



## Mineralogical and oxygen isotope composition of inorganic dust-fall in Wrocław (SW Poland) urban area – test of a new monitoring tool

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We have analysed the mineralogical and oxygen isotope composition of solid inorganic atmospheric particles (SIAP) in Wrocław (SW Poland) to determine potential natural and anthropogenic sources of deposited dust. The mineralogical compositions of SIAP and local soils are very similar and quite typical. Dust sources were attributed to high emission sources (two large coal-fired power generation plants, i.e., “Wrocław” and “Czechnica”) and low emission sources (mostly small furnaces for home heating). A mullite phase was confirmed in the non-magnetic fraction of high emission dust. The  $\delta^{18}\text{O}$  (SIAP) values collected during the study period (from 20th November 2003 to 25th May 2005) vary between 8.6 and 21.8‰. The  $\delta^{18}\text{O}$  values of soil gathered nearest to the passive dust collector vary between 9.3 and 16.0‰. The  $\delta^{18}\text{O}$  values obtained for hypothetical anthropogenic sources of atmospheric inorganic particles are: (1) 7.4‰ for *low emission* and (2) from 13.4 to 16.1‰ for high emission dust components. The range of  $\delta^{18}\text{O}$  values obtained for SIAP, soil and hypothetical anthropogenic sources do not allow the unambiguous partitioning of anthropogenic particles using isotopic mass balance. However, mineralogical and geochemical evidence suggests that a major source (natural or anthropogenic) of dust deposited in Wrocław probably lies outside of the city. The predominant south-west wind direction suggests that agricultural areas, quarries, the Sudety Mountains, or industrial centres are possible origins of SIAP in Wrocław. We also do not exclude hypothetical long-transport processes as a source of dust deposited in Wrocław.

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### INTRODUCTION

Atmospheric dust ranging from the finest particles ( $\text{PM}_{10}$  – particles less than  $1\ \mu\text{m}$ ) to total suspended particles (TSP) and dust-fall can impair human health (Dockery and Pope, 1996; Siegman *et al.*, 1999; Inyang and Bae, 2006, van Zelm *et al.*, 2008) and cause damage to buildings (Wilczyńska-Michalik, 2004). In spite of modernization of all branches of industry, the dust problem in large urban areas, including Wrocław (SW Poland), remains critical. The conurbation of Wrocław, with ca. 640 000 inhabitants, still has an old complex road system, which results in problems with air quality. Generally, two types of anthropogenic atmospheric pollutants are usually present in urban areas: (1) low emission (from local heating and traffic pollutants); (2) high emission (from large industrial emitters). Two heat and power plants are present within the borders of the

Wrocław conurbation: “Wrocław” (a larger one, situated in the central part of the city) and “Czechnica” (a smaller one, situated in the suburbs, in Siechnice). Although these two plants supply the majority of the conurbation with heat and electricity, many parts of the city, especially the old buildings downtown, are still heated by individual home heaters. Classical methods of monitoring atmospheric pollutants in general only provide information about the amount of the pollutants (concentration or deposition) but do not provide qualitative information on the pollutants’ origin. The main problem in classical monitoring is how to distinguish an anthropogenic input of pollutants from the natural background level.

Mineralogical and geochemical studies to determine dust origins have been performed in other parts of Poland (Wilczyńska-Michalik, 1981; Manecki *et al.*, 1988; Schejbal-Chwastek and Tarkowski, 1988, Jabłońska and Janeczek, 2000; Jabłońska *et al.*, 2003) and elsewhere in Eu-

rope (Querol *et al.*, 2002; Moreno *et al.*, 2004). Air quality in Wrocław has been investigated by other authors and concerned: (1) daily fluctuations of CO and NO<sub>x</sub> concentration between high buildings (Mikołajczyk *et al.*, 1999); (2) SODAR (Sonic Detection And Ranging) methods to quantify atmospheric pollutants (Drzeniecka *et al.*, 2000); (3) PM<sub>2.5</sub> and PM<sub>10</sub> (dust particles of diameter less than 2.5 and 10 micrometer, respectively) concentrations (Zwoździak and Zwoździak, 2006; Sówka *et al.*, 2010); (4) variations in δ<sup>34</sup>S (SO<sub>4</sub><sup>2-</sup>) and δ<sup>18</sup>O (SO<sub>4</sub><sup>2-</sup>) in precipitation and composition of dust (Jędrysek, 2000, 2003; Górka and Jędrysek, 2004; Górka *et al.*, 2008); and (5) carbon isotope composition of organic particles in dust-fall (Górka and Jędrysek, 2008).

The geochemical and mineralogical analyses presented here are part of a multiparameter investigation of dust-fall in Wrocław during 2003–2005. Carbon isotope compositions from the organic fraction of dust-fall have already been published and illustrate potential pitfalls in the use of passive collection methods for geochemical analysis of dust-fall in a temperate climate (Górka and Jędrysek, 2008). The main problem concerning carbon isotopes in organic matter as described by Górka and Jędrysek (2008) was decomposition and maturation processes connected with the growth of algae, fungi and bacteria in collectors and possible contamination of the samples collected. According to investigations by other authors (Jackson, 1981; Jires *et al.*, 2002), influence of passive collecting method on the inorganic fraction of dust-fall, which is the case here.

In this study we apply two analytical techniques (i.e., mineralogical composition and oxygen isotope analyses of the inorganic fraction) of deposited dust to determine relative contributions of natural and anthropogenic sources. The oxygen isotope composition of aerosol-hosted quartz grains has been used to trace dust origin (Jackson, 1981; Mizota *et al.*, 1996; Aléon *et al.*, 2002) or to distinguish between marine and terrestrial sands (Yang *et al.*, 2008). Many authors have used the oxygen and carbon isotope composition of carbonate to trace the origin of fugitive dust (Wang *et al.*, 2005; Cao *et al.*, 2008). The most recent mineralogical and isotope geochemical techniques have been able to apply single particle analysis (Coz *et al.*, 2009; Kita *et al.*, 2009).

The potential application of the oxygen isotope tool to discriminate between the primary natural soil minerals (mainly quartz) and secondary anthropogenic minerals (mainly quartz and mullite), is supported by three assumptions: (1) that anthropogenic minerals are enriched in <sup>18</sup>O due to isotopic exchange with atmospheric oxygen (δ<sup>18</sup>O value about +23.5‰) in industrial processes; (2) that natural soil minerals have different oxygen isotopic compositions from anthropogenically generated minerals; (3) that deposited atmospheric dust collected in Wrocław has intermediate oxygen isotope compositions due to two-component mixing (Equation 1). The above assumptions should allow us to calculate the anthropogenic impact on Wrocław using isotopic mass balance (Equations 2 and 3).

$$\delta^{18}\text{O}_{\text{NAT}} < \delta^{18}\text{O}_{\text{ATMO}} < \delta^{18}\text{O}_{\text{ANTH}} \quad [1]$$

$$\delta^{18}\text{O}_{\text{ATMO}} = X_{\text{NAT}} \times \delta^{18}\text{O}_{\text{NAT}} + X_{\text{ANTH}} \times \delta^{18}\text{O}_{\text{ANTH}} \quad [2]$$

$$\% \text{ANTH} = \frac{\delta^{18}\text{O}_{\text{ATMO}} - \delta^{18}\text{O}_{\text{NAT}}}{\delta^{18}\text{O}_{\text{ANTH}} - \delta^{18}\text{O}_{\text{NAT}}} \quad [3]$$

The δ<sup>18</sup>O value of natural quartz derived from igneous and metamorphic rocks varies between 8 to 16‰, whereas quartz of low temperature origin (chert) shows δ<sup>18</sup>O values from 14 to 33‰ depending on formation temperature (Jackson, 1981).

The idea mineral oxygen may exchange with oxygen in air has been reported in experiments of oxygen exchange in the BaSO<sub>4</sub>-O<sub>2</sub> system (Hałas *et al.*, 1982) or the melting of basalt glass (Burkhard, 2001). Hałas *et al.* (1982) reported oxygen isotopic exchange between barite and oxygen in air at 800°C. Burkhard (2001) confirmed that the oxygen isotopic composition of basaltic glass (δ<sup>18</sup>O value about 4.8‰) became enriched in <sup>18</sup>O (to about 10.8‰) when heated to its melting temperature of 1250°C in the presence of air. Lower temperatures did not influence the oxygen isotopic composition of glass. A very slight oxygen exchange with gaseous oxygen in an extremely thin layer (1–20 nm) has been also documented in experimental studies with SiO<sub>2</sub> (Trimaille and Ganem, 1997) and mullite (Fielitz *et al.*, 2003).

On the other hand, in the archaeological investigations, one of main assumptions using the oxygen isotopic composition is the invariability of isotopic composition of silica sand in glass production process. It is commonly assumed that the melting time and temperature do not influence the final oxygen isotopic composition of glass, which depends only on the primary oxygen isotopic signature of used silica (Brill, 1970; Henderson *et al.*, 2005; Silvestri *et al.*, 2010).

In summary, we infer that in our case the dust generated in heat and power stations Wrocław will show altered oxygen isotope compositions due to isotopic exchange with oxygen in air during combustion at temperatures of 1200–1400°C, and that this is different from that of natural soil deflated dust.

## EXPERIMENTAL PROCEDURES

Nine periods of sampling of atmospheric particles have been carried out in Wrocław (SW Poland). Passive collectors, built of non-reactive materials (plastic) as described by Jires *et al.* (2002), were located throughout the city (Fig. 1). Collectors were located 2.5 m above the ground. The collecting area of the collector was 0.0398 m<sup>2</sup> and the volume *ca.* 5 L. To avoid deposition of large non-dust components (leaves, insects) each collector was covered by a plastic grid (mesh size 2 mm).

12 passive collectors were placed in areas of predominantly old-compact settlements, high traffic pollution, and distributed 1–3 km around the hard coal-fuelled heat and power station “Wrocław”, the largest single emitter in Wrocław (Fig. 1). All the collectors were installed in November 2003 and the samples were gathered every two months for nine collection-periods.

Before oxygen isotope and XRD (X-Ray Diffraction) analyses, the dust material was dried, weighed and washed in 0.3 M HCl solution (1 hour) in order to remove inorganic carbon phases (mainly carbonates and hydroxides) (Connin *et al.*, 1997; Collins *et al.*, 1999). Afterwards, the samples were

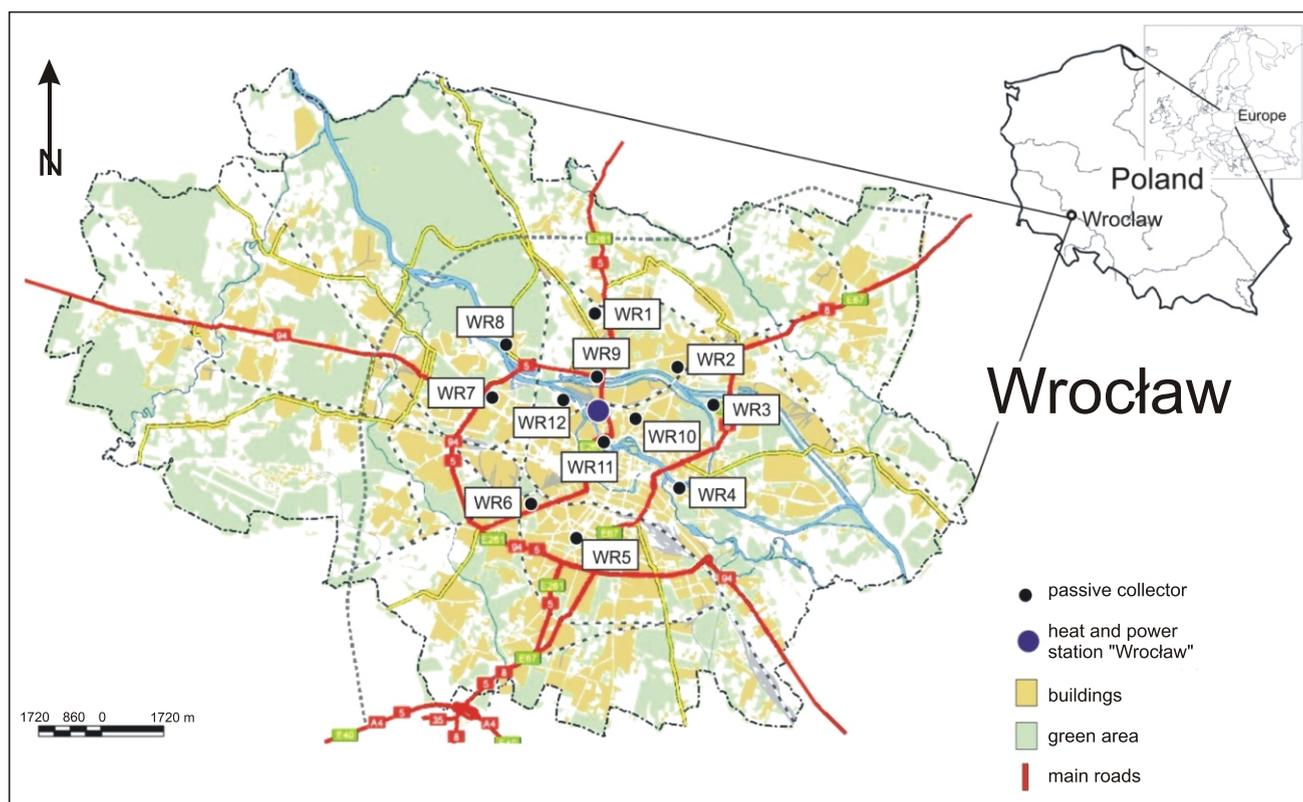


Fig. 1. Location of the 12 passive collectors in Wrocław

washed with hydrogen peroxide (30%  $\text{H}_2\text{O}_2$ ) in order to remove organic matter (solid organic atmospheric particles – SOAP), as described by Jackson (1985) by 3–4 weeks. The contribution of the organic fraction to total dust has been determined by the weight loss and the total dust, the inorganic mineral fraction (acid-insoluble inorganic dust; SIAP) and the organic fraction (SOAP) were calculated and expressed in  $\text{mg}/\text{m}^2/\text{day}$ . Afterwards, representative samples were chosen representing: (1) the summer season (period 5: from 20.07.2004–23.09.2004) for all collectors; (2) the winter season (period 7: from 22.11.2004–26.01.2005) for all collectors and (3) the whole study period (from 20.11.2003 to 25.05.2005) from one collector WR9 situated 1 km north of the heat and power station “Wrocław”. These selected samples have been analysed for mineralogical and isotopic compositions. The mineralogical compositions were determined using the XRD method (XRD Philips, Institute of Geological Science, University of Wrocław). No additional mineralogical treatment or separation of inorganic dust phases and soils was carried out before oxygen isotopic analysis. The anthropogenic ash from the electro-filters from heat and power station “Wrocław” and “Czechnica” was separated as magnetic and non-magnetic fractions using a permanent magnet. Before the  $\delta^{18}\text{O}$  analysis samples were dehydrated at  $300^\circ\text{C}$ . The  $\delta^{18}\text{O}$  analyses were made using the laser fluorination method (Sharp, 1990; Wiechert and Hoefs, 1995; Jędrysek and Weber-Weller, 2000) at the Laboratory of Isotope Geology and Geocology, University of Wrocław. The reagent gas was  $\text{BrF}_5$  and a  $\text{CO}_2$  laser was used. Oxygen produced in the reaction was cryogeni-

cally purified (on two  $\text{N}_2$ -traps). Final purification was in a *Toepler* mercury pump, where any possible fluoride reaction product not frozen in the two  $\text{N}_2$ -traps, was caught by mercury filling the pump. Finally, oxygen was converted to  $\text{CO}_2$  using a graphite/platinum reactor. Oxygen isotopic ratios were determined using a *Finnigan MAT Delta E* mass spectrometer. The analytical uncertainty of the  $\delta^{18}\text{O}$  determination was below 0.2‰. The oxygen isotope standards used were the *IAEA NBS-28* quartz and two inter-laboratory standards (*Laussane 1 Quartz*  $\delta^{18}\text{O} = 18.15\text{‰}$  and *GeeWhiz Quartz*  $\delta^{18}\text{O} = 12.55\text{‰}$ ). The  $\delta^{18}\text{O}$  values are expressed in ‰ relative to the V-SMOW international standard.

The same analytical methods were used to analyse the potential sources of inorganic atmospheric dust. The mineralogical and oxygen isotope compositions of soil minerals, anthropogenic high emission dust, anthropogenic low emission ash and minerals from the nearest building cover were analysed. Soil samples were collected next to each passive collector during one sampling (on the 24.03.2005). The representative samples of electro-filter dust (from the “Wrocław” heat and power plant), ash (from the “Czechnica” plant and from local home heaters) and building plaster were collected once during the entire sampling process, homogenized and analysed.

Meteorological data were obtained from the Meteorological Observatory of Wrocław (University of Wrocław). Complete meteorological data were collected every minute. Predominant wind directions and wind velocities were calculated as a sum of frequency within individual angle intervals. Maps of the spatial distribution of passive collectors in Wrocław and

the distribution of soil  $\delta^{18}\text{O}$  values were made using the *Golden Software Surfer 8.0*, whereas graphs and correlations were determined using the *Golden Software Grapher 6.0* software.

## RESULTS

The geochemical and mineralogical data of inorganic phases of soil next to passive collectors are reported in [Table 1](#). The mass of the particles collected using the passive collectors has been calculated as totals and inorganic dust de-

Table 1

Mineral composition, concentration and average  $\delta^{18}\text{O}$  values of inorganic particles in soil

Sample name	Soil sample near passive collectors		
	$\delta^{18}\text{O}_{\text{V-SMOW}}$ [‰]	Inorganic matter of soil [%]	Mineral composition of soil (XRD)
WR 1	14.0	97.67	quartz, microcline
WR 2	13.2	98.53	quartz, microcline, albite
WR 3	13.4	96.39	quartz, albite
WR 4	13.8	95.91	quartz, microcline
WR 5	15.7	99.12	quartz, microcline
WR 6	12.5	99.09	quartz, albite
WR 7	16.0	97.76	quartz, microcline
WR 8	9.3	96.78	quartz, microcline, muscovite
WR 9	12.1	97.91	quartz, albite
WR 10	15.4	97.47	quartz, microcline, albite
WR 11	15.5	96.78	quartz, microcline, albite
WR 12	13.0	98.05	quartz, microcline
MIN	9.3	95.91	
MAX	16.0	99.12	
AVERAGE	13.6	97.62	

Table 2

Mineral composition and average  $\delta^{18}\text{O}$  values of anthropogenic potential sources of SIAP

Anthropogenic inorganic sources of SIAP		
Origin of sample	$^{18}\text{O}_{\text{V-SMOW}}$ [‰]	Mineral composition of matter (XRD)
Non-magnetic fraction of industrial dust from heat and power station "Wrocław" in Wrocław	15.6	quartz, mullite, graphite, gypsum
Magnetic fraction of industrial dust from heat and power station "Wrocław" in Wrocław	16.1	maghemite, chromite, hematite
Non-magnetic fraction of industrial ash from heat and power station "Czechnica" in Siechnica	13.4	quartz, mullite
Ash from local home heater	7.4	quartz, calcite, portlandite, anhydrite
Plaster from buildings cover	n.a.	quartz, calcite, gypsum, anorthoclase

n.a. – not analysed

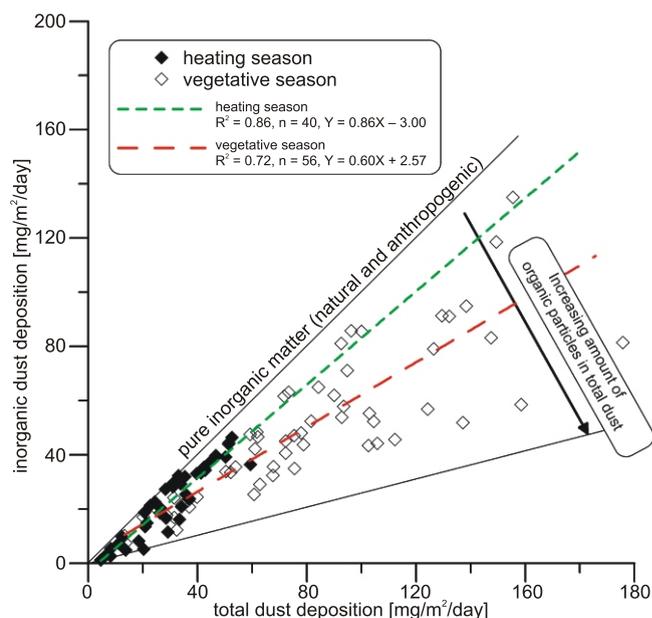


Fig. 2. Relations between deposition of total and inorganic dust in Wrocław in the period 20.11.2003–25.05.2005

position [ $\text{mg}/\text{m}^2/\text{day}$ ] for all the dust samples collected during the entire study period from all the passive collectors. The deposition of the total dust varied from 4.53 to 195.76  $\text{mg}/\text{m}^2/\text{day}$  ([Fig. 2](#)) with a minimum value in January 2004 and a maximum value in July 2004; the average value for each sampling period varied from 18.56 to 86.85  $\text{mg}/\text{m}^2/\text{day}$ . The deposition of inorganic dust varied from 1.20 to 135.08  $\text{mg}/\text{m}^2/\text{day}$  ([Fig. 2](#)) with a minimum value in December 2003 and a maximum value in August 2004; the average for each sampling period varied from 10.29 to 55.89  $\text{mg}/\text{m}^2/\text{day}$ . A positive correlation ( $R^2 = 0.78$ ,  $n = 97$ ,  $p < 0.05$ ) between total and inorganic dust deposition has been observed ([Fig. 2](#)). In [Figure 2](#) the samples are divided into 2 groups: vegetative season (representing periods from late spring to early autumn) and non-vegetative season (representing periods from late autumn to early spring). The concentration of inorganic particles in soils varies from 95.91 to 99.12% ([Table 1](#)), whereas their  $\delta^{18}\text{O}$  values vary from 9.3 to 16.0‰ ([Table 1](#)). The mass of the particles collected using the passive collectors has been calculated as totals and inorganic dust deposition [ $\text{mg}/\text{m}^2/\text{day}$ ] for all the dust samples collected during the entire study period from all the passive collectors. The deposition of the total dust varied from 4.53 to 195.76  $\text{mg}/\text{m}^2/\text{day}$  ([Fig. 2](#)) with a minimum value in January 2004 and a maximum value in July 2004; the average value for each sampling period varied from 18.56 to 86.85  $\text{mg}/\text{m}^2/\text{day}$ . The deposition of inorganic dust varied from 1.20 to 135.08  $\text{mg}/\text{m}^2/\text{day}$  ([Fig. 2](#)) with a minimum value in December 2003 and a maximum value in August 2004; the average for each sampling period varied from 10.29 to 55.89  $\text{mg}/\text{m}^2/\text{day}$ . A positive correlation ( $R^2 = 0.78$ ,  $n = 97$ ,  $p < 0.05$ ) between total and inorganic dust deposition has been observed ([Fig. 2](#)). In [Figure 2](#) the samples are divided into 2 groups: vegetative season (representing periods from late spring to early autumn) and non-vegetative season

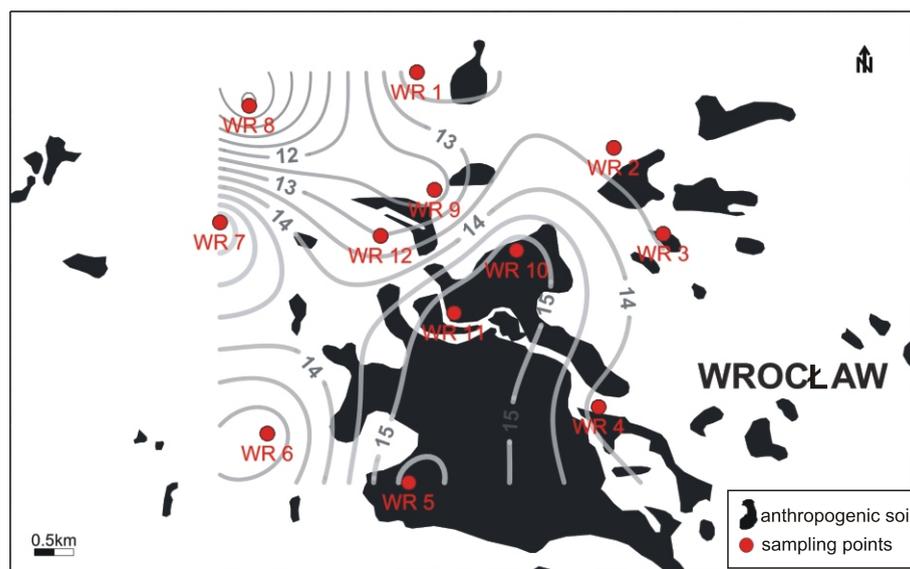


Fig. 3. Spatial distribution of  $\delta^{18}\text{O}$  values of soil minerals next to the 12 passive collectors in Wrocław (background: layer of anthropogenic soil in Wrocław)

(representing periods from late autumn to early spring). The spatial distribution of isotope signatures in soil inorganic particles next to the 12 passive collectors in Wrocław is shown graphically in Figure 3.

The geochemical and mineralogical data of inorganic phases of the potential anthropogenic sources of dust collected in Wrocław are shown in Table 2. Their  $\delta^{18}\text{O}$  values (Table 2)

vary from 7.4‰ (ash from local heaters) to 16.1‰ (magnetic fraction of industrial dust).

The geochemical and mineralogical data of inorganic phases of dust gathered using all 12 passive collectors in period 5 (20.07.2004–23.09.2004) representing summer and period 7 (22.11.2004–26.01.2005) representing winter are shown in Table 3. The  $\delta^{18}\text{O}$  values of inorganic particles in summer vary from 10.9 to 18.8‰ and in winter from 8.6 to 21.8‰ (Table 3).

Table 3

Mineral composition and average  $\delta^{18}\text{O}$  values of SIAP from Wrocław during two periods: period 5 (20.07.2004–23.09.2004) representing summer (vegetative) particles, while period 7 (22.11.2004–26.01.2005) reporting winter (heating) particles

Solid Inorganic Atmospheric Particles (SIAP) from 12 passive collectors						
Collector name	Period 5 (summer) (20.07.2004–23.09.2004)			Period 7 (winter) (22.11.2004–26.01.2005)		
	$^{18}\text{O}_{\text{V-SMOW}}$ [‰]	Mineral composition of SIAP (XRD)	SIAP in total particles fall [%]	$^{18}\text{O}_{\text{V-SMOW}}$ [‰]	Mineral composition of SIAP (XRD)	SIAP in total particles fall [%]
WR 1	18.8	n.a.	62.40	19.3	quartz, microcline, muscovite, hematite	98.12
WR 2	14.0	n.a.	40.63	19.1	quartz, albite, illite	84.03
WR 3	16.8	n.a.	84.81	19.1	quartz, albite, muscovite	n.a.
WR 4	12.7	n.a.	86.50	18.2	quartz, albite, muscovite	91.17
WR 5	10.9	n.a.	n.a.	n.a.	quartz, microcline, muscovite	95.38
WR 6	18.4	n.a.	86.87	17.3	quartz, albite, illite, hematite	94.25
WR 7	18.1	n.a.	58.09	18.8	quartz, microcline, albite, muscovite	86.69
WR 8	16.5	n.a.	53.50	n.a.	n.a.	n.a.
WR 9	n.a.	n.a.	45.76	14.3	quartz, microcline, illite	70.42
WR 10	14.9	n.a.	68.62	18.6	quartz, microcline, albite, muscovite	88.38
WR 11	16.7	n.a.	56.25	21.8	quartz, microcline, albite, muscovite	91.26
WR 12	n.a.	n.a.	64.32	8.6	quartz, microcline, muscovite	79.14
MIN	10.9		40.63	8.6		70.42
MAX	18.8		86.87	21.8		98.12
AVERAGE	15.8		64.34	17.6		87.88

Explanations as in Table 2

Table 4

Mineral composition and average  $\delta^{18}\text{O}$  values of SIAP from Wrocław in 9 periods (from 20.11.2003–25.05.2005) from passive collector WR 9

Solid Inorganic Atmospheric Particles (SIAP) from passive collector WR9		
Period	$^{18}\text{O}_{\text{V-SMOW}}$ [‰]	Mineral composition of SIAP (XRD)
20.11.2003–13.01.2004	n.a.	quartz, muscovite
05.01.2004–15.03.2004	14.1	quartz
11.03.2004–19.05.2004	15.9	quartz, microcline, muscovite
17.05.2004–22.07.2004	18.2	quartz, albite, muscovite
20.07.2004–23.09.2004	n.a.	quartz, albite, microcline, muscovite
21.09.2004–24.11.2004	n.a.	quartz
22.11.2004–26.01.2005	14.3	quartz, microcline, illite
24.01.2005–24.03.2005	14.3	quartz, muscovite, microcline
23.03.2005–25.05.2005	14.1	quartz, albite, muscovite
MIN	14.1	
MAX	18.2	
AVERAGE	15.1	

Explanations as in Table 2

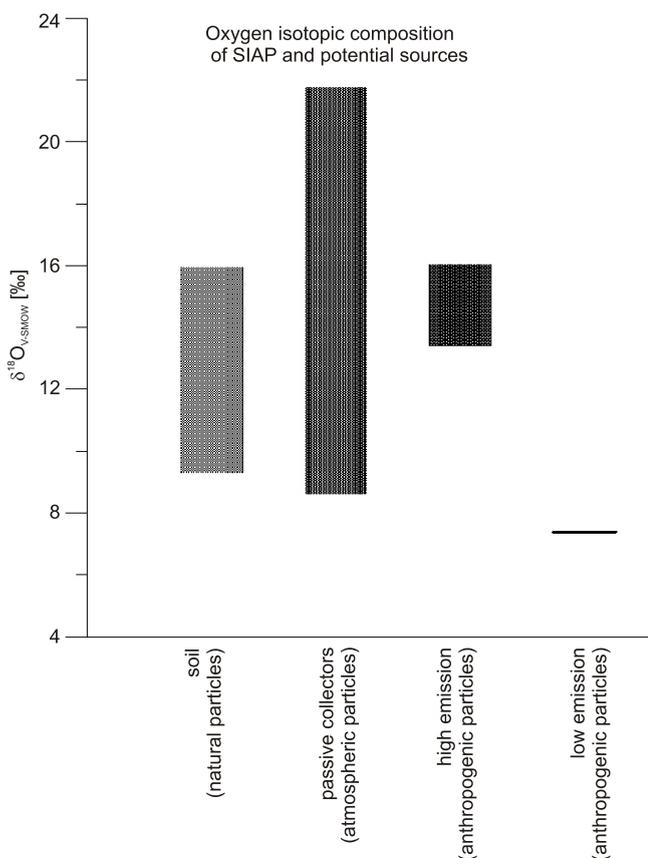


Fig. 4.  $\delta^{18}\text{O}$  values of SIAP collected in Wrocław and their potential natural (soil origin) and anthropogenic (industrial and local heater origin) sources

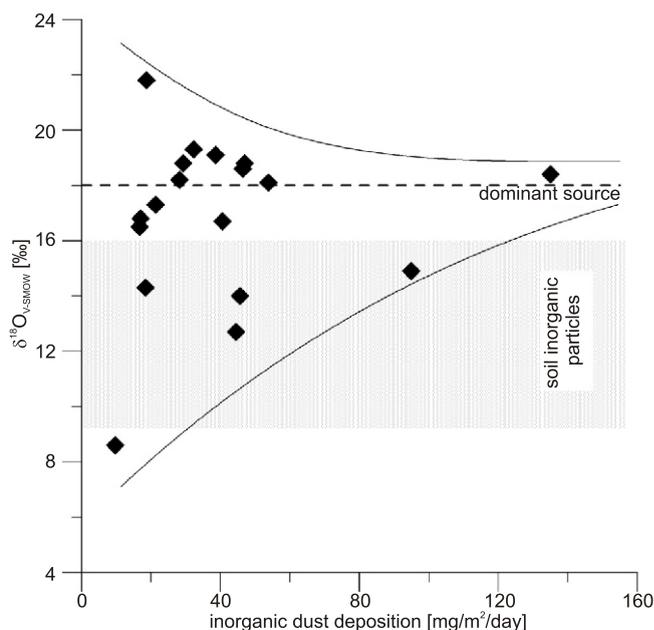


Fig. 5. Relation of isotopic composition to amount of inorganic dust deposition (mention: for all sites – periods 5 and 7)

The geochemical and mineralogical data of inorganic phases of dust gathered by collector WR9 during the entire study period (20.11.2003–25.05.2005) are shown in Table 4. The  $\delta^{18}\text{O}$  values of inorganic particles vary from 14.1 to 18.2‰ (Table 4).

Figure 4 shows the  $\delta^{18}\text{O}$  values of inorganic atmospheric particles collected in Wrocław and all the assumed natural and anthropogenic sources. The relation between the isotope ratios and amount of inorganic dust deposition is shown in Figure 5.

The meteorological data for the study period indicate that the predominant wind directions in Wrocław are south-west and north-east, and additionally south-east (except in summer). Winds in Wrocław are typically of low speed (lower than  $3 \text{ ms}^{-1}$ ). However, direct comparison of geochemical and meteorological data is not possible due to differences in the spatial localisation of geochemical sampling points (spatial data) and of meteorological monitoring stations (single point data).

## DISCUSSION

Seasonal variations in total dust concentration (organic and inorganic) as well as in the concentration of inorganic dust phases have been observed. During the vegetative season (from late spring to early autumn) deposition of total dust and inorganic phases of dust in Wrocław is higher than in the heating (winter) season (Fig. 2). A similar pattern was observed by Norra and Stüben (2004) in Karlsruhe, Germany. The larger amount of total dust and inorganic dust phases during the vegetative season are due to easier deflation processes (Norra and Stüben, 2004; Górka and Jędrysek, 2008). During the heating season the frozen and snow-covered soil is more resistant to deflation, hence the lower amount of deflated particles, both inorganic and organic. On the other hand, the amount of total and

organic dust phases is controlled by the higher concentration of organic matter in the atmosphere during the vegetative season (pollen, fragments of plants, insects, *etc.*; Norra and Stüben, 2004; Górka and Jędrysek, 2008).

Therefore, during heating seasons we observed lower deposition of total dust and strong correlation ( $R^2 = 0.86$ ) with inorganic phases of dust (Fig. 2), which is caused by lower concentrations of atmospheric organic particles and lower local deflation. Consequently, SIAP in heating season originate mainly from anthropogenic sources or from long-transport processes (i.e. deflated in other regions). During vegetative seasons the deposition of total dust is significantly higher and we noted a lower correlation ( $R^2 = 0.72$ ) with inorganic phases of dust (Fig. 2) than in heating seasons. During vegetative seasons, the higher total dust deposition is probably caused by higher amounts of the organic particles and higher local deflation. Consequently, SIAP in vegetative season originate mainly from local deflation, as well as from anthropogenic sources or from long-transport processes. The wide dispersion of vegetative season samples from “pure inorganic matter line” reported on Figure 2 is caused by higher concentrations of organic matter in the atmosphere during the vegetative season influencing the proportional amount of SIAP in total deposited dust.

We supposed that one of the major natural sources of collected atmospheric dust could be represented by particles deflated in nearest neighbourhood of collectors and transported over short distances. The mineralogical and oxygen isotopic composition of analysed soils reported in Table 1 is typical of temperate climate soils (Jackson, 1981; Mizota *et al.*, 1992; Norra *et al.*, 2006). The spatial distribution of  $\delta^{18}\text{O}$  values from whole inorganic soil matter demonstrate good graphical correlation with anthropogenically degraded soils (Fig. 3). An  $^{18}\text{O}$  enrichment is observed in Wrocław areas with anthropogenic soils ( $\delta^{18}\text{O} > 15\text{‰}$ ), when compared to areas without anthropogenic soils ( $\delta^{18}\text{O} \approx 13\text{‰}$ ; Fig. 3). In our opinion, possible explanations for these values are: (1) significant amounts of rubble (thermally treated building materials) in soils characterised by higher  $\delta^{18}\text{O}$  values or (2) differences in mineralogical composition between anthropogenic and natural soils.

The range of  $\delta^{18}\text{O}$  values obtained for the chosen hypothetical anthropogenic sources of atmospheric inorganic particles was rather surprising. In spite of the existence of mullite (a mineral formed at high temperature) in non-magnetic phases of industrial dust, the highest  $\delta^{18}\text{O}$  value (about 16‰) is lower than expected if isotopic exchange with air oxygen (23.5‰) is assumed. We supposed that sediment (igneous origin) quartz in coal will get enriched in  $^{18}\text{O}$  as it is burned due to exchange with oxygen in air resulting in very high  $\delta^{18}\text{O}$  values of generated dust. But the  $\delta^{18}\text{O}$  values obtained suggest that the hypothesis of total exchange of oxygen isotopes during high temperature combustion must be rejected. However, when comparing the  $\delta^{18}\text{O}$  values of high emission (magnetic and non-magnetic industrial dust) and low emission (home heater ash) dust samples, significant differences were observed ( $\delta^{18}\text{O}$  about 15 and 7‰, respectively, Table 2). The observed enrichment in  $^{18}\text{O}$  of high emission samples may be a result of distinct combustion temperatures of both processes. Possibly the exchange may occur only partially in the very thin layer of quartz grains

(Trimaille and Ganem, 1997; Fielitz *et al.*, 2003) and the magnitude of the exchange layer depends on the combustion temperature: the higher the temperature, the larger the layer of exchange and the higher the  $\delta^{18}\text{O}$  value. But the difference in isotopic composition of high and low emission samples can be also caused by the different mineralogical composition of dust formed in these combustion processes (Table 2). Thus, we infer that the dust-hosted silicate minerals either do not exchange oxygen isotopes with atmospheric oxygen during burning (Brill, 1970; Henderson *et al.*, 2005; Silvestri *et al.*, 2010) or the exchange occurs in a very thin surface layer (Trimaille and Ganem, 1997; Fielitz *et al.*, 2003). Probably, the experimentally confirmed enrichment in  $^{18}\text{O}$  (Burkhard, 2001) does not occur in typical burning processes (heat and power station as well as home heater coal burning) due to insufficient temperatures of the combustion process or insufficient combustion time to allow complete isotopic exchange. In the experiment mentioned above (Burkhard, 2001)  $^{18}\text{O}$  enrichment has been observed only after melting processes at a temperature of 1250°C. Such conditions do not occur in home heater burning processes, and may occur only partially during industrial burning, hence the observed enrichment is lower than initially expected.

The  $\delta^{18}\text{O}$  values obtained for aerial dust samples (Table 3) have shown a wide range from 10.9 to 18.8‰ for the summer period (20.07.2004–23.09.2004) and from 8.6 to 21.8‰ for the winter period (22.11.2004–26.01.2005). Comparing the average  $\delta^{18}\text{O}$  values obtained for the summer period (15.8‰) and the winter period (17.6‰; Table 3) with the earlier conclusions concerning the deposition of total and inorganic particles in vegetative and heating seasons it can be concluded that the observed enrichment of the SIAP in  $^{18}\text{O}$  in winter is caused by increased amounts of anthropogenically changed particles in the total pool of SIAP generated *in situ* or derived from long distance transport. Conversely, the enrichment of SIAP in  $^{18}\text{O}$  in summer is lower than in the winter period due to a larger amount of soil originated particles (average 13.6‰, Table 1) in the total SIAP and a lower input of anthropogenically changed particles generated *in situ* or derived from long distance transport. Unfortunately, for the final isotopic mass balance calculation, the majority of the  $\delta^{18}\text{O}$  data obtained from the passive collectors are higher than those of the proposed natural and anthropogenic sources for Wrocław dust (Fig. 4 and Tables 3, 4). But when analysing the relation of isotope composition and amount of SIAP in the dust samples collected (Fig. 5) a dominant source of SIAP can be identified. This source isotopic composition differs from the soil inorganic particles showing higher  $\delta^{18}\text{O}$  values (about 18‰). The  $\delta^{18}\text{O}$  values obtained for quartz dust measured in the northern hemisphere (Jackson, 1981) for long-range particles varies from 17 to 21‰. Therefore, a possible explanation is that the most of inorganic particles collected as dust-fall in Wrocław originates from long-distance transport rather than from locally deflated soil particles. In this case, a part of the inorganic dust phase deposited in Wrocław is derived from outside of the city. The south and south-west predominant wind direction indicate the possible sources for this external dust input:

- deflation of particles from agricultural fields surrounding Wrocław;

- mineral phases originating from the Sudety Mountains situated about 80–100 km SW from Wrocław or from quarries localised about 40 km S and SW of Wrocław;
- production of inorganic dust by industrial centres (such as the copper works situated about 70 km W from Wrocław).

The 1.5 year long (9 periods) mineralogical and oxygen isotopic record for a passive collector (WR 9 – located 1 km northward from heat and power station “Wrocław”) is shown in Table 4. The mineralogical composition of these samples is very similar to those collected during summer and winter periods (Table 3) and from the nearest soil (Table 1). The  $\delta^{18}\text{O}$  values scatter around 14%, excluding two periods (11.03.2004–19.05.2004 and 17.05.2004–22.07.2004), when an  $^{18}\text{O}$ -enrichment appears.

One of the major goals of this study was to assess the input of the anthropogenic atmospheric particles in the total mass of dust deposited in Wrocław. The range of  $\delta^{18}\text{O}$  values obtained for SIAP, soil and hypothetical anthropogenic sources do not fulfil the conditions of equation 1. We did not find any hypothetical sources (natural or anthropogenic) with high enough  $\delta^{18}\text{O}$  to explain all the SIAP deposited in Wrocław. Therefore, in this case, calculation of the amount of anthropogenic particles using isotopic mass balance equations 2 and 3 is not possible.

## CONCLUSIONS

The larger amount of total dust and inorganic dust phases observed during the vegetation period are due to easier deflation processes. During the heating period the frozen and snow-covered soil is more resistant to deflation, hence the lower amount of deflated particles, as inorganic as well as organic. In our opinion, the atmospheric dust in the heating season originates mainly from anthropogenic sources or from long distance transport processes, whereas in the vegetative season it originates mainly

from local deflation, as well as from anthropogenic sources or from long distance transport processes.

The mineralogical composition of SIAP deposited in Wrocław is very similar to the soil nearest the passive collector location. However, the  $\delta^{18}\text{O}$  values of SIAP and soil obtained show different ranges and, as a consequence, exclude local soil as a major potential natural source of SIAP.

The  $\delta^{18}\text{O}$  values obtained for hypothetical anthropogenic sources (low and high emission sources) are not enriched in  $^{18}\text{O}$  as would be expected in the case of isotope exchange processes with atmospheric oxygen. Therefore, the oxygen isotope exchange between minerals and oxygen in air probably does not occur in typical combustion process (representing as high as well as low emissions).

The lack of known sources enriched in  $^{18}\text{O}$  (higher than or equal to SIAP) makes it impossible to construct an isotopic mass balance equation and to calculate the amount of anthropogenic particles in the total dust. This suggests the dominance of other sources of inorganic dust than originally assumed.

Mineralogical and geochemical data indicate that the major source (natural or anthropogenic) of inorganic dust deposited probably lies outside Wrocław. The predominant south-west wind direction may indicate agricultural areas, quarries, the Sudety Mountains, or industrial centres as sources of SIAP in Wrocław. We also do not exclude long-distance dust transport as an additional source of dust deposited in Wrocław.

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