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SOLID ATMOSPHERIC PARTICLES AND WET PRECIPITATIONS
IN WROCLAW (SW POLAND): MINERALOGICAL AND ISOTOPIC
PRELIMINARY STUDIES

Abstract: The atmospheric dry (particles) and wet precipitations in Wrocław downtown (SW Poland) were investigated (between 20.11.2003 and 15.03.2004). However the mineral composition of pure industrial dust (heat and power station “Wrocław” – the biggest individual pollutant in Wrocław) is as follows: magnesioferrite, magnesiochromite, hematite, quartz, mullite and graphite. The mineral composition of the mineral fraction of dust collected in various points in Wrocław is composed of: quartz, muscovite, biotite, microcline, albite, anorthite. $\delta^{13}\text{C}$ value of organic particles in the dust varies from -25,04 to -27,78 ‰ and the $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value in precipitation varies from +6,36 to +13,12 ‰. The obtained data indicate correlations with meteorological observations and evidence multiple sources of pollution in Wrocław.

Keywords: pollutants, Wrocław, sulphur and carbon isotopes, RTG analyses, mullite

INTRODUCTION

Two periods of sampling atmospheric dust and precipitations in Wrocław downtown (SW Poland) have been carried out. The analyzed samples, were collected into 12 passive collectors (Jires et al. 2001), where old type of buildings and traffic pollutants, predominates. Two types of the anthropogenic environmental atmospheric pollutants are usually discriminated: 1) *low emission* (from the local home hearths and traffic pollutants) and 2) *high emission* (from the large industrial plants). This paper report the results of mineralogical and isotopic studies of solid atmospheric particles and rainwater sulfates studies. Basic problems of the air quality in Wrocław have been described by other authors (e.g. Drzeniecka et al. 2000, Jędrysek 2000, 2003, Mikołajczyk et al. 1999).

The main goal of this work was: 1) to determine quantitatively the role of potentially largest pollutants emitter (heat and power station “Wrocław”) in the atmospheric pollution mass balance in Wrocław mean of RTG analysis; 2) to find the potential zonation with respect to atmospheric pollutants using isotopic analysis and meteorological observations.

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METHODS OF INVESTIGATION

The passive collectors were located onto two radiuses at a 1 and 3 km distains from heat and power station “Wrocław”. Each collector was 2.5 m high and had 0.0398 m² of the collecting surface. They were installed in November 2003 and the samples were gathered once per two months. This work reports the results of 2 collection-periods (2 months each). Before the RTG analyses, the part of the collected dust has been washed out with 30% H₂O₂ in order to remove the organic matter. The industrial dust have been separated, with a magnet, to the magnetic and non magnetic fractions. Before carbon isotope analyses, the dust material has been dried and washed out with 0.3M HCl (1 hour) in order to remove other carbon phases (mainly carbonates and hydroxides). The total dust fall, separately mineral and organic one expressed in mg/m²/day. The sulfate in precipitation is shown as SO₄²⁻ deposition in mg/m²/day.

The organic dust particles were combusted, using cooper oxide (CuO) wire, under vacuum at 900 °C. The CO₂ obtained was cryogenically purified and collected to pyrex ampoules. The BaSO₄ were reacted with V₂O₅ reagent, next the SO₂ obtained was cryogenically purified and collected to pyrex ampoules.

RTG analyses have been made by Siemens RTG (Institute of Geologic Studies, UW_r). C and S isotopic ratios were analyzed using the mass spectrometer MI-1305 with special device for nano-mole gas analysis (UMCS, Lublin) and Finnigan Mat Delta E mass spectrometer (Laboratory of Isotope Geology and Geoecology ,UW_r, Wrocław).

RESULTS

The geochemical, mineralogical and isotopic data obtained for periods 20.01.2003-13.01.2004 and 13.01.2004-15.03.2004 are as follows (Tab. 1):

Table 1. The data obtained for periods 20.01.2003-13.01.2004 and 13.01.2004-15.03.2004 (n.a. – not analysed).

	20.01.2003-13.01.2004	13.01.2004-15.03.2004
The SO ₄ ²⁻ deposition varies between sample points [mg/m ² /day]	0,05 ÷ 1,85	0,52 ÷ 4,01
The deposition of total dust [mg/m ² /day]	4,53 ÷ 38,04	8,21 ÷ 59,34
The deposition of organic particles of dust [mg/m ² /day]	3,32 ÷ 15,02	2,79 ÷ 22,90
The deposition of mineral fraction of dust [mg/m ² /day]	1,20 ÷ 25,44	5,42 ÷ 39,72
δ ¹³ C value of organic particles of the dust [‰]	-25,04 ÷ - 26,02 ‰;	-25,93 ÷ - 27,78 ‰;
δ ³⁴ S(SO ₄ ²⁻) value in precipitation [‰]	+6,36 ÷ +13,12 ‰.	n.a.
RTG analysis of mineralogical fraction of dust fall	quartz, muscovite, biotite, microcline, albite, anorthite	n.a.

The RTG analysis of industrial dust from heat and power station “Wrocław” have been carried out. The magnetic fraction of dust represented mainly by: magnesioferrite, magnesiochromite and hematite. The non-magnetic fraction of dust represented mainly by: quartz, mullite (high temperatures mineral) and graphite.

DISCUSSION

A positive correlations between total dust fall and mineral fractions ($R^2=0,89$) and between the deposition of the dust mineral particles and SO_4^{2-} depositions ($R^2=0,79$) for period 20.01.2003-13.01.2004 might be explained by the nucleation role of atmospheric dust particles in formation of SO_4^{2-} -rich droplets of precipitations. Increasing dust in air resulted in increasing frequency of precipitations and in consequence to increasing SO_4^{2-} depositions.

It has been observed a zone with preferential deposition of mineral fraction of dust for period 20.01.2003-13.01.2004 and 13.01.2004-15.03.2004 on the direction SW-NE (Fig.1 and 2) respectively. This is in agreement with highest velocity of winds but perpendicular to the highest frequency of predominant winds in Wrocław downtown.

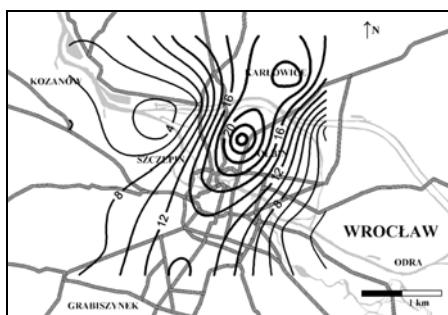


Fig.1 Distribution of mineral fractions of dust fall [$mg/m^2/day$] in Wrocław (20.11.2003-13.01.2004).

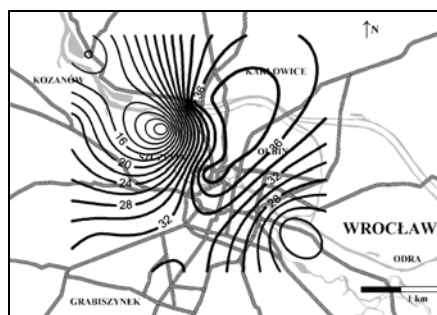


Fig.2 Distribution of mineral fractions of dust fall [$mg/m^2/day$] in Wrocław (13.01.2004-15.03.2004)

Carbon isotope analysis of organic dust particles indicated two regions of Wrocław with the highest $\delta^{13}C$ values and it correspond with exist regions with predominant low air pollutant emission.

Unusually high $\delta^{34}S(SO_4^{2-})$ value has been observed as compare the data obtained earlier in the Wrocław downtown (Jędrysek 2000, 2003). We do not know the reason of this and further investigations will be carried out.

The RTG analyses of mineral fraction of dust fall did not show any traces of the mullite phase. This may indicate a negligible (if any) role of the heat and power station “Wrocław” in the general mass balance of pollutants, or amount high temperatures mineral (mullite) in dust fall samples is below the limit of detection.

The lower total dust fall and the mineral fraction in that dust between (20.11.2003-13.01.2004) as compared to the period (13.01.2004 - 15.03.2004) may

resulted from the elevated dust deflation from the soil in the second period (no snow cover and the soil was not frozen in second period).

CONCLUSIONS

The presented results indicate several types of sources of air pollution in investigated part of Wrocław downtown. The old compact settlement, so called low air pollutant emission regions, are the dominant source of dust and atmospheric sulfates in Wrocław. In contrast to velocity of wind, the role of predominant wind direction in spread of pollutions, is not important factor. The heat and power station "Wrocław" is not the major local pollutant source in Wrocław downtown.

ACKNOWLEDGEMENTS: Meteorological data have been obtained from Meteorological Observatory of Wrocław (Section for Meteorology and Climatology, Wrocław University). Great thanks are due to Dr A. Kałużny for help in field works.

This study was supported from 1017/S/ING/03-IX, 2022/W/ING/03-49 2022/W/ING/03-12 grants.

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