Mineralogical Composition of the Total Suspended Particles as a Tool for Emissions Sources Identification

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Abstract

The total dust deposition was analyzed by X-ray diffraction in the Moravian-Silesian Region (the Czech Republic) three times during years 2013–2014. The results of mineralogical composition of the total dust deposition were used to distinguish the sources of air pollution in selected localities in the Moravian-Silesian Region. Sampling sites were selected according an estimate for the prevailing influence of the pollution source (metallurgical industry, local house heating, transport and background localities in mountains). Mineral phases in the total dust deposition can be divided into three groups. The first group contains common clastic components which are transported from soils or from the dust on roads by resuspension (quartz, feldspars – albite, orthoclase and microcline, phyllosilicates – muscovite, chlorite and kaolinite, carbonates – calcite, siderite and magnesite). The second group is formed by minerals from raw materials used in metallurgical industry (hematite, magnetite, graphite and calcite) and minerals originated during technological processes (akermanite, mayenite and spinel). The third group contains salts which are present in secondary aerosols (sulphates – boussingaultit and lecontite, chlorides – sal-ammoniac, halite). Proportion of secondary minerals was in the nine out of ten sampling sites higher during the winter season than during summer season. The percentage of resuspended particles is from 1.2 to 7.5 times higher in the summer season, compared with the winter period. The influence of metallurgical industry was proved by the presence of hematite and magnetite at 9 out of 10 sampling sites. At the localities Ostrava Radvanice and Třinec, iron oxides form up to 50% of crystalline phases in the total dust deposition.

Keywords: total dust deposition, X-ray diffraction, the Moravian-Silesian Region

Introduction

Distinguishing between natural and anthropogenic origin of polluting substances in the atmosphere represents one of the main problems in the study of air pollution. The global estimates show that more than two thirds of dust originates from natural sources (Tondera et al., 2007). Mineralogical composition of dust particles represents one of the possibilities to distinguish the sources of air pollution (Song et al., 2014; Krueger et al., 2005). Atmospheric dust – total suspended particles (TSP) is formed by dust particles of the size from 1 to 75 µm.

The mineralogical composition of dust varies in dependence upon the soil type and the land use, road surface, traffic intensity, emission sources and long-distance transport (Amato et al., 2009; Kumar et al., 2014; Li et al., 2013; Alastuey et al., 2004).

The particle size class of PM10 contains approximately 50 wt. % of the crystalline fraction, the remaining part is formed by amorphous particles of fly ash (containing Si, Al, Ca and Fe), soot released from road vehicles and from combustion (black carbon) as well as biological material of natural origin (Song et al., 2014). Gunawardana et al. (2012) identified in the road dust approximately 60% of crystalline substances, the remaining 40% are formed by amorphous phases.

Minerals present in total suspended particles can be classified according to their origin (Loosmore and Hunt 2000, Smith and Lee 2003). The resuspended particles in the vicinity of roads are formed very often by carbonates: dolomite and calcite, alkali feldspars: albite, orthoclase, microcline; phyllosilicates: muscovite, clinochlore, chlorite and kaolinite; oxides: quartz; and sulphates: gypsum (Amato et al., 2011; Jancsek-Turóczi el al., 2013).

The industrial and construction activity can also be a source of calcite, quartz, gypsum and

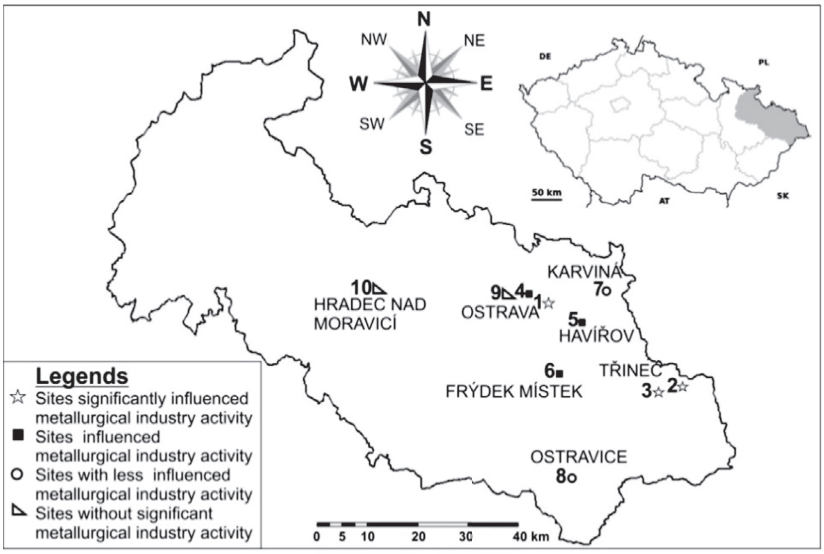

Fig. 1. Sampling sites: Ostrava Radvanice (1), Třinec (2), Třinec Oldřichovice (3), Ostrava Mariánské Hory (4), Havířov (5), Frýdek-Místek (6), Karviná (7), Ostravice (8), Ostrava Poruba (9), Hradec nad Moravicí (10)

Rys. 1. Miejsca pobierania próbek: Ostrava Radvanice (1), Třinec (2), Třinec Oldřichovice (3), Ostrava Mariánské Hory (4), Havířov (5), Frýdek-Místek (6), Karviná (7), Ostravice (8), Ostrava Poruba (9), Hradec nad Moravicí (10)

siderite (Jancsek-Turóczi el al., 2013; Song et al., 2014). Gypsum, calcite and dolomite are formed during cement production and desulphurisation of flue gases (Vester, 2007). The presence of gypsum in the atmospheric gas is related to the bonding of SO_2 with calcium (Kumar and Rajkumar, 2014).

The secondary minerals are formed in the atmosphere as a result of physical and chemical processes (Cvetković et al., 2012). Sulphates and chlorides are the most common secondary anthropogenic minerals (Song et al., 2014; Cvetković et al., 2012). Among sulphates, koktaite, boussingaultite, gypsum, anhydrite, mascagnite, ammonium-nitrite sulphate and lecontite were identified. Chlorides prevalently consist of sal-ammoniac (Song et al., 2014). Sulphates and chlorides are produced as the main products by chemical reactions of already existing alkaline particles with SO_2 and NO_x in the atmosphere (Song et al., 2014).

Iron oxides (magnetite, hematite) are formed during combustion of fossil fuels in dependence on the conditions of burning (Muxworthy et al., 2001). Combustion of coal with increased concentrations of K and Ca can lead to the origin of syngenite similarly as gypsum. Other possible source can be cement production (Xie et al., 2005). Particles with high content of iron (hematite) are characteristic for metallurgy (Tavares at al., 2014). The dust particles contain both minerals originated during metallurgical processes (akermanite, mayenite, spinel) and minerals which are components of input raw materials (hematite, magnetite and/or maghemite), but also graphite (Journet et al., 2014; Menéndez et al., 2007). The Moravian-Silesian Region located in north - eastern part of the Czech Republic (Fig.1) has large industrial concentrations in its territory. The main sources of air pollution (metallurgy and power plants) are located in Ostrava conurbation and in the town of Třinec. Large metallurgical complexes are located in the eastern part of Ostrava as well as in Třinec.

The aim of this work is the determination of mineralogical composition of crystalline phase in the total dust deposition and utilization of this information for a source identification of atmospheric pollution in the Moravian-Silesian Region.

Sampling sites and analytical methods

The sampling of TSP was performed during three sampling intervals in the years 2013/2014 (winter 2013, summer and winter 2014) at 10 localities (Fig. 1) of the Moravian-Silesian Region. The sampling sites were selected by the Health Institute with the seat in Ostrava. The total dust deposition was collected in the plastic vessels fixed in the height of 2.5 m above surface of land. The sampling was performed simultaneously at all the sampling sites during one month in the respective sampling season. After collecting, the samples were dried and washed out of vessels by acetone.

The samples were prepared for analysis by homogenization in agate mortar and filled in the silicon sample holder with low background. Min-

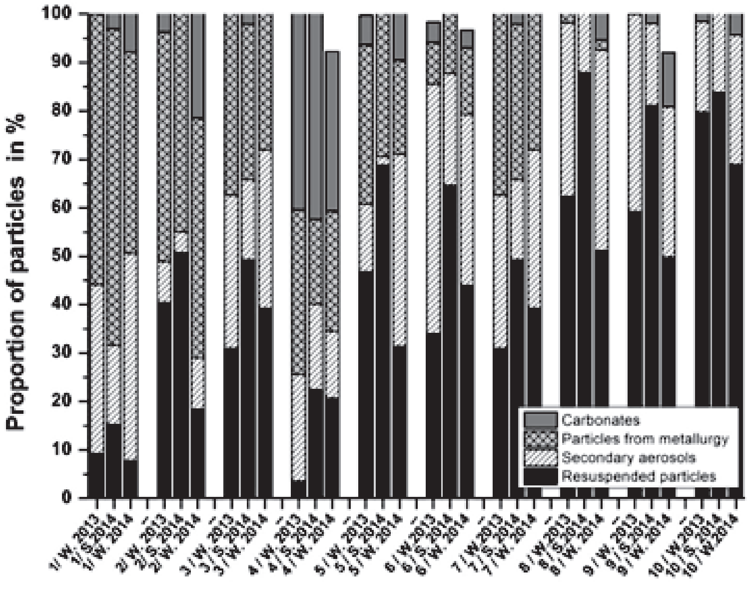

Fig. 2. Proportion of particles divided into four groups, 10 sampling sites, 3 sampling seasons

Rys. 2. Ilości cząsteczek podzielone na cztery grupy, 10 miejsc poboru próbek, 3 okresy próbkowania

eralogical phase composition was determined by the method of X-ray diffraction using the instrument Bruker-AXS D8 Advance, with geometry of measurement theta/2 theta, semiconductor detector LynxEye, CoKα radiation with Fe filter, 40 kV, 40 mA, step size 0.014°, interval at the step 0.25 s, sum of 5 repeated measurements. The qualitative determinations were performed by means of the Bruker Diffrac.Eva program, the semiquantitative evaluation was performed by Rietveld method - Bruker Topas version 4.2. The results of semiquantitative analyses are related to the sum of 100% crystalline phases, amorphous components were neglected.

Results and discussion

Minerals which were present in bulk samples of the total atmospheric depositions, were divided into four groups. Fig. 2 illustrates the proportional differences of the distinguished groups at the ten sampling sites during three sampling seasons. The first group is formed by resuspended minerals: albite, orthoclase, microcline, muscovite and chlorite. The second group contains secondary minerals: gypsum, boussingaultite, sal-ammoniac, halite and lecontite. The third group is formed by minerals originated in metallurgy: iron oxides (hematite and magnetite) and also minor concentrations of graphite, akermanite, mayenite, spinel. The fourth group contains carbonates of uncertain origin: calcite and magnesite. Besides resuspension, carbonates can originate in construction activities or from limestone which is used in blast furnaces. The sampling site Ostrava Mariánské Hory in urban environment had anomalous high content of calcite during the entire sampling period. The content of calcite in crystalline phase of total dust deposition was 40% in winter season 2013, 42% in summer 2014 and 33% in winter 2014.

Gypsum had the dominant representation in the group of secondary minerals during the entire sampling period. Concentrations of secondary minerals are considerably different in summer and winter seasons. The occurrence of bassanite versus gypsum represents the most striking difference which is influenced by relative humidity. In winter season, gypsum was identified at all sampling sites as well as an increased content of halite (especially at the sampling sites Ostrava Poruba and Frýdek-Místek).

The increased content of halite can be influenced by winter maintenance of roads. Boussingaultite and lecontite were also present in TSP during the winter season.

Particles released from metallurgy form an important group of minerals. During summer months, only hematite and magnetite were found among particles. Additional mineral phases - graphite, akermanite, mayenite and spinel were identified during winter months. Increased proportions of maghemite (26.6%) and syngenite (42.1%) were determined in TSP from the sampling site Třinec. Syngenite in concentration of 60% was identified in the sampling site Karviná.

The ratios of individual groups of minerals (resuspended particles, secondary minerals, particles

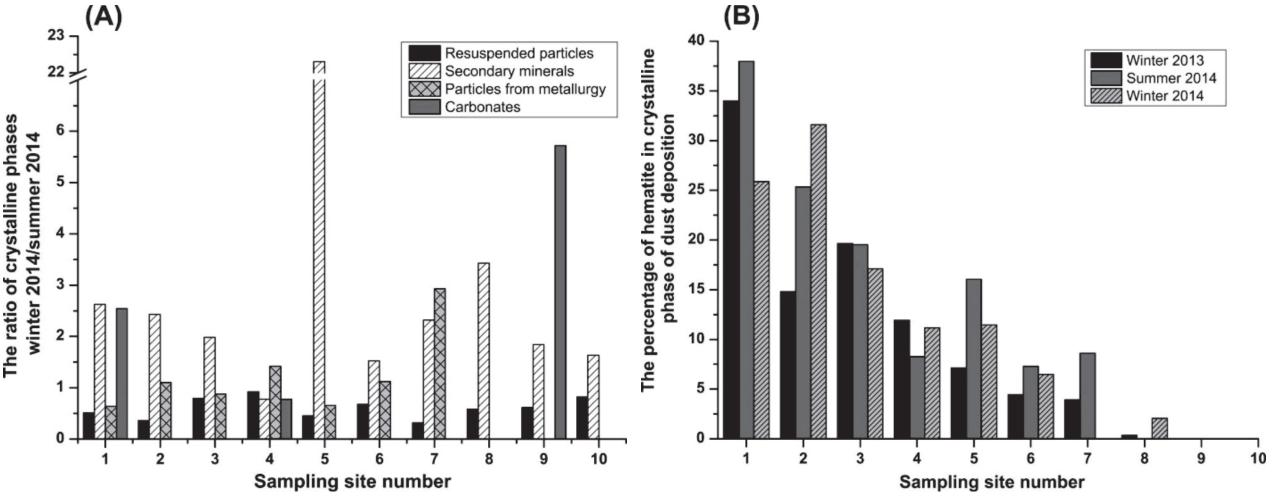

Fig. 3. (A) The ratios at 10 sampling sites – winter 2014/summer 2014, percentages of four mineral groups, (B) Concentrations of hematite at 10 sampling sites during three sampling seasons

Rys.3. (A) Wskaźniki dla 10 miejsc poboru próbek – zima 2014/lato 2014, udział czterech grup minerałów, (B) Zawartość hematytu w 10 miejscach poboru próbek, w czasie trzech sezonów próbkowania

from metallurgy and carbonates) in the summer and winter seasons 2014 are illustrated in Figure 3A. Nine out of ten sampling sites have the proportion of secondary minerals higher during the winter season than during summer season (from 1.5 times to 22 times higher). The percentage of particles originating from metallurgy was higher during winter than during summer at the sampling sites Třinec, Ostrava Mariánské Hory, Frýdek-Místek and Karviná. The increased percentage of carbonates during winter was observed for the sampling sites Ostrava Radvanice and Ostrava Poruba.

The significant enrichment by hematite was determined at 8 out of 10 sampling sites. Iron oxides form almost 50% of the crystalline phase of total dust deposition at the sampling sites Ostrava Radvanice and Třinec. On the basis of hematite percentages, the sampling sites were divided into four groups. The first group is formed by sampling sites which are significantly influenced by metallurgy (locations 1, 2 and 3). The percentage of hematite in the crystalline phase of total dust deposition is higher than 17% during all sampling seasons. The second group is formed by sampling sites with middle influence of metallurgy (4, 5, 6). The concentration of hematite in crystalline phase of TSP varies in the range from 6 to 16 %. The third group contains the sampling sites with low influence by metallurgy (7 and 8). Hematite concentration in crystalline phase of TSP is lower than 6%. The last group is formed by sampling sites without any significant influence of metallurgy (9 and 10). Hematite was not identified in TSP from these locations (Figure 3B).

Conclusions

The results of mineralogical analysis of TSP proved that this method provides the important possibilities for identification of pollution sources. The presence of hematite, which has source in metallurgy, was documented at 8 out of 10 sampling sites (including Ostravice located in mountains). The sampling sites with significant load by particles from metallurgy include Ostrava Radvanice, Třinec, Třinec Oldřichovice, Havířov, Ostrava Mariánské Hory and Karviná. The percentage of secondary minerals is higher during winter than during summer (with the exception of the sampling site Ostrava Mariánské Hory). Compared with the winter season, the percentage of resuspended particles is from 1.2 to 7.5 times higher in the summer period. An average content of resuspended particles in TSP is 21% for all three sampled periods and all sampling sites. The lowest concentrations of resuspended particles were found for sampling sites Třinec (near the metallurgical plant) and Havířov.

Acknowledgements

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Skład mineralogiczny pyłu zawieszonego jako narzędzie do identyfikacji źródeł emisji zanieczyszczeń

Osadzanie pyłu zostało trzykrotnie przeanalizowane w latach 2013–2014, przy pomocy dyfrakcji rentgenowskiej w regionie Morawsko-Śląskim (Republika Czeska). Wyniki oznaczenia składu mineralogicznego osadzonego pyłu posłużyły do rozpoznania źródeł zanieczyszczeń powietrza w wybranych lokalizacjach w regionie Morawsko-Śląskim. Wybrano miejsca, które według ustaleń w znacznym stopniu odgrywają rolę źródła zanieczyszczeń (przemysł metalurgiczny, domowe instalacje grzewcze, transport oraz miejscowości zlokalizowane na uboczu, na terenach górzystych). Fazy mineralne w osadzanym pyle można podzielić na 3 grupy. Pierwsza zawiera typowe składniki klastyczne, które są przenoszone z gleb oraz pyłu ulicznego poprzez powtórne rozpylenie (kwarc, skalenie – albit, ortoklaz, mikroklin, krzemiany – muskowit, chloryn,kaolinit, węglany – kalcyt, syderyt, magnezyt). Druga grupa uformowana jest z minerałów pochodzących z surowców używanych w przemyśle metalurgicznym (hematyt, magnetyt, grafit i kalcyt) oraz minerałów powstałych podczas procesów technologicznych (akermanit, majenit i spinel). Trzecia grupa zawiera sole obecne we wtórnych aerozolach (siarczany – baussingaultyt i lekontyt, chlorki – salmiak, halit). Stosunek minerałów wtórnych w 9 na 10 miejsc testowych był wyższy w sezonie zimowym niż letnim. Procent powtórnie zawieszonych cząsteczek był od 1,2 do 7,5 raza wyższy w sezonie letnim w porównaniu do zimowego. Wpływ na zanieczyszczenie przez przemysł metalurgiczny został udowodniony przez obecność hematytu i magnetytu w 9 na 10 terenów próbnych. W miejscowościach Ostrava Radvanice i Třinec, tlenki żelaza uformowały do 50% fazy krystalicznej przy osadzaniu całkowitego pyłu.

Słowa kluczowe: zanieczyszczenie powietrza, osadzanie pyłu, pył zawieszony, dyfrakcja rentgenowska, region Morawsko-Śląski