

SPE AND GC–MS INVESTIGATION OF ORGANIC CONTAMINANTS IN ATMOSPHERIC PRECIPITATION

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SUMMARY

The seasonal and regional variability of organic contaminants in atmospheric precipitation has been investigated in the Sosnowiec region (Upper Silesia, southern Poland) for a twelve-month period during 2002 and 2003. Contaminants were isolated by solid-phase extraction (SPE) and analyzed by gas chromatography–mass spectrometry (GC–MS) to compare the chemical composition of organic contamination and the semi-quantitative content of selected compound groups. During the heating season, the dominating source of pollution is coal combusted in the region. Characteristics of organic contamination in precipitation sampled after the heating season indicate they are related to traffic emission. Regional differences between organic pollutant content suggest that the low emitters, for example individual house fires, are important source of organic contamination in the Upper Silesia agglomeration.

INTRODUCTION

In the natural environment precipitation is important in scavenging gaseous constituents from the air and dissolving fine particles suspended in the air and transporting all the material to the earth's surface [1–4]. Little is known, however, about how this process participates in the systems in which organic compounds migrate to soil, and to surface and ground water. The rapid development of civilization has been responsible for introducing into the environment many synthetic chemicals which pollute air, water, and soil [5–10].

The objective of this investigation was to compare seasonal changes in both quantitative content and chemical composition of the organic pollutants in precipitation (rain and snow) in the Sosnowiec region. It was

also of interest to determine the extent of differences between samples from different parts of the region (urban, non-industrial, industrial). The results obtained enable assessment of the main origins of the organic pollutants present in the precipitation in this region.

EXPERIMENTAL

Twenty four precipitation samples (rain and snow) from the Sosnowiec region were collected between August 2002 and August 2003 in the meteorological plot situated close to the Faculty of Earth Sciences, University of Silesia (Sosnowiec, Poland). Regional variations were investigated by sampling precipitation in the area of the Upper Silesia agglomeration both during the heating season (twelve samples in February and March) and afterwards (twelve samples in April and May).

Organic compounds were separated from the aqueous phase by solid-phase extraction (SPE) on Bakerbond C₁₈ columns (octadecyl on silica gel carrier; 3 g, vol. 6 mL). The extraction procedures used were those described in Bakerbond Application note EN-19 (Extraction of PAH from Drinking Water). Total recovery of PAH >85% is assumed for these columns. Precipitation samples were filtered at a rate of 8–10 mL min⁻¹. Organic substances were eluted from the columns with several portions of

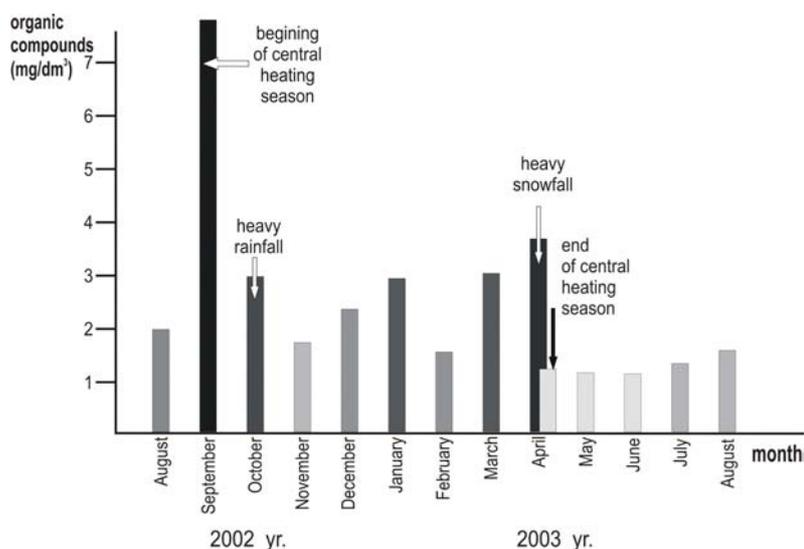


Fig. 1

Seasonal variation of the concentrations of organic compounds

dichloromethane (~0.5–1 mL) and eluates were combined. The solvents were evaporated at room temperature and organic compound yields were calculated (Fig. 1).

Contaminants were analyzed by gas chromatography–mass spectrometry by means of an Agilent Technology 6890 gas chromatograph coupled with the Agilent Technology 5973 mass spectrometer. Compounds were separated on a 60 m × 0.25 mm i.d. × 0.25 μm film HP-5 column. Dilute samples (1.5 μL) were injected with a 1:10 split ratio. He (purity 99.90%) was used as carrier gas. The oven temperature was maintained at 50°C for 2 min then programmed first at 10° min⁻¹ to 175°C, then at 6° min⁻¹ to 225°C, and finally at 4° min⁻¹ to 300°C which was held for 20 min. Total programming time was 90 min. The mass spectrometer was operated in electron-impact ionization mode, electron energy 70 eV. Full-scan spectra were acquired in the mass range 50 to 650 Da. Acquired data were processed with Hewlett–Packard Chemstation software. All compounds were identified from their mass spectra, by comparison of their retention times with those of standard compounds and with literature data, and by interpretation of MS fragmentation patterns [11]. Evaluation of semi-quantitative composition was achieved by use of total-ion chromatograms.

RESULTS AND DISCUSSION

The amount and composition of organic contamination in atmospheric precipitation varies substantially with season (Fig. 1). The beginning of the heating season in September was marked by a large increase in the concentration of organic pollutants emitted to the atmosphere and the end of the heating season (April) resulted in a distinct decrease in concentration. Abundant precipitation in October and November caused an obvious decrease in the concentration of organic compounds in samples taken subsequently.

The organic compound groups identified in the atmospheric precipitation samples were: *n*-alkanes, branched alkanes and acyclic isoterpanes ($m/z = 71$), *n*-alkenes ($m/z = 69$), alkylcyclohexanes ($m/z = 83$), alkylcyclobenzenes ($m/z = 91$), diterpenes ($m/z = 123$), and polycyclic aromatic hydrocarbons (PAH) with three, four, or five condensed aromatic rings, for example retene ($m/z = 183$), phenanthrene and anthracene ($m/z = 178$), fluoranthene and pyrene ($m/z = 202$), chrysene ($m/z = 228$), and benzo-fluoranthenes, benzo(*a*)pyrene, benzo(*e*)pyrene, and perylene ($m/z = 252$). Most of the PAH were accompanied by their alkyl derivatives of chain

length from C₁ to C₅, although the unsubstituted parent PAH, except retene, occurred in much higher concentrations than the alkyl derivatives, indicating combustion as their source [4,6]. PAH with more than five rings were not found in the precipitation samples analyzed. Phenol derivatives and methylquinolines were identified among substituted compounds.

It was found there were two main sources of organic pollutants (Fig. 2):

1. coal combusted in central heating plants and individual houses; and
2. traffic pollution with the features of crude oil.

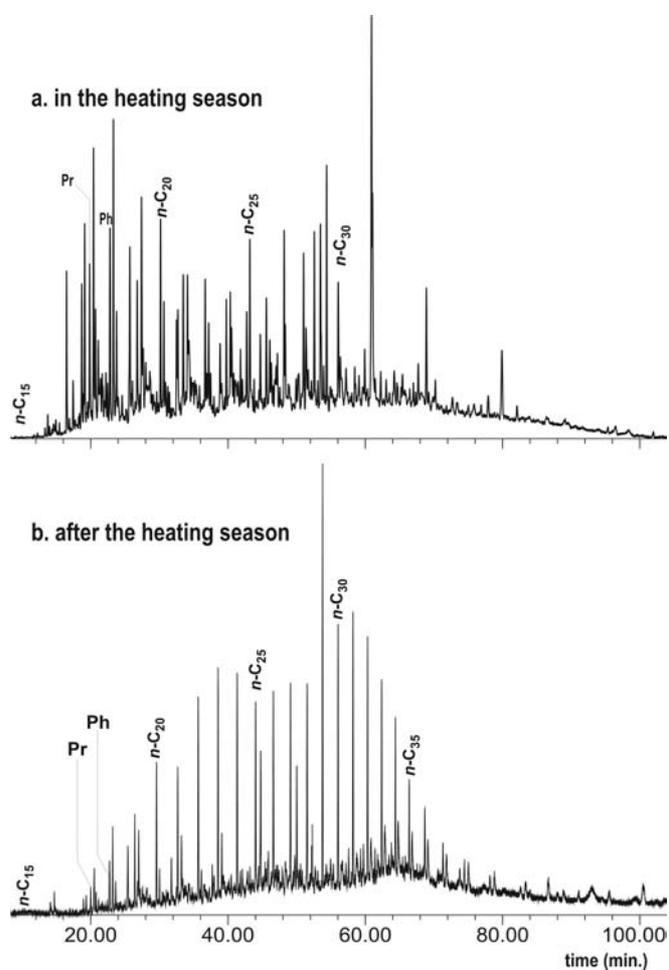


Fig. 2

Seasonal changes in the composition of organic pollution found in precipitation in the Sosnowiec region: (a) the heating season; (b) after the heating season

is monomodal and similar to that in the most crude oils (Fig. 2b). Diterpenes, retene, simonellite, alkylbenzenes, and alkylcyclohexanes are absent or occur at very low concentrations (0.0–0.7%) in these samples. The summer samples are strongly depleted in five-ring PAH (less than 0.3% of the total, compared with 1.4–10.8% in the heating season). They do, however, contain phenanthrene and chrysene, and their methyl derivatives.

CONCLUSIONS

The composition of the organic compounds found in precipitation suggests that traffic is the main source of organic pollution during late spring, summer, and early autumn whereas incomplete combustion of coal is dominant during the central heating season. Alkylcyclohexanes, alkylbenzenes, diterpenes, retene, and simonellite, indicators of coal combustion [4–6,12], are absent in the late spring–early autumn precipitation whereas these compounds occur in all winter samples. Because these compounds originate from organic matter which contains a significant terrestrial content, for example coal, their occurrence confirms these findings. Regional differences in organic pollutant content suggest that low emitters such as individual house fires are important sources of organic contamination in the Upper Silesia agglomeration. Samples containing the highest concentration of organic substances do not come from the industrial districts but from those with individual houses.

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