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# Geochemical and isotopic analyses of PM10 in Lower Silesia - preeliminary data

KEY WORDS:
PM10 dust, carbon isotopic analyses, Lower Silesia, atmospheric pollutants

## ABSTRACT

The main aim of the study was to determine the origin of particulate air pollution in Lower Silesia. Samples of PM10 dust were collected on quartz filters Whatman QM-A by employees of Voivodship Inspectorate for Environmental Protection (VIEP) in Wroclaw in 2011. As a pilot researches in Lower Silesia were selected two monitoring points of VIEP: (i) Osieczów and (ii) Zgorzelec. Air sampling point in Osieczów is a point of regional background and it is an excellent reference base for the analyses of PM10 in Lower Silesia. The aim of monitoring in this point is to assess the exposure of ecosystems to air pollution. Sampling point in Zgorzelec reflects the urban background and the measurements will be compared, in the future, to the results of the sampling points investigated the impact of industry and local transport on air quality in the whole Lower Silesia. For further geochemical and isotopic analyses were selected 25 samples from each sampling point, average every two weeks measurement. The concentration of PM10 dust for Osieczów ranged from 7 $\mu g \cdot m^{-3}$ (11.10.2011r.) to 89 $\mu g \cdot m^{-3}$ (4.03.2011r.) with an average of 24 $\mu g \cdot m^{-3}$ and for Zgorzelec between 10 $\mu g \cdot m^{-3}$ (11.10.2011r.) and 85 $\mu g \cdot m^{-3}$ (9.11.2011r.) with an average of 26 $\mu g \cdot m^{-3}$. The mean percentage contribution of carbon in PM10 samples from Osieczów was 47%, while in Zgorzelec 42%. The obtained values of $\delta^{13}C$ (PM10) in Osieczów varied from -31.1‰ (5.02.2011r.) to -25.5‰ (26.10.2011r.) with an average of -27.6‰, whereas in Zgorzelec between -28.6‰ (15.07.2011r.) and -25.2‰ (6.01.2011r.) with an average of -26.8‰. At the current stage of research is clearly discernible the different carbon isotope record in the material dust (qualitative information), despite the identical range of concentrations of PM10 in both analysed points (quantitative information). This confirms the appropriateness of the choice both research method and monitoring points.

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## Introduction

In XXI century air pollution is a very important civilization issue. All of substances which have negatively influence on people's health, properly working ecosystems or for people's products (buildings, sculptures etc.) are called pollution (VIEP 2011). Due to their physical character they are distinguished for dust and gaseous pollution. Gaseous pollutants are i.a. sulphur dioxide ($SO_2$), carbon dioxide ($CO_2$), carbon monoxide (CO), nitrogen oxides ($NO_x$), while dust pollutants are TSP (total suspended particles), PM10 (particulate matter with particle diameter less than 10 μm), PM2.5 (<2.5 μm) and PM1 (<1 μm). A group of elevated risk: children, elderly people and pregnant women are mainly subjected to negative influence of dust pollutants. Dust concentration cutting in atmospheric air is also very important issue because very often very high value of dust regional background are measured. According to Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (also known as CAFÉ Directive) 24-hour standards of maximum levels for the content of PM10 in Poland is 50 $\mu g \cdot m^{-3}$ - maximum 35 times per year (black line on Fig. 3) but yearly average limit is 40 $\mu g \cdot m^{-3}$. Currently for PM2.5 are allowed to exist some overruns but till 2015 the level of PM2.5 must be 25 $\mu g \cdot m^{-3}$ and till 2020, the level could not exceed 20 $\mu g \cdot m^{-3}$ (CAFE Directive). Among all air pollution dust hazards are one of the most dangerous for the environment and human health because of their mobility and can affect all ecosystem elements - water, air, soil and life forms.

It should be emphasized that the PM2.5 is up to 90% of PM10. At the same time there is no clarified threshold below which effects of PM2.5 is not harmful to humans. So fine particles have the ability to penetrate the human respiratory system down to the level of the alveoli and further into the bloodstream. They are causes of respiratory diseases (silicosis, asthma, chronic allergies) and circulatory system acid (Juda-Rezler 2000). European Union Member States shall make every effort to reduce air pollution, especially in areas densely populated by humans. In the cities people are exposed mainly to the negative effects of pollution from industry, transport, and from the so-called low emissions from the home furnances. Outside the cities the problem of air pollution may come from agriculture, biomass burning and in coastal areas from sea spray. Network monitoring of the PM10 and PM2.5 concentration is well developed in Poland by Voivodship Inspectorates for Environmental Protection measuring stations. They measure only the amount of harmful substances but not indicate the origin of analysed pollutants whether the direction of transport. The aim of this study was to determine the geochemical composition of the dust in Lower Silesia basing on isotopic analyses of $\delta^{13}C$. The analyses of isotopic ratios of the substances help to determine the origin of air pollutants. In earlier studies of carbon isotope composition of PM10 it is recognized that basing on known isotopic signal is possible to distinguish the individual dominant sources of pollution in the atmosphere (Widory et al. 2004, Kelly et al. 2005, Lòpez-Veneroni 2009).

Fig. 1 Monitoring points of Voivodship Inspectorates for Environmental Protection selected for studies: Osieczów and Zgorzelec.

## Study area and sampling

The study of this work is part of a larger project carried out for the whole province of Lower Silesia which covers nine points. For the pilot researches two points of air monitoring in Lower Silesia were selected:

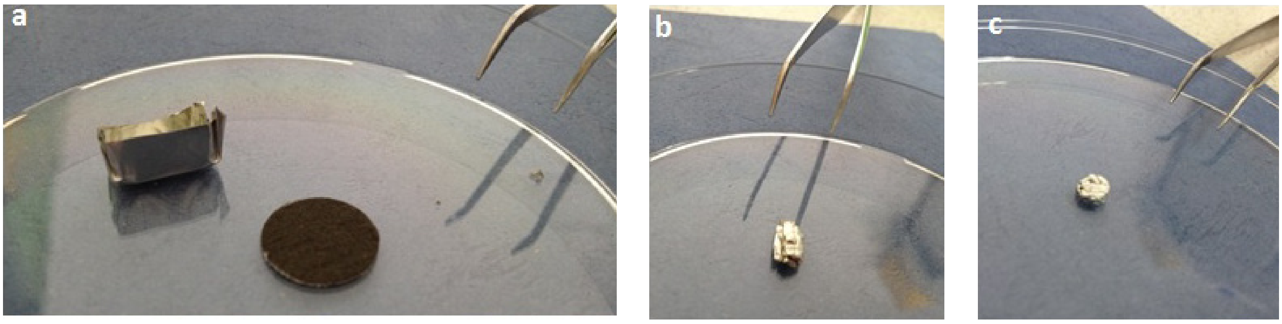
(i) Osieczów - point of regional background where ecosystems exposure to atmospheric pollution is studied; it is an excellent basis for comparison of the entire study area; latitude: E 15° 25'54 ", longitude: N 51° 09'04"

(ii) Zgorzelec - point of urban background where the impact of anthropogenic pollution in the urban environment of Zgorzelec city is studied; it is a background for comparison with other similar points in Lower Silesia; latitude: E 15 ° 01'30 ", longitude: N 51 ° 08'40 ".

For this studies were selected samples with PM10 dust deposited on a Whatman quartz filters gathered approximately every two weeks in 2011 by employees of the Voivodship Inspectorate for Environmental Protection in Wroclaw. Geochemical and isotopic analyzes were carried out for 25 samples inclusively of both points. The samples with diameter of 6 mm were filters and packed in tin capsules with dimensions of 6 x 6 x 12 mm.

Concentrations of C and N were carried out by Elemental analyzer NC Instruments NC 2500, while isotopic analyses of $\delta^{13}C$ were carried out by IsoPrime100 CF-IRMS coupled to an elemental analyzer Vario Micro Cube. Analyses were carried out at Université du Québec à Montréal.

Fig. 2 Sample prepared for analyse.




## Results

Fig. 3 Concentration of PM10 dust in Osieczów (blue) and Zgorzelec (green) in 2011 (data of VIEP).

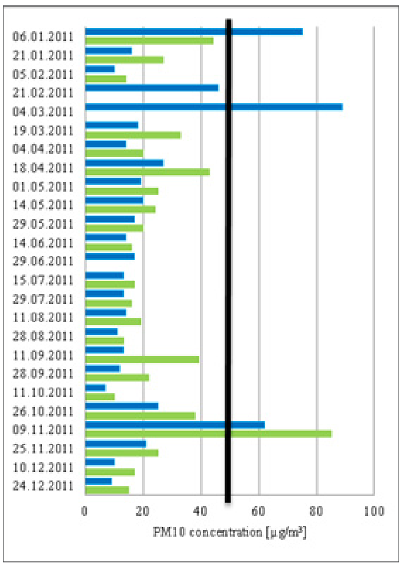
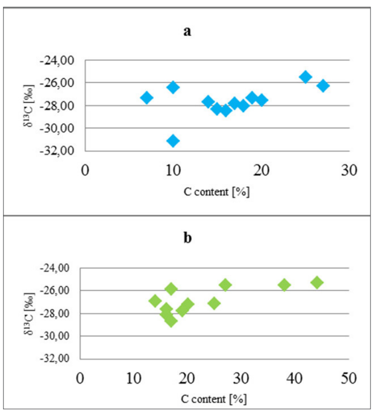


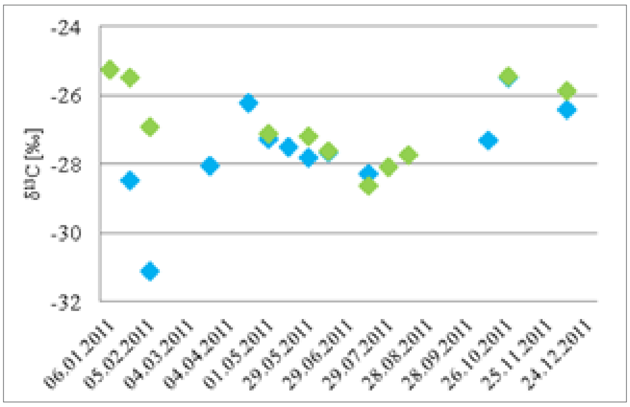

Fig. 4 Relationship of percentage contents of C in PM10 dust and $\delta^{13}C$ values in PM10 dust samples (a – Osieczów, b – Zgorzelec).




The levels of PM10 concentrations of chosen points in 2011: (i) Osieczów (blue) and (ii) Zgorzelec (green) are presented in Fig. 3. In Osieczów in 2011 concentration of PM10 ranged from 7 μg·m$^{-3}$ to 89 μg·m$^{-3}$ (4.03.2011) to with mean value of 24 μg·m$^{-3}$. In Zgorzelec in 2011 concentration of PM10 ranged from 10 μg·m$^{-3}$ (11.10.2011) 85 μg·m$^{-3}$ (9.11.2011) to with mean value of 26 μg·m$^{-3}$.

In Osieczów (Fig. 4a) percentage contents of C ranged from 32.97 % (14.05.2011r.) to 77.84 % (11.10.2011r.) with mean value of 47 %. In Zgorzelec (Fig. 4b) percentage contents of C ranged from 30.78 % (1.05.2011r.) to 60.73 % (21.01.2011r.) with mean value of 42 %. The $\delta^{13}C$ values (PM10) in Osieczów varied from -31.1‰ (5.02.2011r.) to -25.5‰ (26.10.2011r.) with mean value of -27.6‰ (Fig. 5 blue solid symbols). The $\delta^{13}C$ values (PM10) in Zgorzelec varied from -28.6‰ (15.07.2011r.) to -25.2‰ (6.01.2011r.) with mean value of -26.8‰ (Fig. 5 green solid symbols).

Fig. 5 Isotopic composition of δ13C in PM10 dust in 2011 (blue solid symbols – Osieczów, green solid symbols - Zgorzelec).




## Discussion

The aim of this study was to identify potential sources of dust in Lower Silesia using δ13C isotopic analyses of PM10 dust and to try to assess effect of human impact in the study area. To this pilot researches two points were determined: (i) the regional background in Osieczów and (ii) urban background in Zgorzelec.

The highest concentration of PM10 in Osieczów in 2011 was 89 μg·m-3 with an average of 24 μg·m-3, while in Zgorzelec the highest concentration of PM10 was 85 μg·m-3 with an average of 26 μg·m-3. In sampling points in Lower Silesia overruns of maximas were noted three times for Osieczów and one for Zgorzelec (Fig. 3). It should be remembered that for this studies were selected only 25 days in 2011. At the sampling point in Osieczów there were expected to get the minimum number of days per year with exceeded of limits, because it is a point of regional background, which means that it should be the least contaminated. Basing on a number of previous studies on particulate matter we know that dust pollution are not only issued in situ, but they can come up with some long-range transport (Cachier et al., 1986, Grivas et al. 2008). To ensure there are needed additional modeling analyses of movement of air masses. Sampling point in Zgorzelec showed once exceeding the limit values for dust among measurement days selected for the analyses, and the yearly average concentration was slightly higher than in the case of the regional background in Osieczów.

The values of isotopic composition of δ13C in sampling points differed greatly depending on the sampling point. In Osieczów δ13C (PM10) values varied from -31.1‰ to -25.5‰, which point at presence of many potential sources of dust pollution on studied area (Fig. 4a). Basing on the known values of δ13C for individual emitters in Osieczów source of contamination can be determined from plant fragments (about -31.1 ‰) (Kelly et al. 2005). In 2003-2005 Górka and Jędrysek obtained values of δ13C for pollutants in Wrocław, Lower Silesia. Values of δ13C for fragments of plants were: for grass -30,5 ‰ and for leaves -27,3 ‰ (Górka and Jędrysek 2008). From the combustion of diesel and other liquid fuels (-26.5 ‰ ± 0.5) as well as from the combustion of coal (about -25 ‰) (Widory et al. 2004). In Wrocław For the combustion of fossil fuels δ13C values were obtained: low-quality coal -24,2 ‰, high-quality coal -25,7 ‰, diesel and gasoline soot -28,3 ‰ and -26,8 ‰ respectively (Górka and Jędrysek 2008). Assuming that sampling point in Osieczów is chosen as regional background point it was expected that there will not be one dominant source, but a mixture of pollutants, both anthropogenic and natural, what could be observed in Fig. 5. In Zgorzelec can be observed a seasonal variability of dust pollution sources depending on the season. During the heating season (January-April and October-December) δ13C values range from -26.90 ‰ to -25.24 ‰, while in the growing season -28.63 ‰ (Fig. 4b, Fig. 5). Enrichment of 13C isotope during the heating season clearly underlines the dominant contribution of pollutants from the combustion of fossil fuels and transport (Widory et al. 2004). Significant depletion in 13C during the growing season indicates a natural origin of dust (eg. plant fragments) (Kelly et al. 2005).

## Summary

An important signal is the absence of one dominant source of dust pollution in Osieczów, which indicates the presence of a mixture of natural and anthropogenic pollutants in the studied area. Osieczów is therefore an ideal point for regional background where a comparison with the remaining area of Lower Silesia is observed. The seasonal variability of the distribution of dust in Zgorzelec at urban background point is observed. During the winter in the city the dominant source of PM10 are impurities from the low emissions, mainly from burning coal and from transport. During the summer there are observed depletion in $^{13}C$: (i) sources derived from combustion of liquid fuels - transport or (ii) the fragments of C3 plants.

Results of pilot researches show that sampling points (i) the regional background in Osieczów and (ii) the urban background in Zgorzelec have been well selected for analyses and will become points of reference for further research into the origins of dust in Lower Silesia. Overruns of PM10 dust concentrations on studied area require reduction and qualitative researches of atmospheric pollution may be a very useful tool.



## References

Cachier H., Buat-Menard P., Fontugne M., and Chesselet R., Long-range transport of continentally- derived particulate carbon in the marine atmosphere: evidence from stable isotope studies, 1986 *Tellus B* 38, 161-177.

Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (CAFE)

Górka M. and Jędrysek M., δ13C of organic atmospheric dust deposited in Wrocław (SW Poland): critical remarks on the passive method, *Geological Quartely* (2008), 52 (2), 115-126

Grivas G., Chaloulakou A., Kassomenos P., An overview of the PM10 pollution problem, in the Metropolitan Area of Athens, Greece. Assessment of controlling factors and potential impact of long range transport, *Science of the Total Environment (2008)*, 389, 165-177.

Juda-Rezler K.,Oddziaływanie zanieczyszczeń powietrza na środowisko, (2000), Warszawa

Kelly S.D., Stein C., Jickells T.D., Carbon and nitrogen isotopic analysis of atmospheric organic matter, Atmospheric Environment 39 (2005), 6007-6011

Lòpez-Veneroni D., The stable carbon isotope composition of PM2.5 and PM10 in Mexico City Metropolian Area air, *Atmospheric Environment 43* (2009), 4491-4502

Regional Inspectorate for Environment Protection, Report on state of Environment in Lower Silesia 2011

Widory D., Roy S., Le Moullec Y., Goupil G., Cocherie A., Guerrot C., The origin of atmospheric particles in Paris: a view through carbon and lead isotopes, *Atmospheric Environment* 38 (2004), 953-961



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