Atmospheric deposition of chlorinated organophosphate flame retardants (OFR) onto soils

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A B S T R A C T

This study highlights the influence of dry and wet deposition on concentrations of chlorinated organophosphate flame retardants (OFR) in soil. Soil samples were collected in 2010/11 during a period of snow falling to snow melting, a period of rainfall and a dry period. Snow and rainwater samples were also collected from the soil sampling site. Tris(2-chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl)phosphate (TDCP) were analysed in soil samples using a combination of Twisselmann extraction and solid-phase microextraction (SPME), followed by gas chromatography-mass spectrometry (GC-MS). SPME/GC-MS was applied to analyse TCEP, TCPP and TDCP in aqueous samples.

Concentrations of TCEP were between 236 and 353 $ng\,L^{-1}$ in snow and 78 and 234 $ng\,L^{-1}$ in rain. TCPP concentrations were between 226 and 284 $ng\,L^{-1}$ in snow and 371 and 385 $ng\,L^{-1}$ in rain. In soil samples, concentrations ranged from 5.07 to 23.48 $ng\,g^{-1}$ dry weight (dwt) for TCEP and 5.66 to 19.82 $ng\,g^{-1}$ dwt for TCPP. Concentrations of TDCP in rainwater and snow samples were rather low (46 and 100 $ng\,L^{-1}$, respectively); concentrations of TDCP were below the limit of detection in soil samples.

Snow melting caused enhanced soil concentrations of TCEP and TCPP, but greater effect of snow melting was observed for TCEP than for TCPP soil concentrations. No significant correlation between precipitation amounts and soil concentrations was observed. The influence of wet deposition on soil contents of TCEP and TCPP may be covered by volatilisation or by the mobility of both compounds in soil and their transport to deeper soil zones with seepage water. Snow was found to be a more efficient scavenger and transporter of chlorinated OFR into soil than rainwater. During dry weather, the soil concentrations of both compounds seemed to be driven mainly by air concentrations, which are determined by source emission strengths and photochemical degradation in the atmosphere.

Values of calculated air concentrations were between 0.0034 $ng\,m^{-3}$ for TCEP and 0.99 $ng\,m^{-3}$ for TCPP. Total OFR specific loads were 3756 $ng\,m^{-2}\,day^{-1}$ within the first 24 h and 3028 $ng\,m^{-2}\,day^{-1}$ within the next 24 h. Fugacity calculations (0.011 to 0.103 for TCPP and 0.005 to 0.073 for TCEP) indicated net deposition from air to soil for both compounds.

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1. Introduction

Chlorinated organophosphate flame retardants (OFR) such as tris(2-chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl)phosphate (TCPP) and tris(1,3-dichloro-2-propyl)phosphate (TDCP) are used widely as alternative flame retardants to polybrominated diphenyl ethers (PBDEs) (European Commission, 2008a,b, 2009). Their migration to the surface of the products, followed by their release to ambient air, cause OFR to be emitted into the atmosphere from buildings and vehicles. Total continental emissions for TDCP and TCPP are estimated to be 15.33 $kg\,d^{-1}$ and 89.56 $kg\,d^{-1}$, respectively. Loss of TCEP to air from outdoor and indoor services results in a total release of 1.30 $kg\,d^{-1}$ (European Commission, 2008a,b; OECD, 2004).

Estimated half-lives based on an OH radical concentration of 5×10^5 molecules mL^{-1} in air for TCPP and TDCP are 8.6 h and 21.3 h, respectively (European Commission, 2009). In the risk

assessment for TCEP, photooxidation in air was assumed to represent a major degradation path for TCEP in the environment based on its estimated half-life of 17.5 h (European Commission, 2003). However, detection of TCEP (1950 ng g^{-1}) and TCPP (763 ng g^{-1}) in pine needles in the Sierra Nevada Mountains, United States, suggest the long-range air transportation of these compounds (Aston et al., 1996). Analysis of background air and deposition samples in Pallas, northern Finland, also confirmed that some organophosphate esters (tri(n-butyl)phosphate (TnBP), TCEP and TCPP) are subjected to long-range air transportation (Marklund et al., 2005).

Organic chemicals, which occur as gases or are sorbed to particles in the atmosphere, could be scavenged by ice crystals in clouds (Fries et al., 2007, 2008) or by falling snow and rain (Meyer and Wania, 2011; Lei and Wania, 2004; Stocker et al., 2007; Meyer et al., 2009a,b). Precipitation scavenging of particles was found to be typically more important than dry deposition, accounting for the vast majority of the wet deposition of hydrophobic organic chemicals (McLachlan and Sellstrom, 2009).

Due to relatively high soil organic carbon − water partitioning coefficients (log K_{oc}) of 3.11 for TCPP, 3.97 for TDCP and 5.67 for tris(2-butoxyethyl)phosphate (TBEP)) and low volatility (vapour pressure of 1.4×10^{-3} for TCPP, 5.6×10^{-6} for TDCP and 1.6×10^{-4} for TBEP at 25 °C), it was assumed that most TDCP, TBEP and TCPP emitted to the atmosphere adsorb to particulate matter, which may then be washed out by rainfall (European Commission, 2008a; OECD, 2004; WHO, 2000). OFR (TCEP, TCPP, TDCP, TnBP, TBEP) have already been detected in urban and rural rainwater and snow samples in Italy and Germany in concentrations between 2 and 448 ng L^{-1} (Regnery and Püttmann, 2009; Bacaloni et al., 2008; Fries and Püttmann, 2003). In previous field experiments it was assumed that precipitation played an important role as an entry pathway for OFR into the aquatic and terrestrial environment (Regnery and Püttmann, 2009). However, all of these field studies were limited to monitoring OFR in bulk snow, meltwater and rainwater samples taken in urban, rural or remote areas.

Theoretical modelling has demonstrated the important role played by snow cover in the concentrations of organic chemicals in the terrestrial environment (soils and vegetation) (Daly and Wania, 2004; Lei and Wania, 2004; Stocker et al., 2007). Organic chemicals scavenged by falling snow could be released in air, water or soil during a short melt period, resulting in temporarily elevated concentrations (Daly and Wania, 2004). Thus, snow acts as a transfer medium, taking up chemicals from the air and releasing them to water or soil during the snowmelt period. In laboratory studies by Meyer et al. (2009a,b), it was concluded that water-soluble organic substances (atrazine and lindane) were released in high concentrations at the early stage of melting, whilst hydrophobic substances (phenanthrene, pyrene and benzo(ghi)perylene)

attached to particles accumulated near the snow surface and were released at the end of the melting process.

According to the absence of any point source of OFR, e.g. irrigation with river water or the spreading of sewage sludge, the detection of TCEP, TCPP and TBEP in soil samples indicated atmospheric deposition as a diffuse input source of OFR for the first time (Fries and Mihajlović, 2011; Mihajlović et al., 2011).

In the present study, the impact of atmospheric deposition on soil concentrations of OFR was studied in detail. Field experiments were designed such that a distinction can be made between the role of wet and dry deposition. Soil samples were collected in 2010/11 during a period of snow falling to snow melting, a period of rainfall and a dry period. In addition, rainwater samples were collected between soil sampling events to analyse the presence of OFR in precipitation and to calculate the specific loads deposited by rainwater. Snow samples were also collected at the soil sampling site. Finally, the potential for the accumulation of OFR in soil based on the air-soil exchange was estimated.

2. Materials and methods

2.1. Soil sampling and analysis

As a sampling site, 1 m^2 was selected close to the university campus of Osnabrueck (52°16′56.85″N, 8°1′12.51″E) located about 3 km from the city centre (Germany, about 160,000 inhabitants). The sampling site was located in the Westerberg district, a semi-urban area of the City of Osnabrueck with a population density of 1873 people/km^2. The surrounding university buildings are around 120 metres from the sampling site. The buildings are constructed in reinforced concrete sections, the external walls and facades are made of non-combustible materials with a large proportion of glass.

Sampling was performed at twelve different sampling times in different meteorological situations so as to investigate the influence of different deposition processes. Table 1 shows the sampling design, sampling date and time, number of sampling events, precipitation quantity between two sampling events (for the first sampling event, the precipitation on that day), minimum (min) and maximum (max) daily air temperature (measured 2 m above the surface) on the sampling day. Data for daily air temperatures were taken from the German Weather Service for monitoring station 10315 (Muenster-Osnabrueck), whilst precipitation quantity data were obtained by collecting rainwater samples in a Hellmann rainwater gauge. During sampling to study the influence of rain, the amount of rainfall was measured at the same time as collecting the soil samples (see Section 2.2).

After three days without any wet deposition, soil samples were collected on 29/11/10 (sampling event #1). Prior to sampling, it

Table 1
Sampling design, precipitation between two sampling dates (L m^{-2}), min and max daily air temperature (°C).

Sampling design	Sampling time (date/h)	Sampling event number	Precipitation between two sampling dates (L m^{-2})	Min/max daily air temperature 2 m above surface (°C)
Snow started	29/11/2010/17:30 h	#1	0.8	−3.1/0.0
24 h after snow started	30/11/2010/17:30 h	#2	0.0	−5.0/−0.3
7 days after snow started	06/12/2010/17:30 h	#3	10.6	−6.0/2.4
Snow melted	12/12/2010/9:30 h	#4	17.2	−4.2/5.4
24 h after snow melted	13/12/2010/9:30 h	#5	0.0	−7.0/−1.1
Rain started	17/01/2011/16:15 h	#6	0.0	2.9/10.1
1 h after rain started	17/01/2011/17:15 h	#7	0.2	2.9/10.1
24 h after rain started	18/01/2011/16:15 h	#8	6.2	3.5/9.2
48 h after rain started	19/01/2011/16:15 h	#9	5.0	0.6/5.4
Dry deposition 1st day	07/02/2011/12:00 h	#10	0.0	7.1/12.6
Dry deposition 2nd day	08/02/2011/12:00 h	#11	0.0	−2.1/8.2
Dry deposition 3rd day	09/02/2011/12:00 h	#12	0.0	−3.7/7.5