders and healthy controls.

Particulate matter (PM) can function as a surface platform to mediate and catalyze chemical processes that are important for human health. In such case, redox biochemistry involving the production of reactive oxygen (ROS) and reactive nitrogen species (RNS), depends strongly on the composition of the airborne particulate matter, particulate mass, solubility and morphology (structure, porosity, size distribution, surface area, etc.). The latter controls the surface area available and thus the efficiency of the catalytic activity of such particles in multi-phase aqueous chemistry. The toxicity of organic compounds, both volatile and those as components of PM, is based mainly on specific interactions between molecules and biomolecules, the activity of TMCPM should be predominantly based on redox chemistry. This implies the need to distinguish the role of organic and transition metal-based pollutants in the induction of autoimmune responses.

PM10 and PM2.5 fractions are better known and characterized than PM1. Many studies focused on coarse and fine particulate matter (Viana et al., 2008; Zwozdziak et al., 2012; Cuccia et al., 2013), but the submicron PM1 was investigated only rarely (Gugamsetty et al., 2012; Spindler et al., 2013; Casale et al., 2009; Ramgolam et al., 2008). Such PM can originate from industrial emissions, traffic pollution, construction activities, soil dust, sea salt, and from fossil fuel and biomass combustion (Viana et al., 2008; Masiol et al., 2014a; Amato et al., 2016a; Karagulian et al., 2015). The lifetime of the smaller size particles (PM2.5 and PM1) can range from days to weeks, whereas larger particles (PM10) have a lifetime of hours to days (Wilson and Suh, 1997).

A significant number of European cities are affected by highly polluted air. Recent reports have pointed to Poland as one of the countries in Europe with the highest air pollution. This means that there may be more than 35 days per year of exceeding the PM10 limit concentration of 50 $\mu g/m^3$, especially during the cold season of the year (EU Directive, 2008) (Anonymous, 2008). Polish regulations (Regulation of the Minister of Environment, 2012) follow the EU directive (Anonymous, 2012). Although the problems related to submicron PM1 are essential to environmental health issues, an appropriate regulation does not exist.

According to existing data, Krakow is one of the most polluted cities in Poland and in Europe. According to reports from the Inspectorate of Environmental Protection, sources of pollution in Krakow come from Arcelor Mittal Poland S.A., a steel factory, the power plant in Krakow, the power plant in Trzebinia, the nitrogen plant in Tarnów, Synthos Dwory in Oswiecim and TAMEH Poland Tauron Arcelor Mittal Energy Holding. Samek et al. and Bokwa et al. reported results for PM10 studies in Krakow (Samek, 2012; Samek et al., 2016a; Bokwa, 2008). The reports of Samek et al. deal with the characterization of the PM10 content and application of statistical analysis for source identification and apportionment. The characterization of the PM2.5 fraction was also presented in several other reports (Samek et al., 2015, 2016a, 2016b). Homogeneity of air particulate matter samples, source identification, and apportionment of PM2.5, were evaluated (Samek et al., 2015). In other studies the concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) adsorbed on PM2.5 particles were studied at 4 locations in the Silesia and Małopolska regions. The highest PM2.5 related PAH concentrations in summer and winter seasons, were observed in Krakow as a result of industrial and traffic pollution, and seasonal, household heating (Samek et al., 2016b). The content of carbon and sulfur in PM2.5 and PM10 in ambient air of the center of Krakow was also studied (Ćwiklak et al., 2007). In contrast to the extensive studies on the PM10 and PM2.5 fractions, characterization of submicron particles in Krakow was rarely reported. Wilczynska-Michalik et al. showed that PM1 dominated in aerosol with respect to particle numbers (Dziugieł et al., 2012). However, the concentrations and chemical composition were not studied. Even the annual reports of the Voivodship Inspectorate for Environmental Protection (WIOŚ) concerning air pollution in Krakow, omitted the PM1 fraction (Wilczynska-Michalik et al., 2015). This is an unfortunate gap in the available information that needs to be resolved due to the higher reactivity of the smaller fractions of PM and resulting adverse health effects. Therefore, the goal of the present study is to focus on the role of PM1 in terms of its composition and contribution to environmental health issues, i.e. aspects that are of essential interest to the APARIC project.

Samples of fine (PM2.5) and submicron (PM1) fractions of particulate matter were collected at an urban site in Krakow. The concentrations and ratio of PM1 and PM2.5 fractions were determined. The concentration of selected elements was determined by X-ray fluorescence spectrometry. The content of redox-active elements in the collected particulate matter was compared to standard reference material (SRM) for urban air pollutants (SRM 1648a from the US National Institute for Standards and Technology, NIST). Commercially available SRM is nowadays widely used as the reference sample in both chemical and biological studies (Viana et al., 2008; Zwozdziak et al., 2012) (WIOŚ, 2016; Auger et al., 2006). The SRM 1648a sample contains elements similar to those