



Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff

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ABSTRACT

To investigate seasonal fluctuations and trends of organophosphate (flame retardants, plasticizers) concentrations in rain and snow, precipitation samples were collected in 2007–2009 period at a densely populated urban sampling site and two sparsely populated rural sampling sites in middle Germany. In addition, storm water runoff was sampled from May 2008 to April 2009 at an urban storm water holding tank (SWHT). Samples were analyzed for tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) by gas chromatography–mass spectrometry after solid phase extraction. Among the six analyzed organophosphates (OPs), TCP dominated in all precipitation and SWHT water samples with maximum concentrations exceeding 1000 ng L⁻¹. For all analytes, no seasonal trends were observed at the urban precipitation sampling site, although atmospheric photooxidation was expected to reduce particularly concentrations of non-chlorinated OPs during transport from urban to remote areas in summer months with higher global irradiation. In the SWHT a seasonal trend with decreasing concentrations in summer/autumn is evident for the non-chlorinated OPs due to in-lake degradation but not for the chlorinated OPs. Furthermore, an accumulation of OPs deposited in SWHTs was observed with concentrations often exceeding those observed in wet precipitation. Median concentrations of TCP (880 ng L⁻¹), TDCP (13 ng L⁻¹) and TBEP (77 ng L⁻¹) at the SWHT were more than twice as high as median concentrations measured at the urban precipitation sampling site (403 ng L⁻¹, 5 ng L⁻¹, and 21 ng L⁻¹ respectively).

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1. Introduction

The environmental occurrence of organophosphates (OPs), employed as flame retardants, plasticizers, antifoaming agents, and additives in many products and materials, is exclusively man-made as these compounds do not occur naturally. They are triesters of phosphoric acid and comprise non-halogenated or halogenated alkyl groups as well as aryl groups (Verbruggen et al., 2005). The chlorinated compounds tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCP), tris(1,3-dichloro-2-propyl) phosphate (TDCP) are preferentially applied as flame retardants whereas the non-chlorinated esters tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) are used as plasticizers, antifoaming agents and additives in many applications (Bester, 2006). All these OPs are listed as European Union (EU) High Production Volume Chemicals (HPVCs) with production/import volumes exceeding 1000 t per year and are considered as emerging contaminants in

the environment (Reemtsma et al., 2008). Due to their physico-chemical properties, the chlorinated flame retardants TCEP, TCP, and TDCP and the non-chlorinated plasticizers TBEP, TiBP and TnBP can be classified as semi-volatile organic compounds (Wensing et al., 2005) with water being a preferred environmental compartment of distribution (Verbruggen et al., 2005). Several studies have pointed to a wide range of adverse biological effects for some OPs (Bester, 2006); therefore TCEP, TCP, and TDCP are subject of the EU risk assessment process (European Commission, 2006, 2007a,b). Furthermore, the resistance of chlorinated flame retardants to biodegradation and conventional potable water and wastewater treatments is well documented (Meyer and Bester, 2004; Stackelberg et al., 2007).

Transport of OPs via the atmosphere after emission from urban settlements and road traffic has been discussed previously (Marklund et al., 2005; Bacaloni et al., 2008; Regnery and Püttmann, 2009). When used as plastic additives, migration to the surface and release into the environment by volatilization, abrasion and dissolution can occur, as these ingredients are not chemically bound to the polymer matrix. According to the field of application, flame retardants constitute about 5–14% (w/w) of the finished

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product, e.g., polyurethane insulation or assembly foams (Leisewitz et al., 2001). For instance, approximately 40% of TCPP, used in a finished product is available for release (European Commission, 2007a). As a result of increasing vapor pressure, higher proportions of released OPs in indoor and outdoor environments are expected when ambient temperature is rising (Marklund et al., 2003; Hartmann et al., 2004; Staaf and Östman, 2005; Wensing et al., 2005).

The atmospheric wash-out of OPs by precipitation or dry deposition and local contamination sources such as treated and untreated wastewater discharges, are presumed to be the main entry-pathways for OPs into the aquatic environment (Bacaloni et al., 2008; Regnery and Püttmann, 2009). However, so far the available amount of data is too low for an estimation of the proportion by which the possible sources of OPs contribute to the currently observed surface water pollution. Moreover, data on the seasonal fluctuations and trends of OP concentrations in precipitation are required for the assessment of the influence of photodegradation on the OP concentrations in precipitation.

To investigate seasonal fluctuations and trends of OP concentrations in rain and snow, precipitation samples were collected in the period 2007–2009 at a densely populated urban sampling site and two sparsely populated rural sampling sites in middle Germany. In addition, storm water runoff was sampled bi-weekly from May 2008 to April 2009 at a storm water holding tank (SWHT) next to the urban precipitation sampling site.

2. Materials and methods

2.1. Chemicals

TCEP, TiBP, TnBP, TBEP and squalane (internal standard) were purchased from Sigma Aldrich (Steinheim, Germany). TCPP (a mixture of three isomers) and TDCP were supplied by Akzo Nobel (Amersfoort, The Netherlands). Acetonitrile (ultrapure HPLC grade) was obtained from J.T. Baker (Deventer, the Netherlands). All other organic solvents were purchased from Merck (Darmstadt, Germany) at analytical grade and were distilled before use. Ultrapure water was generated with an Astacus ultrapure water purification system from MembraPure (Bodenheim, Germany).

Individual stock solutions of each compound were prepared in methanol/acetonitrile (1/1 v/v) at $1 \mu\text{g } \mu\text{L}^{-1}$ concentration. Hexane was used to prepare the stock solution ($1 \mu\text{g } \mu\text{L}^{-1}$) of the internal standard squalane. Working standard solutions were obtained by appropriate dilution of stock solutions.

2.2. Sampling locations

The three locations chosen for sampling of precipitation are located in middle Germany. Sampling sites and sampling procedures are described in detail in Regnery and Püttmann (2009). All-season precipitation sampling took place at the urban sampling site Frankfurt am Main (November 2007–April 2009; 90 samples), the small village Bekond nearby Mosel River (December 2007–March 2009; 48 samples) and the Taunus University Observatory on Mount Kleiner Feldberg (November 2007–January 2009; 29 samples). Precipitation was collected using a stainless steel sampler on top of the Geosciences Center of Frankfurt University (Riedberg campus) and large glass or stainless steel funnels at the two other sampling sites.

The SWHT Kalbach (N° 50 10570; E° 8 38060) next to the precipitation sampling site in the north of the urban center of Frankfurt am Main, is a technical installation for the collection of surface drainage of public streets, lanes and squares as well as private properties. The SWHT is not affected by local contamination

sources such as sewage inflow. It has a total surface area of about 35,000 m² and consists of two basins: a small settling pond in the inlet area and a greater pond with a throttle structure controlling the runoff into a small creek. The basins are connected to each other via overflow pipes. The water depth averages between 1.5 and 2.0 m. To avoid contact between surface water and groundwater, the basin bottom was sealed off using calcinations (<http://www.umweltamt.stadt-frankfurt.de>). Sampling of the SWHT Kalbach was carried out bi-weekly from May 2008 to April 2009. Water samples of 2 L volume were collected just below the water surface at each of the basins. Additional, few spot samples of surface water (2 L) were collected from a small SWHT (N° 49 51420; E° 6 47430) next to the precipitation sampling site Bekond. The basin is located in a public park and dewateres a small area zoned for economic activities.

Within this study a total of 167 rain and snow samples (1–2.5 L) and 52 surface water samples (2 L) have been collected and analyzed regarding their concentrations of TCEP, TCPP, TDCP, TBEP, TiBP and TnBP.

2.3. Analytical methods

The analytes were extracted and enriched from the water, rain, and melted snow samples by use of solid phase extraction (SPE). Prior to SPE all water samples were subjected to pressure filtration with a 142 mm diameter borosilicate glass fiber filter (filter pore size 1 μm ; type A/E, Pall, Dreieich, Germany) to avoid cartridge plugging during SPE. After filtration the samples (1–2.5 L) were extracted by a styrene–divinylbenzene polymeric SPE cartridge (Bond Elute PPL, 1 mL, Varian Darmstadt, Germany), eluted with 1 mL methanol/acetonitrile (1/1 v/v), and analyzed by GC–MS in full scan mode. Quantification was carried out using squalane as internal calibration standard. See reference Regnery and Püttmann (2009) for a detailed specification of the applied analytical method.

From November 2007 to July 2008 quantitative analyses were performed using a Fisons gas chromatograph GC 8000 coupled to a Fisons MD 800 mass spectrometer (Thermo Fisher, Dreieich, Germany) as described in Regnery and Püttmann (2009). Since August 2008 samples were analyzed by a Trace GC Ultra gas chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich, Germany). Method and instrument parameters remained constant. Acquired data were processed using Excalibur software (Thermo Fisher Scientific, version 2.0.7). The limit of detection (LOD) for each of the six substances was estimated on the basis of measured calibration curves in accordance with DIN 32645 (DINTest, University of Heidelberg, $\alpha = 1\%$). The LODs for TCEP (2 ng L^{-1}), TCPP (1 ng L^{-1}), TDCP (1 ng L^{-1}), TBEP (3 ng L^{-1}), TnBP (1 ng L^{-1}), and TiBP (2 ng L^{-1}) using the Fisons GC–MS system were somewhat higher than those obtained for the Thermo Scientific GC–MS system (LOD of 1 ng L^{-1} for each of the six substances). The limit of quantification (LOQ) was estimated as three times the LOD according to DIN 32645 and ranged between 3 ng L^{-1} (TCEP) and 4 ng L^{-1} (TBEP) for the Thermo Scientific GC–MS system and 2 ng L^{-1} (TDCP) and 8 ng L^{-1} (TBEP) for the Fisons GC–MS system.

All laboratory equipment used in this study consisted of glass, stainless steel, or Teflon and was regularly controlled to be OP-free. Glass bottles were rinsed with ultrapure water and methanol, respectively, and finally heated to 110 °C over night before using for sampling. The glass fiber filters were heated for more than 2 h at 400 °C. Blanks for analyses were ultrapure water and tap water treated in the same way as field samples, to test for sample contamination during transportation and preparation. To avoid losses of target compounds, all samples were stored in brown glass bottles at 5 °C until they were extracted within 7 d after sampling.

The mean blank values (ultrapure water, $n = 11$) for TDCP (14 ng L^{-1}), TBEP (6 ng L^{-1}) and TiBP (1 ng L^{-1}) were subtracted

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