Identification of Pollution Sources in the Urban Atmosphere

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Abstract

Identification of PM_{10} particles in the city of Olomouc (the Czech Republic) was aimed at determining the proportion of inorganic and organic compounds. Organic compounds in PM_{10} represent 30–36% of PM_{10}, of which 21–25% is biogenic material (spores were identified). The rest of 10 to 15% of organic matter is represented by anthropogenic processes. Combustion processes (35.1 to 40.9% of PM10) and emissions from transport (20.0 to 22.9% of PM_{10}) have the main share in the PM particles, minerals from resuspension – weathering processes and mechanical processes of construction activity account for around 9% of the particles and Fe – particles also constitute about 9%. The iron concentration in the aerosol is in accordance with the values measured in other European cities. Mineral phases in the inorganic aerosol were determined by X-ray diffraction. Both natural and anthropogenic crystalline phases were identified – quartz, clay minerals (kaolinite), feldspar, calcite, dolomite, iron oxides (magnetite), gypsum, boussingaultite, mascagnite and koktaite.

Keywords: air pollution, PM_{10}, Secondary inorganic aerosol, koktaite, x-ray diffraction, back particle trajectory

Introduction

The sharp rise in urbanization, industrialization, increased population migration and the increasing traffic volume in urban areas contributed to the increase in particles released into the air. The main compounds of PM (Particulate Matter) forming up to 99% of the total weight of the particles, include: primary inorganic particles, carbonaceous materials (organic carbon – OC and elementary carbon – EC), sea aerosol, secondary inorganic aerosols – SIA (consisting of sulphates, nitrates and ammonia). PM secondary components (metals) are represented by units, maximum of tens of percent (Lozano et al., 2007; Wang, 2010). The composition of PM varies depending on the sampling site and weather conditions. The amount of sulphates and EC in PM_{10} are lower in rural areas than in urban areas. Percentages of OC + EC in PM_{10} ranges from 20 to 45% for Central Europe, from 12 to 37% for Southern Europe, and from 12 to 20% for Northern Europe (Querol et al., 2004). Mineral dust in PM_{10} represents 5–15% in Central Europe, 12–40% in Southern Europe and 20–70% in Northern Europe. SIA in PM_{10} represents 25–55% in Central Europe and 13–45% in Southern and Northern Europe (Querol et al., 2004). The content of organic compounds in PM_{10} in Europe (OM) ranges from 16 to 22% and an unidentified compound forms 19 to 28% of PM_{10} (Putaud et al., 2004).

The aim of this article is to identify the composition of PM_{10} in relation to the sources of pollution in the summer season in the localities in Olomouc.

Methodology and Sampling

Olomouc is a city in Moravia – eastern part of the Czech Republic (Figure 1). This city is an administrative centre of the Olomouc Region and the sixth largest city in the Czech Republic today. The city of Olomouc has a long tradition of industrial production. The dominant sectors are food processing and machinery. The chemical industry, production of electronics, plastics processing and construction industry are represented in this place as well.

Sampling of air pollution (PM_{10}) was conducted by the Institute of Public Health in Ostrava (ZUOVA) on the quartz filters (diameter 16 cm) using high-volume samplers. Sampling took place during the summer months (June – July) in 2015. PM_{10} samples were collected in the locality Olomouc Řepčín (Machova Street) and Olomouc Slavonín (Kyselovská Street). The sampling locality Řepčín can be characterized as an area of houses on a flat terrain near full-grown trees. The locality may be affected by traffic on the access road to the houses and Moravské železárny (Moravian Ironworks, a.s.), which is situated about 10 meters from the sampling site.

The sampling locality Slavonín can be characterized as an area of family houses on a flat terrain with

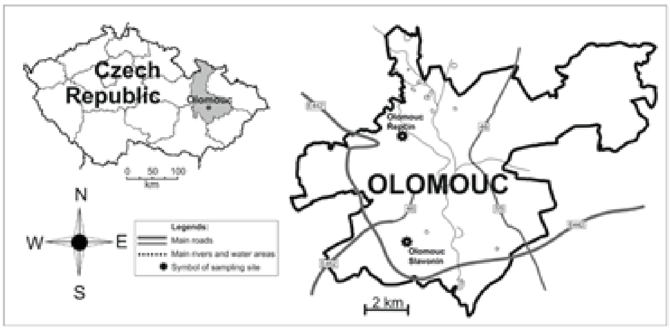

Fig. 1 Sampling sites in the city of Olomouc

Rys. 1 Miejsca poboru próbek w mieście Ołomuniec

Tab. 1 Comparison of ion content (µg/m^3) in the SIA in Olomouc and Zabrze, Poland

Tab. 1 Porównanie zawartości jonów (µg/m^3) w SIA w Ołomuńcu oraz Zabrzu, Polska

Sample	Reference	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-/SO_4^{2-}
Zabrze, Poland	*Kozlowska et al., 2013*	775	1,046	1,927	273	962	191	345	79	0.84
Slavonín	*This study*	71.1	633	3,360	824	1,212	1,125	119	1,046	0.18
Řepčín	*This study*	61.2	462	2,420	163	838	398	1,099	806	0.19

tree cover in the nearby neighbourhood. The locality may be affected by passenger traffic on the nearby road. There is no more significant industrial enterprise near the sampling site.

Identification of the particulates collected on the filters was performed using the following methods: determination of elemental carbon (EC) and organic carbon (OC), the chemical composition of the secondary inorganic aerosols (SIA) – the method of ion chromatography in water-soluble fraction prepared by ultrasonic extraction in water, the identification of crystalline mineral phases using the method of X-ray diffraction, and other inorganic particles by scanning electron microscopy (SEM) with the energy dispersion (EDAX).

To create backward trajectories, the model HYSPLIT (Hybrid Single – Particle Lagrangian Integrated Trajectory) was used; it was developed by the National Oceanic and Atmospheric Administration, (NOAA) in the USA. Modelling was performed by the company E–Expert, s.r.o, Ostrava.

Results

Carbonaceous particles

Carbonaceous particles are an essential part of the atmospheric aerosol; they represent 10 to 50% of the total weight of PM$_{10}$ (Duarte et al., 2008). When the values of the ratio OC/EC exceed 1, it can be assumed that OC in PM is of secondary origin (US EPA, 2012). The organic material was calculated as the concentration of OC multiplied by the value of the factor 1.4 (Putaud et al., 2004, Sillanpää et al., 2005). The concentration of OC and OM (Organic Matter) in the locality of Olomouc Řepčín was 3.9 g µg/m^3 and 5.4 µg/m^3, respectively, while in the locality of Olomouc Slavonín, the OC and OM concentration was 5.1 µg/m^3 and 7.2 µg/m^3, respectively. Organic matter accounted for 30–35% of PM$_{10}$. Carbon from combustion processes (EC) constitutes about 4–5% of PM$_{10}$. These EC, OC, OM concentrations are comparable with the results of selected sites in Europe, published by Yttri et al., (2007). The ratio OC/EC 4.3 (Řepčín) and 6.4 (Slavonín) shows that PM$_{10}$ contains a larger amount of secondary organic particles, which arise from primary organic carbon due to photochemical reactions in the atmosphere.

Water-soluble ions (secondary inorganic aerosols)

The dominant compounds of the secondary inorganic aerosol (SIA) in Europe and the USA are represented by nitrates, sulphates, and ammonium ions (Yao et al., 2003). The concentration of sulphates in the inorganic matter (water–soluble fraction) is generally higher than the concentration of nitrates. The source of the occurrence of nitrates in aerosols is transport, and the occurrence of sulphates is related to the combustion processes. The source of pollution can be specified using the ratio $(NO_3)^-/(SO_4)^{2-}$. In the event that the value of the ratio $(NO_3)^-/(SO_4)^{2-} > 1$, emissions come from mobile sources (transport), for the value < 1, ions originate from combustion processes (Pachauri, 2012). The ratio $(NO_3)^-/(SO_4)^{2-}$ is < 0.2 for both localities. Water-soluble anions come in particular from combustion processes.

The analysed anions constitute 31.6% of PM$_{10}$ in the locality of Řepčín and 46.4% in the locality of Sla-

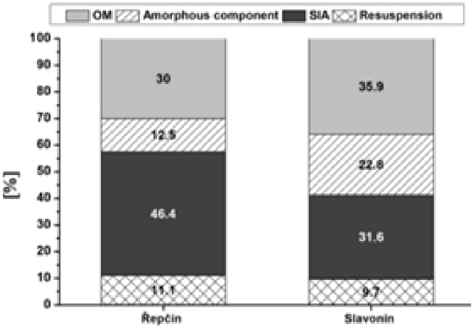

Fig. 2 Identification of the origin of the components in PM_{10} from Olomouc

Rys. 2 Identyfikacja pochodzenia składników PM_{10} w Ołomońcu

Tab. 2 The results of X-ray fluorescence for the samples from Olomouc

Tab. 2 Wyniki fluorescencji rentgenowskiej dla próbek z Ołomuńca

Locality	Cr [µg/m^3]	Fe [µg/m^3]	Zn [µg/m^3]	% Fe from PM_{10}
Řepčín	0.193	1.721	0.799	9.50
Slavonín	0.189	1.147	0.314	8.64

vonín. The concentrations of anions in the SIA from the two samples taken in Olomouc (Table 1) are in relative agreement with the results from the Polish Zabrze (Rogula-Kozlowska et al. 2013). In both locations in Olomouc, significantly lower concentrations of chlorides and nitrates were measured. The concentrations of ammonium ions in the locality of Řepčín (1,212 µg/m^3) were slightly higher than in Zabrze and in the locality of Slavonín (838 µg/m^3). In the samples from Olomouc, several times higher content of potassium, magnesium and calcium was found. The calcium content is affected by the dissolution of gypsum and koktaite, which were identified by X–ray diffraction in the two samples. Potassium is probably released from dead biogenic matter present on the filter. In comparison with other localities, a significantly higher content of Mg^{2+} was demonstrated. In the crystalline phase, quartz that comes from the re-suspension (particle morphology), ammonium sulphate $(NH_4)_2SO_4$ – mascagnite, calcium ammonium sulphate: koktaite $(NH_4)_2Ca(SO_4)_2.H_2O$ were identified in both samples. In the sample Řepčín, gypsum was identified as well. In the sample Slavonín, feldspar (albite), which comes from resuspension and erosion of soils was identified. The identification of the origin of the components in the aerosol is shown in Figure 2.

The crystalline phase content in PM_{10} represents about 50%. It is accompanied by amorphous silicate particles from high – temperature thermal processes (particles containing Si, Al, Ca and Fe-rich particles), particles from transport, biogenic material and organic particles formed during combustion processes (Song et al., 2014). The crystalline phase consists of particles of natural and anthropogenic character. The particles of natural character are formed by the earth's crust minerals, and they are released from the soil or from building materials (quartz, clay minerals). The particles of anthropogenic character contain predominantly sulphates and nitrates. Calcite and dolomite can be formed by human activities, and they may be natural. Fly ash particles are generally spherical in nature and typically they are composed of Si, Al, Ca and Fe. Other compounds identified in PM_{10} include kaolinite (18%), boussingaultite $Mg(NH_4)_2(SO_4)_2.6H_2O$ (38%), ammonium chloride, NH_4Cl (4%), mascagnite $(NH_4)_2SO_4$ (7%), and ammonium-nitrite-sulphite $(NH_4)_5(NO_3)_3SO_4$ (10%). Sulphates, koktaite, boussingaultite, gypsum and mascagnite were identified in PM_{10} from the industrial areas around the world (Gianini et al., 2012). The stability of sulphates is influenced by the temperature, and particularly by relative humidity. Mori et al. (1998) reported that koktaite may be formed by reacting calcite and ammonium sulphate after one day at a temperature of 22°C and RH = 70%, gypsum is formed after 7 days. The same reaction proceeded even at RH = 40%, when koktaite or gypsum were identified using the method of X-ray diffraction (Mori et al., 1998).

$$CaCO_3 + 2(NH_4)_2SO_4 \rightarrow (NH_4)_2Ca(SO_4)_2.H_2O + 2NH_3 + CO_2 \qquad (1)$$

$$(NH_4)_2Ca(SO_4)_2.H_2O + H_2O \rightarrow CaSO_4.2H_2O + (NH_4)_2SO_4 \qquad (2)$$

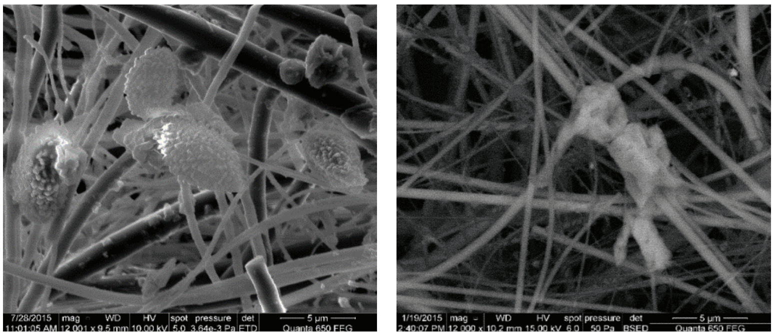

Fig. 3 Spores – a biogenic component of aerosol, gypsum – $CaSO_4$ (secondary aerosols)

Rys. 3 Zarodniki – składnik biogeniczny aerozolu, gips CaSO4 (wtórne aerozole)

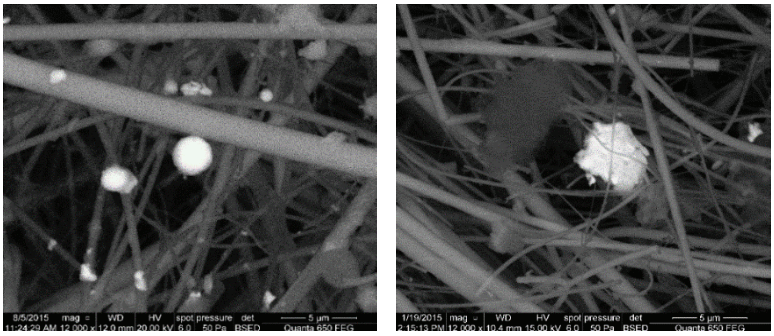

Fig. 4 Fe oxides (on the left from combustion), on the right another origin

Rys. 4 Tlenki żelaza (na lewo od spalania), na prawo inne związki

Carbonates are minerals which can neutralize the acidity of SO_2 and NO_x in the air. Song et al. (2014) did not identified them in aerosol samples presumably because of their reaction with SO_2 and NO_x. CaO particles are released during the combustion of coal; they are capable of neutralizing SO_2 while gypsum is formed (Song et al., 2014).

The Analysis of the Primary Particles

From biogenic particles, spores were identified (Figure 3). Using the analysis of the primary particles, aluminosilicates formed during the combustion process were found in PM_{10} at the locality of Slavonín. PM_{10} sample contains particles with a high content of Fe, Si and O. The particles have a spherical shape, which is typical for incineration processes. In the location of Řepčín, particles with a higher content of Fe were identified; they are irregularly limited and do not form aggregates. Its origin is different – they probably originate from transport or industry (Moravské železárny (Moravian Ironworks, a.s.). Furthermore, particles with irregularly limited particles and a high content of Pb–Cr–Mn were identified (Figure 4). On the basis of their morphology, it can be assumed that are not formed during combustion, but during the technological process. Fe particles produced by transport do not contain Pb, but more than 50% of Fe + Cu, Cr, Zr, Mn, and Zn (Moreno et al., 2013).

The high content of Fe particles collected on the filters (approximately 1/3 of the analysed particles comprise Fe oxides) lead to the need of identifying Fe in PM_{10}, which was performed by X-ray fluorescence. The results shown in Table 2 were compared with the concentrations of metals that were defined for the USA within (US EPA, 2001). They all met the conditions reported by US EPA for the urban environment.

In addition to trace elements specified in Table 2, the content of Pb, Mn, Zn, Cu, Sn, V, Mo, Cd, Rb, Ni, Sr, Li, Sb, Cr, Co, Ga, Bi, Ag, Te, Tl, U, and Pt was analysed in the PM particles. The concentrations of trace elements were similar to those found in other cities (Muranszky et al., 2011) with the exception of Mn, Ga, Rb, and Cd, which were in lower concentrations. The highest concentration in PM_{10} fraction was found in Fe, Zn, Pb, Cu, and Mn; Fe constitutes about 87% of the monitored trace elements (Muranszky et al., 2011). Trace elements usually represent only 5% of the total amount in PM_{10}. Within this amount (5%), iron represents 87%, and the other elements form 13%. Fe-rich particles contain about 69% of Fe, their share in PM_{10} is approximately 4% (Choël et al., 2007). The results of the chemical analysis of Fe show that the concentrations occur in the ranges defined for a metropolitan area according to US EPA, and they are consistent with the results of Muranszky et al., (2011) in Budapest. They correspond to the concentrations observed for Berlin

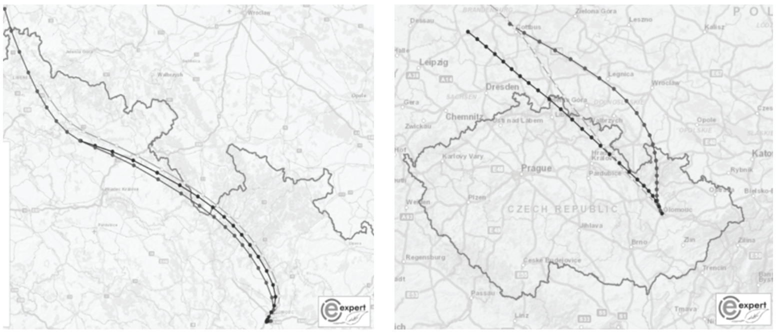

Fig. 5 Back trajectories for the transport of particles – 24 hours with 1-hour interval

Rys. 5 Trajektorie wsteczne dla transportu ziaren – 24 godziny z przedziałem godzinowym

(2,048 ng/m3), Zurich (1,611), Florence (1,520), and Madrid (1,930), but they do not correspond to the concentrations observed for Vienna (181 ng/m3), where the measured concentration is about 10 times lower.

The combination of all the applied methods of analysis of PM_{10} particles has shown that the largest amount of particles on both localities is related to thermal processes (combustion + other technologies producing SO_2), namely 35.1–40.9% of PM_{10} (the concentration of secondary inorganic aerosols in the sample). The second largest group was represented by biogenic sources (20.6–24.8% of PM_{10}), and the contribution of transport (20.0–22.9%) was almost comparable had PM_{10}. Resuspension and Fe particles comprised less than 10% of PM_{10}.

The course of back trajectories for the transport of particles during sampling PM_{10} (Figure 5) shows that the particles were brought from areas northwest of the Czech Republic and along the track.

Conclusions

Carbon from combustion processes (EC) constitute about 4–5% of PM_{10}. Organic compounds constitute about 30–36% of PM_{10}, 21–25% of the particles if of a biogenic nature. The largest share of PM_{10} consists of secondary inorganic aerosols (SIA) – Řepčín 46%, Slavonín 32%. Inorganic aerosols contain gypsum, mascagnite and koktaite. The principal ions that are involved in the formation of these phases are SO_4^{2-}, Ca^{2+} and NH_4^+. The presence of individual phases and their relative proportion is affected by the temperature and humidity. The primary inorganic particles comprise minerals from resuspension (quartz, feldspar) 8–9%, amorphous particles based on alumosilicates, and Fe oxides formed during thermal processes – combustion (8–15%). Iron forms 8–9.5% of PM_{10}. Most particles of Fe has angular shape, or they form crystalline aggregates. The morphology of these particles does not correspond to particles produced during combustion processes (spherical nature of the particles – magnetite). It can be assumed that the particles have different origin; they probably come from transport and industry (Moravské železárny, a.s.). The presence of other elements in the Fe particles (especially Pb) shows that they could come from Moravské železárny, a.s. Fe contents determined by X-ray fluorescence correspond to the concentrations measured in other urban areas. For both localities, the main identified components of air pollution include combustion, emissions of biogenic material, transport, resuspension, and of particles containing Fe.

Acknowledgments

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Identyfikacja źródeł zanieczyszczeń atmosfery na obszarach zurbanizowanych

Celem pracy była identyfikacja ziaren PM_{10} *w atmosferze w mieście Ołomuniec (Czechy) w celu określenia proporcji składników organicznych i nieorganicznych. Składniki organiczne w* PM_{10} *stanowią 30–36%, z czego 21–25% jest materiałem biogenicznym (zidentyfikowano zarodniki). Pozostałe 10 do 15% materii organicznej powstała w wyniku procesów antropogenicznych. Procesy spalania (przyczyna powstania 35,1 do 49,9% ogółu* PM_{10}*) oraz emisja z transportu (20,0 do 22,9% ogółu* PM_{10}*) mają główny udział w ziarnach PM, minerały wtórne pochodzące z procesów mechanicznych związanych z budownictwem to około 9% ziaren a ziarna stanowią również kolejne 9%. Stężenie żelaza w aerozolu jest podobne do wartości zmierzonych w innych miastach Europy. Fazy mineralne w aerozolu nieorganicznym zostały zmierzone za pomocą dyfrakcji rentgenowskiej. Zarówno naturalne, jaki antropogeniczne fazy krystaliczne zostały zidentyfikowane, stwierdzono występowanie kwarcu, minerałów glinu (kaolinit), skalenie, kalcyt, dolomit, tlenki żelaza (magnetyt), gips, boussingaultyt, maskagnit oraz koktait.*

Słowa klucze: zanieczyszczenie powietrza, PM_{10}*, wtórny aerozol nieorganiczny, dyfrakcja rentgenowska, trajektoria wsteczna ziarna*