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Technical note

Occurrence of 4-Nonylphenol in rain and snow

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Abstract

The present technical note reports on the endocrine disruptor 4-nonylphenol (4-NP) in rain and snow. In July 2001, November 2001 and January 2002, rain and snow sampling was conducted at different urban, suburban and rural areas in Germany and Belgium. The mean concentration of 4-NP in rain water and roof run off was 0.253 $\mu g\,dm^{-3}$ ($n=8$) with a higher mean concentration in suburban areas at 0.534 $\mu g\,dm^{-3}$ and considerable lower mean concentrations in rural and urban areas at 0.099 and 0.062 $\mu g\,dm^{-3}$, respectively. The mean concentration of 4-NP at 0.099 $\mu g\,dm^{-3}$ ($n=3$) was significantly lower in summer rain than in winter rain at 0.346 $\mu g\,dm^{-3}$. In snow samples, 4-NP was detected with a mean value of 0.242 $\mu g\,dm^{-3}$ ($n=8$). A higher mean value of 4-NP in snow at 0.478 $\mu g\,dm^{-3}$ ($n=4$) was found at urban sites whereas in snow from suburban areas the mean concentration of 4-NP at 0.030 $\mu g\,dm^{-3}$ ($n=2$) was much lower. 4-NP was never detected above its determination limit in snow samples from rural areas.

Keywords: 4-Nonylphenol; Alkylphenol polyethoxylates; Endocrine disruptors; Non-ionic surfactants; Rain; Snow; Solid-phase extraction; GC/MS

1. Introduction

Alkylphenol polyethoxylates (APnEOs) are an important group of non-ionic surfactants commonly used as household and industrial detergents. In 1995, about 500,000 tonnes of APnEOs were produced worldwide (Renner, 1997). Nonylphenol polyethoxylates (NPnEOs) are the most important APnEOs accounting for about 80% of the total APnEOs. 4-Nonylphenol (4-NP), a complex mixture of isomers, occurs in the environment as a product of the microbial breakdown of NPnEOs (Giger, 1987). 4-NP is also used as an adjuvant in pesticides (McLeese et al., 1981). It has been reported that 4-NP has a three times higher estrogenic activity than DDT (Soto et al., 1991). 4-NP causes deformities and reproductive problems in wildlife (Jobling and Sumpter, 1993; Oehlmann, 2000). The compound might be involved in breast cancer increases and sperm count declines in humans (Sonnenschein, 1998). Removal of organic compounds from the atmosphere takes place through chemical transformation as well as through dry and wet deposition (Duce et al., 1983; Prospero et al., 1983). So far, an atmospheric input of 4-NP to the aquatic environment has not been considered yet. However, evaporation of semi-volatile compounds (SVOCs) to the atmosphere from water surfaces, soil bodies and vegetation has been recognized as an important source for such contaminants in the atmosphere (Nelson et al., 1998). The vapor pressure at 1×10^{-6} atm (at 298 K) classifies 4-NP as a SVOC with a moderate tendency to volatilize. The Henry's law constant (H) for 4-NP at $3.5\times10^{-5}\,atm\,m^3\,mol^{-1}$ (at 298 K) is high enough to support gaseous air–water exchange of 4-NP to the atmosphere (Dachs, 1999). Dachs et al. (1999) and Van Ry et al. (2000) detected

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concentrations of 4-NP in the atmosphere ranging from at 0.0081–0.0253 $\mu g\,m^{-3}$ resulting mostly from volatilization of 4-NP from free water surfaces. However, the atmospheric half-lives (<1 day) of 4-NP is suggested to be short (Howard et al., 1991).

To the best of our knowledge, to date there are no studies dealing with the occurrence of 4-NP in rain water and snow. In the present study, we collected rain and snow samples in Germany and Belgium to investigate wet deposition as a source of 4-NP in the environment. To study the spatial and temporal distributions rain and snow samples were collected from urban, suburban and rural areas at summer and winter time.

2. Experimental and methodology

2.1. Sampling

Samples of rain, roof runoff and snow were collected from urban, suburban and rural areas of Germany and Belgium at three different sampling times. Information about sample types, sampling sites and sampling occasions are given in Table 1. In July 2001, one sample of rain water and two samples of roof runoff were taken from three different rural areas in the east of Germany. The rain water sample was collected in a 10-l PVC bin close to the village Küstrin (R6r) (2000 inhabitants). The two samples of roof run off were collected in 5-l glass vessels from roof downspouts in the small towns Müncheberg (6000 inhabitants) (R7r) and Straußberg (25,000 inhabitants) (R8r). In November 2001, five samples of rain water were sampled in several glass vessels. Two samples of urban rain were collected from the city Frankfurt/Main (650,000 inhabitants) (R1u and R2u) and three samples of rain from the villages Eisingen (R3su) and Dammbach (R4su, R5su). Both villages are located in the west of Germany 5 km distant from the city Würzburg (130,000) inhabitants and 40 km distant from the city Aschaffenburg (70,000 inhabitants), respectively. The volume of each rain water and roof run-off sample was 5 l. All rain water samples were filled in precleaned amber glass bottles and kept at 4°C <2 days until analysis.

In January 2002, freshly fallen snow was collected from areas in Germany and Belgium (Table 1). Four urban snow samples were taken from Sossenheim (S1u), Lohrberg (S2u), and Schwanheim (S3u, S4u). All three areas are located <10 km distant from the city Frankfurt/Main. The latter is located 5 km distant from the Rhein/Main Airport. Additionally, two snow samples were collected from a rural site in Belgium close to the small village Sourbrodt (S5r and S6r). Two more snow samples were taken from the suburban areas Dammbach (S8su) and Feldberg (S7su). The latter is located 20 km distant from the city Frankfurt/Main. The snow samples were collected from snow packs after a fresh snowfall in precleaned aquaria. After melting, all samples were transferred into precleaned amber glass bottles and kept at 4°C for less than 2 days until analysis. The final analysis-volume of each melted snow samples was 5 l.

2.2. Analytical procedures

Since 4-NP is a complex technical mixture of different isomers with a varying isomer composition a sophisticated method was developed to determine different 4-NP isomers in environmental samples. The applied method is composed of solid-phase extraction (SPE)

Table 1
Grid values of the monitoring stations (Nov = November; Jan = January)

Sample ID	Sample type	Sampling site	Sampling occasion	Easting	Northing
R1u	Rain	Frankfurt/Main	Nov 01	3475150	5553460
R2u	Rain	Frankfurt/Main	Nov 01	3475310	5553650
R3su	Rain	Eisingen	Nov 01	3559790	5414040
R4su	Rain	Dammbach	Nov 01	3522100	5525050
R5su	Rain	Dammbach	Nov 01	3522130	5525080
R6r	Rain	Küstrin	July 01	5446125	5854510
R7r	Roof runoff	Müncheberg	July 01	5441150	5820050
R8r	Roof runoff	Straußberg	July 01	5425490	5828490
S1u	Snow	Lohrberg	Jan 02	3480570	5557050
S2u	Snow	Sossenheim	Jan 02	3469130	5554120
S3u	Snow	Schwanheim	Jan 02	3469720	5549300
S4u	Snow	Schwanheim	Jan 02	3469800	5549350
S5r	Snow	Sourbrodt	Jan 02	2508570	5593500
S6r	Snow	Sourbrodt	Jan 02	2508530	5593490
S7su	Snow	Feldberg	Jan 02	3461490	5566400
S8su	Snow	Dammbach	Jan 02	3522180	5525080