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# Analysis of phenols and nitrophenols in rainwater collected simultaneously on an urban and rural site in east of France

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ABSTRACT

The behaviour of phenols and nitrophenols in the atmosphere is of concern for environmental research as these are known to be toxic to humans and wildlife. To increase the knowledge about these compounds, the concentrations of 20 phenols and nitrophenols in rainwater were studied in an urban (Strasbourg) and a rural (Erstein) site in Eastern France.

The wet rain samples were collected on a weekly basis between January 2002 and July 2003, and analyzed for phenols and nitrophenols using SPME and gas chromatography coupled to mass spectrometry. The compounds were derivatized with MDBSTFA directly in the injection port of the gas chromatograph.

Total concentrations ranged from 0 to 1383 µg $L^{-1}$ in Strasbourg and from 0 to 1215 µg $L^{-1}$ in Erstein. These concentrations are in the same range than those measured in other studies, but considerably higher than the concentrations measured for pesticides (about 10 times) and polycyclic aromatic hydrocarbons (about 1000 times) on the same sites and at the same period.

Phenols, except for o-cresol, were generally less concentrated than nitrophenols. o-Cresol was one of the major compounds, probably due to its role as raw material in pesticide production. The concentrations of phenols and nitrophenols were found to vary with time. No seasonal trend was observed, but significant correlations with rainfall amount were identified.

## 1. Introduction

Atmospheric phenols and nitrophenols received a special interest over the last years because of their known toxicity to humans (Allen and Allen, 1997) and wildlife (Shea et al., 1983; Shafer and Schonherr, 1985), and their supposed contribution to the forest decline in Central and Northern Europe (Rippen et al., 1987; Trautner et al., 1989). Leuenberger et al. (1988) also showed that dinitrophenols induce toxic effects on the plants at rain concentrations between 1 and 10 nM $m^{-3}$ by inhibiting the growing of plants, the assimilation of nutriments and the transpiration (Shea et al., 1983; Leuenberger et al., 1988). These observations have induced the monitoring of nitrophenols on needles and leaves of higher plants (Hinkel et al., 1989; Thompson and Treble, 1995; Natangelo et al., 1999).

The origins of phenols and nitrophenols in the atmosphere can be very diverse. They can be directly emitted through combustion processes in vehicles (Nojima et al., 1983; Tremp et al., 1993), especially diesel engines (Furuta et al., 2008), or through their use as reagents in the manufacture of dyes, drugs, fungicides and pesticides (Tompkins et al., 1992). Other important direct emissions come from plastic and chemical industries, and also the paper manufacture that uses phenols and nitrophenols in important amounts for the protection of wood used for paper production (Rodriguez et al., 2000; Schlett and Pfeifer, 1992). The global production of phenols and nitrophenols associated to these industries was estimated to be 5.5 million tons in 1993 (Ojala et al., 1997).

Phenols and nitrophenols can also be indirectly emitted into the atmosphere, for example through photochemical reactions of benzene, toluene and phenolic compounds with OH and $NO_2$ radicals (Nojima et al., 1975, 1976; Nojima and Kanno, 1977; Atkinson et al., 1980; Grosjean, 1984; Leone and Seinfeld, 1985). Other sources can spill nitrophenols into the atmosphere, namely coal and wood combustion, the biodegradation of organophosphorous insecticides like parathion and methyl-parathion (Kishk et al., 1976; Laplanche et al., 1981) or the use of phenols (bromoxynil, ioxynil) and nitrophenols (DNOC, dinoseb, dinoterb) as herbicides (Leuenberger et al., 1988). Despite the incorporation of many phenolic compounds into the EPA list of hazardous air pollutants (http://www.epa.gov/ttn/atw/188polls.html), only few data about these sources are available, and consequently their significance and importance remain imprecise. Nevertheless, some measurements were performed on rainwater (Nojima et al., 1976;

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Leuenberger et al., 1985, 1988; Kawamura and Kaplan, 1983; Alber et al., 1989; Levsen et al., 1990, 1993; Schüssler and Nitschke, 2001) and fog (Trautner et al., 1989; Richartz et al., 1990).

This paper describes the results obtained by monitoring of 6 phenols (phenol, m-cresol, o-cresol, p-cresol, bromoxynil and ioxynil) and 14 nitrophenols (3-nitrophenol, 2-methyl-3-nitrophenol, 3-methyl-2-nitrophenol, 3-methyl-4-nitrophenol, 4-methyl-2-nitrophenol, 5-methyl-2-nitrophenol, DNOC, dinoseb, dinoterb, 2,5-dinitrophenol, 2,6-dinitro-p-cresol, 2,6-dinitrophenol, 2,4-dinitrophenol and 3,4-dinitrophenol) in rainwater samples in the Eastern France between January 2002 and July 2003.

## 2. Materials and methods

### 2.1. Reagents and material

Acetonitrile of HPLC grade, $HNO_3$ and NaCl were obtained from Prolabo (LPCR, Schiltigheim, France). Ultrapure water was obtained from a Milli-Q water system (Millipore, St. Quentin en Yvelines, France).

The standards of phenols and nitrophenols were supplied as individuals from Aldrich, Riedel-de Haën, Fluka Chemika, Ultra Scientific and Institute of Organic Industrial Chemistry. The levels of purity were higher than 99% for phenol, m-cresol, o-cresol, p-cresol, 4-nitrophenol-$d_4$, 3-methyl-2-nitrophenol, 4-methyl-2-nitrophenol, ioxynil, DNOC, dinoseb and dinoterb. Purity was higher than 98% for 3-nitrophenol, 2-methyl-3-nitrophenol, 3-methyl-4-nitrophenol, bromoxynil, 2,5-dinitrophenol, 2,6-dinitro-p-cresol, and higher than 97% for 5-methyl-2-nitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenol and 3,4-dinitrophenol. A stock solution of each phenol and nitrophenol was prepared at 1 g $L^{-1}$ in acetonitrile.

Working solutions and mixtures of phenols and nitrophenols were also prepared in acetonitrile. Ultrapure Milli-Q water was used to prepare the calibration standard solutions. The final percentage of acetonitrile in all aqueous solutions did not exceed 2.5% for not influencing the efficiency of the solid-phase microextraction (SPME).

MDBSTFA (*N*-Methyl-*N*-[tert-butyldimethyl-silyl]trifluoroacetamide) was purchased from Sigma-Aldrich (St. Quentin Fallavier, France) and SPME manual holders and 85 µm polyacrylate (PA) fibres were obtained from Supelco (Bellefonte, PA, USA). The fibres were conditioned as recommended by the manufacturer.

### 2.2. Sampling site and collection

To draw information about ambient contamination, rain samples were collected at two different sites. The first site was in the botanical garden of Strasbourg University, an urban area situated near to the centre of Strasbourg (400,000 inhabitants).

The second system was installed in a rural area, situated 25 km Southeast of Strasbourg, at 2 km from a small town, Erstein (9000 inhabitants).

Samples were collected simultaneously on the two sites on a weekly basis between January 2002 and July 2003 by using a wet only rainwater sampler (Précis Mécanique, France) agreed by METEO-France. After collection, the samples were stored in darkness at −18 °C before analysis.

In order to eliminate the variations of the concentrations caused by fluctuations of the precipitation levels during the sampling interval, each station was equipped with a graduated open collector (Précis Mécanique, France).

The normalized concentration was calculated according to

$$C_{i1,\mathrm{norm}} = \frac{C_{i1}H_i}{H_m} \qquad (1)$$

where $C_{i1,\mathrm{norm}}$ is the normalized concentration of species 1 in the sample $i$, $C_{i1}$ the concentration of species 1 in the sample $i$, $H_i$ the precipitation level of the sample $i$ and $H_m$ the mean precipitation height.

### 2.3. Extraction procedure

Rainwater samples of 2 mL were placed in SPME amber vials of 4 mL. Then, 20 µL of 4-nitrophenol-$d_4$ at 100 mg $L^{-1}$ (to obtain an internal standard concentration of 1 mg $L^{-1}$), 10 µL of $HNO_3$ at $10^{-3}$ M (to obtain a pH value of about 3.0) and 1.5 g of NaCl were added.

Stirrer bars were put in, then the vials were sealed with PTFE-faced silicon caps and placed into the SPME device to process solutions at ambient temperature. The mixture was magnetically stirred at 400 rpm, and a polyacrylate (PA) SPME fibre was exposed to it for 40 min in immersion mode. Then the fibre was retracted into the holder and introduced into the injection port of the gas chromatograph where the phenols and nitrophenols were desorbed from the fibre.

Approximately 5 s before the introduction of the SPME fibre into the injection port of the GC, 2 µL of MBDSTFA were injected directly into the injection port for silylation of the phenols and nitrophenols (derivatization in the injection port). The injection port was maintained at 280 °C and kept in splitless mode for 5 min (starting with the injection of the SPME fibre). No degradation of the column was observed with this procedure.

Desorption time of the fibre was set to 5 min (splitless time). Carryover was prevented by keeping the fibre in the injector for an additional 5 min with the injector in split mode. Blanks were periodically run to confirm the absence of contamination.

SPME fibres were conditioned at 280 °C for 2–3 h before the first use, and for 30 min before every subsequent use.

### 2.4. Gas chromatography–mass spectrometry

All measurements were performed with a Thermo Quest GC 2000 with a split–splitless injector and a Thermo Finnigan Trace MS detector. For the chromatographic separation, an OPTIMA-210 Macherey-Nagel column (MN-France, Hoerdt) was used (30 m × 0.32 mm, film thickness: 0.25 µm). The carrier gas was helium at a flow rate of 1.9 mL $min^{-1}$.

The injector and the transfer line temperatures were kept at 280 °C and 250 °C respectively. The oven temperature was held at 50 °C for 5 min, then increased to 150 °C at 8 °C/min, held at 150 °C for 1 min, increased to 260 °C at 18 °C/min, held at 260 °C for 1 min, increased to 280 °C at 5 °C/min and finally held at 280 °C for 10 min to purge the column.

The derivatized molecules were analyzed by electron ionisation (EI) at 70 eV in selected ion monitoring mode (SIM) where two or three characteristic ions were selected (Table 1). Details of the entire analytical method were published before by Jaber et al. (2007).

Detection and quantification limits varied between 0.2 µg $L^{-1}$ and 99 µg $L^{-1}$ [LOD] and between 0.7 µg $L^{-1}$ and 331 µg $L^{-1}$ [LOQ]. Uncertainties varied between 8.7% (phenol) and 17.9% (4-methyl-2-nitrophenol). LODs were calculated by comparing the signal-to-noise ratio ($S/N$) of the lowest concentration to a $S/N > 3$ (Jaber et al., 2007).

## 3. Results and discussion

### 3.1. Rainwater sampling

Wet only rainwater samples have been collected between January 2002 and July 2003 in Strasbourg (urban site) and between February 2002 and July 2003 in Erstein (rural site) on a weekly basis. Rainwater samples were collected on the two sites, and the precipitation amount was read directly on a graduated bulk container situated near the wet only rainwater collector. In 2002, 34 samples were collected in Strasbourg and 31 in Erstein, and in 2003, 10 samples were collected both in Strasbourg and Erstein. Details are given in Table 2.