

## **C and S isotope variations in solid atmospheric particles and sulfate in precipitations in Wrocław (SW Poland).**

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### *Introduction*

In spite of tremendous improvement of the air quality in the last 10 years, the problem of clean air is still crucial in large city. Two types of the 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 work describes the results of solid atmospheric particles and rainwater sulfates studies in Wrocław downtown (SW Poland). The samples analyzed, were collected into 12 passive collectors (Jires et al. 2001) in Wrocław, where old type of buildings, showing the *low type emission* and traffic pollutants, predominates. Basic problems of air quality in Wrocław have been described by other authors (e.g. Drzeniecka et al. 2000, Jędrysek 2000, 2003, Mikołajczyk et al. 1999).

The major goal of this work was: 1) to determine participation of the one local large pollutants emitter (heat and power station “Wrocław”) in the atmospheric pollution mass balance in Wrocław; 2) detect the potential zonation with respect to atmospheric pollutants. Carbon and sulphur isotope analysis of solid organic atmospheric particles ( $\delta^{13}\text{C}$ ) and sulfate in precipitation ( $\delta^{34}\text{S}(\text{SO}_4^{2-})$ ) respectively, have been carried out. The isotope analyses have been complemented by meteorological data.

### *Analytical procedures*

The passive collectors were located onto two radiuses at a 1 and 3 km distains from large local pollutants emitter (heat and power station). Each collector was 2,5 m high and had 0,0398 m<sup>2</sup> of the collecting surface. They were installed in November 2003, and this work shows the results of 2 months collection period (one sampling action). 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  $\text{mg}/\text{m}^2/\text{day}$ . The sulfate in precipitation is shown as  $\text{SO}_4^{2-}$  deposition in  $\text{mg}/\text{m}^2/\text{day}$ .

The organic dust particles were combusted, using copper oxide (CuO) wire, under vacuum at  $900\text{ }^\circ\text{C}$ . The  $\text{CO}_2$  obtained was cryogenically purified and collected to pyrex ampoules. The  $\text{BaSO}_4$  were reacted with  $\text{V}_2\text{O}_5$  reagent, according to the method of Yanagisawa and Sakai (1983). The  $\text{SO}_2$  obtained was cryogenically purified and collected to pyrex ampoules.

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, UWr, Wrocław).

### Results

The geochemical and isotopic data obtained for period 20.01.2003-13.01.2004 as follows:

- the  $\text{SO}_4^{2-}$  deposition varies between sample points from 0,05 to 1,85 [ $\text{mg}/\text{m}^2/\text{day}$ ];
- the deposition of total dust varies from 4,53 to 38,04 [ $\text{mg}/\text{m}^2/\text{day}$ ];
- the deposition of organic particles varies from 3,32 to 15,02 [ $\text{mg}/\text{m}^2/\text{day}$ ];
- the deposition of mineral fraction varies from 1,20 to 25,44 [ $\text{mg}/\text{m}^2/\text{day}$ ];
- $\delta^{13}\text{C}$  value of organic particles in the dust varies from -25,04 to -26,02 ‰;
- $\delta^{34}\text{S}(\text{SO}_4^{2-})$  value in precipitation varies from +6,36 to +13,12 ‰.

### 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  $\text{SO}_4^{2-}$  depositions ( $R^2=0,79$ ) might be explained by the nucleation role of atmospheric dust particles in formation of  $\text{SO}_4^{2-}$ -rich droplets of precipitations. Increasing dust in air resulted in increasing frequency of precipitations and in consequence to increasing  $\text{SO}_4^{2-}$  depositions.

It has been observed a zone with preferential deposition of both dust fall and  $\text{SO}_4^{2-}$  on the direction SW-NE (Fig.1 and 2). This is in agreement with highest velocity of winds but perpendicular to highest frequency of predominant winds .

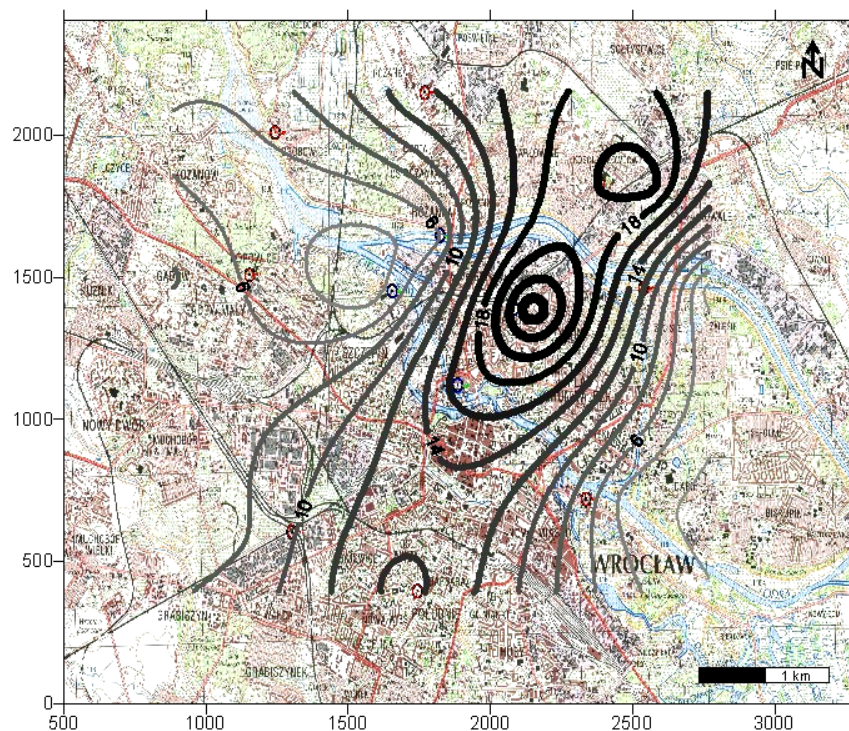


Fig. 1. Distribution of mineral fractions of dust fall [ $\text{mg}/\text{m}^2/\text{day}$ ] in Wrocław (20.11.2003-13.01.2004).

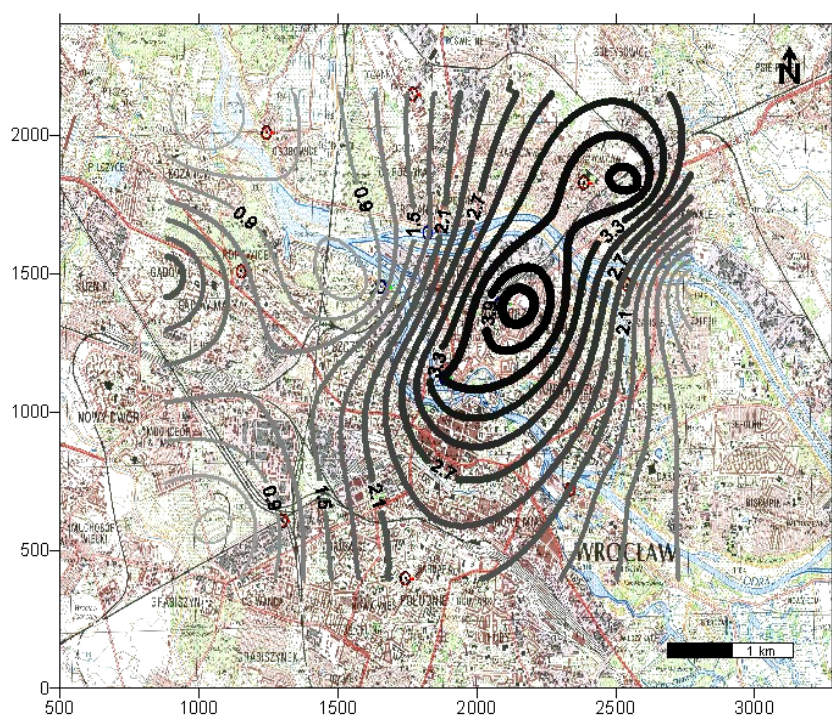
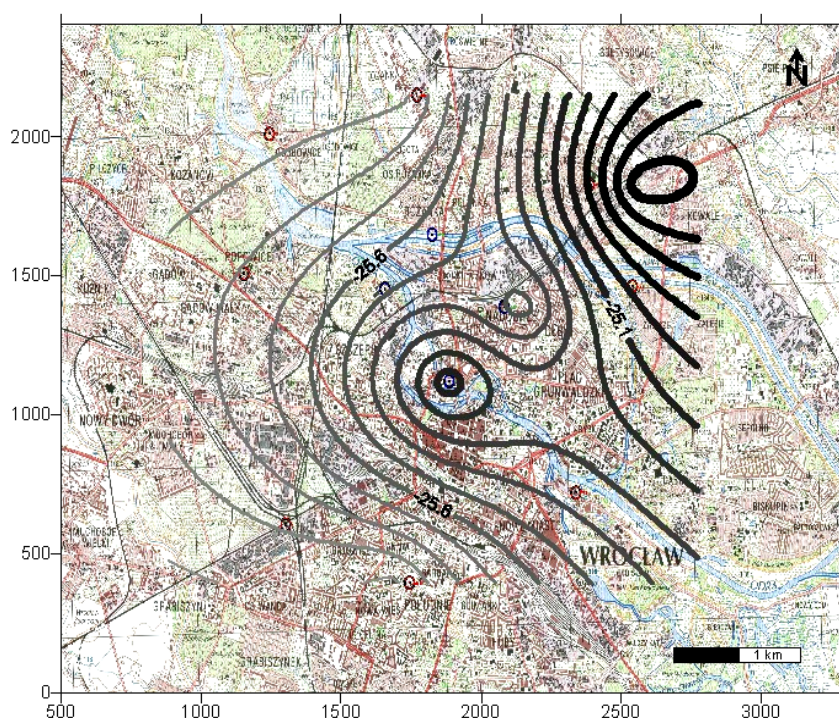


Fig. 2. Distribution of  $\text{SO}_4^{2-}$  deposition [ $\text{mg}/\text{m}^2/\text{day}$ ] in Wrocław (20.11.2003-13.01.2004)

Fig. 3.



Spatial

distribution of  $\delta^{13}\text{C}$  value of organic particles in the dust in Wrocław (20.11.2003-13.01.2004).

Carbon isotope analysis of organic dust particles indicated two regions of Wrocław with the highest  $\delta^{13}\text{C}$  values (Fig. 3). These regions show the predominant low air pollutant emission.

Unusually high  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  value has been observed as compared to 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.

### Conclusions

The presented results indicate several types of sources of air pollutants in the investigated part of Wrocław downtown. The preferential dust and precipitation sulfates deposition are regions with old compact settlement (low air pollutant emission). In contrast to the velocity of wind, the role of the predominant wind direction in the spread of pollutants is not an important factor.

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### **References**

- Drzeniecka A., Pereyma J., Pyka J.L., Szczurek A., 2000. Wpływ warunków meteorologicznych na stężenie zanieczyszczeń powietrza w Śródmieściu Wrocławia, *Chemia i Inżynieria Ekologiczna*, T.7, Nr8/9, 865-882.
- Jędrysek M. O., 2000. Oxygen and Sulphur Isotope Dynamics in the  $\text{SO}_4^{2-}$  of an Urban Precipitation., *Water, Air and Soil Pollution* 117, 15-25.
- Jędrysek M.O, 2003. Nowe dane na temat zmienności  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  i  $\delta^{18}\text{O}(\text{SO}_4^{2-})$  w wodach opadowych: potencjalny znacznik zasilania wód powierzchniowych i podziemnych (New data on  $\delta^{34}\text{S}(\text{SO}_4^{2-})$  and  $\delta^{18}\text{O}(\text{SO}_4^{2-})$  values in precipitation: potential indicator of the origin of surficial and groundwater recharge)., In Polish, English abstract., Ed. H. Piekarek-Jankowska, B. Jaworska-Szulc), *Współczesne Problemy Hydrogeologii (Recent Problems in Hydrogeology)*, Wyd. Politechniki Gdańskiej 11 (2), 157-164.
- Jires A., El-Hasan T., Manasrah W., 2002. Qualitative evaluation of the mineralogical and chemical composition of dry deposition in the central and southern higlands of Jordan, *Chemosphere* 48, 933-938.
- Mikołajczyk A., Pereyma J., Szczurek A., 1999. Ocena wpływu warunków meteorologicznych na jakość powietrza w Śródmieściu Wrocławia, POL-IMIS '99 III Sympozjum OCENA WIELKOŚCI IMISJI ZANIECZYSZCZEŃ POWIETRZA, Wydawnictwo PZITS 764, 71-80.
- Yanagisawa, F., Sakai, H., 1983. Preparation of  $\text{SO}_2$  for sulfur isotope ratio measurements by thermal decompositions of  $\text{BaSO}_4\text{-V}_2\text{O}_5\text{-SiO}_2$  mixtures. *Anal. Chem.* 55, 985-987.