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Dry and wet deposition processes as a source of organophosphate flame retardants (OFR) in soils

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Ivana Mihajlović

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Author’s address: Ivana Mihajlović, Faculty of Technical Sciences,
Department of Environmental Engineering and Occupational Safety and Health, Novi Sad,
Serbia.

Supervised by:
Prof. Dr. Elke Fries (University of Osnabrück)
Prof. emeritus Dr. Mirjana Vojinović Miloradov (University of Novi Sad)

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ABSTRACT

Flame retardants are substances, which addition in various materials (furniture, plastics, electronics equipment, textiles, etc) could save a lot of lives and injuries caused by fires. On the other side, the migration of flame retardants from products during their whole life cycle results in their ubiquitous presence in the environment and reflects negative effects on ecosystems and human health. Global consumption of organophosphate flame retardants (OFR) as alternative substitutes of polybrominated diphenyl ethers has increased sharply in recent years. Studies on the presence and sources of OFR in surface water, ground water, sediments, snow, rainwater, indoor and outdoor air and analyses of OFR in these compartments have also increased in the last decade.

In this doctoral thesis an analytical method was developed to determine six OFR (tris(2-chloroethyl) phosphate (TCEP), tris(2-chlorisopropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri(n-butyl) phosphate (TnBP) and triphenyl phosphate (TPP)) in soil. The method consists of a combination of Twisselmann extraction and solid-phase microextraction (SPME), followed by gas chromatography-mass spectrometry (GC-MS). To develop the method, spiked soils were extracted using a Twisselmann extractor after freeze-drying. The extracts were evaporated to dryness, redissolved, and filtered. A volume of 7 mL was then analysed by SPME, followed by GC-MS. The effects of different parameters on analyte recoveries during sample preparation e.g. solvent for Twisselmann extraction, solvent for redissolving the extract, addition of copper, and filtration of the extract were systematically investigated. Under optimum conditions, 10 g of soil were extracted using toluene, and the extract was redissolved in methanol/water (1:14) and filtered. It was not necessary to add copper. For TnBP, TBEP, TCPP, and TCEP, recoveries ranged from 77.0 % to 89.6 %. Those for TPP and TDCP were much lower, at 31.5 % and 42.0 %, respectively (addition level 22.9-45.8 ng/g). The variability of recoveries under these conditions was between 0.3 and 16.2 % (n = 3). Limits of detection (LOD) were 0.002-3 ng/g.

When ultrasonication was used instead of Twisselmann extraction in the developed method, recoveries were three to four times lower (27.4 % to 30.6 %), but the variability of recoveries was below 3 % (n = 3).

The method was applied to quantify OFR in soils collected from different sampling locations (urban, semi-urban and rural) in Germany. The results indicated for the first time that atmospheric deposition leads to soil contamination by OFR. Since it has been shown in animal experiments (F344/N rats and B6C3F1 mice) that chlorinated OFR were carcinogen and also have negative effects on human health (Matthews et al., 1991, 1993, Johnson, 1999), the further studies were focused on sources of chlorinated OFR. Therefore, the influence of dry and wet deposition processes as a source of chlorinated OFR in soils was systematically investigated. 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. Concentrations of TCEP were between 236 and 353 ng/L in snow and 78 and 234 ng/L in rain. TCPP concentrations were between 226 and 284 ng/L in snow and 371 and 385 ng/L in rain. In soil samples, concentrations ranged from 5.07 to 23.48 ng/g dry weight (dwt) for TCEP and 5.66 to 19.82 ng/g dwt for TCPP. Concentrations of TDCP in rainwater and snow samples were rather low (46 and 100 ng/L, respectively); concentrations of TDCP were below the limit of detection in soil samples.

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

Rainwater concentrations of OFR were used to assess air concentrations from the scavenging ratios at equilibrium conditions and the potential for the accumulation of OFR in soil based on the air-soil exchange was estimated. Calculated values of median air concentrations were 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 hours 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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ABBREVIATIONS AND ACRONYMS

ATSDR	Agency for Toxic Substances and Disease Registry
BDE	Brominated Diphenyl Ethers
BCF	Bioconcentration factor
bwt	Body weight
CAS	Chemical Abstracts Service
DBU	German Environmental Foundation
DIN	German Institute of Standardizations
dwt	Dry weight
EC	European Commission
EFRA	European Flame Retardants Association
EI	Electron Ionisation
ESR	Environmental Science and Research
EU	European Union
GLP	Good Laboratory Practice
GC	Gas Chromatography
HPLC	High-Performance Liquid Chromatography
HPV	High Production Volume Chemicals
H	Henry's law constant
K_{ow}	Octanol-water partitioning coefficient
K_{oc}	Organic carbon-water partitioning coefficient
LD50	Median Lethal Dose
LOD	Limit of Detection
LOQ	Limit of Quantitation
IS	Internal Standard
IPCS	International Programme on Chemical Safety
IUCLID	International Uniform Chemical Information Database
MAE	Microwave-Assisted Extraction
MPC	Maximum Permissible Concentration
MS	Mass Spectrometry
ND	Not Determined
NORMAN	Network of Reference Laboratories for Monitoring of Emerging Environmental Pollutants
OFR	Organophosphate Flame Retardants
OPE	Organophosphate esters
OVAT	One Variable At a Time
P/vP	Persistent/very Persistent
PBDE	Polybrominated Diphenyl Ethers
PDMS/DVB	Polydimethylsiloxane/Divinylbenzene
PEC	Predicted Environmental Concentration
PLE	Pressurized Liquid Extraction
PNEC	Predicted Non Effect Concentration
PUR	Polyurethane
QA	Quality Assurance
RSD	Relative Standard Deviation
SIM	Selected Ion Monitoring
S/N	Signal-to-Noise ratio
SPE	Solid Phase Extraction
SPME	Solid Phase Microextraction

SRI	Science Recruitment Ireland
T	Toxic
TBEP	Tris(2-butoxyethyl) phosphate
TCEP	Tris(2-chloroethyl) phosphate
TCP	Tricresyl phosphate
TCPP	Tris(2-chlorisopropyl) phosphate
TDCP	Tris(1,3-dichloro-2-propyl) phosphate
TiPP	Triisopropyl phosphate
TnBP	Tri(n-butyl) phosphate
TnBP-d27	Deuterated tri(n-butyl) phosphate
TOC	Total Organic Carbon
TPP	Triphenyl phosphate
UK	United Kingdom
U.S. EPA	United States Environmental Protection Agency
WHO	World Health Organization

1. INTRODUCTION

Flame retardants are widely used all over the world in order to meet flammability standards for various materials (furniture, plastics, electronics equipment, textiles, polyurethane foams, coatings etc). Since fire causes a lot of injuries and deaths e.g. recorded fires in 2001 caused 2905 deaths in the six largest EU countries (SRI Consulting, 2004), usage of flame retardants is obviously needed.

Restrictions on the use of polybrominated diphenyl ethers (PBDE) have resulted in the increased use of alternate flame retardant chemicals, such as organophosphate flame retardants (OFR) (European Commission, 2003). The global consumption of OFR was estimated to 186, 000 tons in 2001 (SRI Consulting, 2004). Hence, these compounds are listed as High Production Volume Chemicals (HPV) (IUCLID, 2000). Several chlorinated OFR are included in the EU risk assessments: tris(2-chloroethyl) phosphate (TCEP) in the 2nd ESR Priority List, tris(2-chlorisopropyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCP) in the 4th ESR Priority List (European Commission, 2008a, 2008b, 2009). It was shown that TCEP has carcinogenic and teratogenic effects on organisms (Latendresse et al., 1994). TCEP has demonstrated moderate toxicity after oral application, with oral LD50 for rats in the range of 430-1230 mg/kg bwt (European Commission, 2009). Studies in rats indicated that TCPP is of moderate toxicity via the oral route of exposure, with LD50 values from the better quality studies ranging from 632 mg/kg up to 4200 mg/kg, with the majority of values determined to be <2000 mg/kg (European Commission, 2008a). The substance manufacturers have classified TDCP as a category 3 carcinogen for humans (Steukers et al., 2004). Also, the degradation products of these OFR include the moderately toxic byproduct, 2-ethylhexanoic acid (Rodriguez et al., 2006). Clinical signs of maternal toxicity in rats with 2-ethylhexanoic acid, including increased liver weight, as well as increased resorptions, dead fetuses and growth retardation were observed at 500 mg/kg/day (Hendrickx et al., 1993).

Search for alternative flame retardants caused increased use of similar, probably less toxic compounds. On the other side behavior and fate of these chlorinated OFR in the different environmental media have not been completely investigated.

Individual data on the occurrence of OFR in water and air has increased continuously over the last decade. OFR have been already detected in river water, ground water and rain (Andresen et al., 2004, Fries & Püttmann, 2001, Fries & Püttmann, 2003), in snow (Regnery &

Püttmann, 2009), in outdoor air and dust (Quintana et al., 2007) and sediments (Lach and Steffen, 1997).

However, the occurrence, sources and fate of OFR in soil have not been studied yet. According to relatively high organic carbon-water partitioning coefficients (K_{oc}) of some OFR (U.S. EPA. 2003), OFR accumulation in sediments and soils can be assumed. The application of sewage sludge, usage of waste water for irrigation, the disposal of flame retardant plastics in landfills, the leakage of hydraulic fluids, dry and wet deposition processes could be the potential sources of OFR in the soil (Muir, 1984, Stachel et al., 2007, Passuello et al., 2010). Buildings and traffic, as secondary sources of OFR in the atmosphere could also increase concentrations in soils (Marklund et al, 2005b).

Although the ubiquitous distribution of OFR in the environment has been documented very thoroughly, data on the occurrence of OFR in sediment and soil, however, are rather limited. So far, only very few studies have dealt with determining OFR in sediment samples (Martínez-Carballo et al., 2007, Kawagoshi et al., 1999, García-Lopez et al., 2009). OFR from sediments and other solid matrixes, such as dust and sludge, have been extracted using medium polarity solvents (e.g., dichloromethane, ethyl acetate and acetone), Soxhlet extraction (Bester, 2005), pressurized liquid extraction (PLE) (Quintana et al., 2007, Marklund et al., 2005b), microwave-assisted extraction (MAE) (García et al., 2007) and ultrasonication (Marklund et al., 2003). Kawagoshi et al. (1999) extracted sediment samples by solvent shaking and cleaned extracts by liquid-liquid partitioning into dichloromethane. Unfortunately, recoveries were not reported for this procedure. Sediment samples were also extracted using PLE followed by solid phase extraction (SPE) (García-Lopez et al., 2009). Recoveries for this procedure ranged from 77 % to 111 %.

Only David and Seiber (1999) have analysed tricresyl phosphate (TCP) and TPP in soils at U.S. Air Force Base contaminated with hydraulic fluids. They used ethyl acetate as the solvent for Soxhlet extraction and cleaned the extracts by Florisil column. This is the only study so far on the analysis of OFR in soil. No analytical method for soil has ever been published, however, for chlorinated compounds, e.g., TCPP and TCEP. Additionally, all of the described methodologies for solid matrixes required a cleanup step to decrease the complexity of raw extracts from samples.

Solid-phase microextraction (SPME), introduced by Arthur and Pawliszyn (1990), is considered to be an attractive, valuable, time and cost-effective analytical technique for determining organic pollutants in water without having to filter the sample or clean extracts. This technique was applied to determine organophosphorus pesticides in soil (Bouaid et al., 2001). However, SPME has never been applied to analyse OFR in soil samples. Analytical method for analysis of OFR in soil has not been developed and influence of atmospheric processes on OFR soil concentrations has not been investigated yet.

Organic chemicals, which occur as gases or 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, 2009b). Precipitation scavenging of particles was found to be typically more important than dry deposition and it accounted for the vast majority of the wet deposition of hydrophobic organic chemicals (McLachlan and Sellstrom, 2009).

The important role of wet deposition processes to the concentrations of organic chemicals in the terrestrial environment (soils and vegetation) has been proved in theoretical modelling (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 air and releasing them to water or soil during snowmelt period. In laboratory studies of Meyer et al. (2009a, 2009b) it was concluded that water-soluble organic substances (atrazine and lindane) were released in high concentrations at the early stage of melting, while 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.

2. MOTIVATION AND AIMS

Production and usage of OFR, which served as alternative flame retardants, in the last decade has increased dramatically and caused new potential risk to ecosystems and human health. The terrestrial environment (soils and vegetation) could be an important source of organic chemicals in animals feed as well as main entry pathway of these chemicals in ground water. Thus, the both scenarios could cause elevated daily intake of these compounds for animals and humans. For these reasons it is very important to investigate possible input sources and pathways, behaviour and spatial distribution of toxic contaminants like OFR in soils. Since toxic and carcinogenic effects of chlorinated OFR were confirmed in previous studies, special attention should be focused on the fate of chlorinated OFR. Hence, there is a need to investigate their spatial distribution in soil samples and the possible input sources.

Since field data related to dry and wet deposition processes were not found for OFR in the literature, the main research question of this PhD thesis was to understand influence of these processes to concentrations of OFR in soil samples. Therefore, it was first necessary to develop analytical method to measure OFR in soil and wet precipitation with a special focus on how to obtain high recoveries for the analysis of OFR in soil samples. After developing optimal method with high recoveries of selected OFR and low variability of repeated measurements, the method was applied to analyse environmental samples in order to study input sources of OFR in soil samples. By applying this method to environmental samples the influence of atmospheric deposition processes was proposed and the objective was to study rain and snow as scavengers of OFR. In addition possible atmospheric input pathways of OFR in soil samples were investigated and discussed. The next aim was to answer the question how dry deposition processes change concentrations of OFR in soil samples. Purpose of study was also to calculate air concentrations from measured rainwater concentrations at the equilibrium conditions and to use values of assessed air concentrations in fugacity calculations. It was also planned to adopt an approach to air-soil exchange assessment to investigate the potential for accumulation of OFR in soils. Ultimately, seasonal variations of selected OFR in soil were presented, since precipitation quantity is significantly different during the year and could influence fluctuations in OFR soil concentrations.

3. TARGET COMPOUNDS

According to great worldwide production and usage as well as negative health effects the six OFR, tris(2-chloroethyl) phosphate (TCEP), tris(2-chlorisopropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri(n-butyl) phosphate (TnBP) and triphenyl phosphate (TPP) were selected as target compounds in this research. Their CAS registry numbers and acronyms are presented in Table 1, while their structural formulas are shown in Figure 1. According to Network of reference laboratories for monitoring of emerging environmental pollutants (NORMAN), TCPP, TDCP, TCEP, TnBP, and TPP are classified as emerging substances.

Table 1. CAS registry numbers, acronyms and formulas of OFR.

Compound	Acronym	CAS	Formula
tris(2-chloroethyl) phosphate	TCEP	115-96-8	$C_6H_{12}Cl_3O_4P$
tris(2-chloroisopropyl) phosphate	TCPP	13674-84-5	$C_6H_{18}Cl_3O_4P$
tris(1,3-dichloro-2-propyl) phosphate	TDCP	13674-87-8	$C_9H_{15}Cl_6O_4P$
tris(2-butoxyethyl) phosphate	TBEP	78-51-3	$C_{18}H_{39}O_7P$
tri(n-butyl) phosphate	TnBP	126-73-8	$C_{12}H_{27}O_4P$
triphenyl phosphate	TPP	115-86-6	$C_{18}H_{15}O_4P$

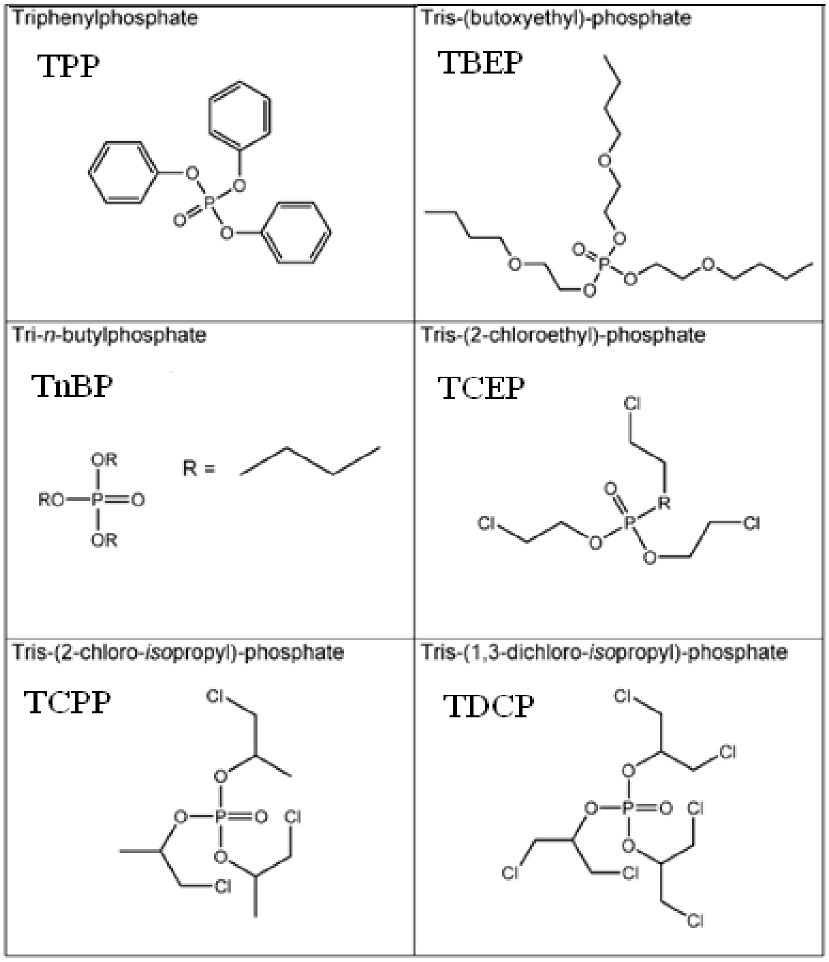


Figure 1. Structural formulas of OFR.

3.1 Production and usage

The production process of OFR is based on reaction of phosphorus oxychloride with an organic epoxide in the presence of a catalyst. The product is then washed and dehydrated to remove impurities, filtered and transferred to storage tanks (European Commission, 2008a, 2008b, 2009).

Ban of brominated diphenyl ethers (BDE) - penta-BDE and octa-BDE in the EU and the entry into force of the Restriction of Certain Hazardous Substances caused higher consumption of alternative flame retardants (European Commission, 2003). Global consumption of OFR was estimated to 186,000 tons pro year in 2001. In the European Union (EU), their consumption raised from 58,000 tons in 1995 to 91,000 tons in 2006 (EFRA, 2007). The annual consumption of OFR in EU (alkyl phosphates as plasticizers not included) increased for 8%

for only two years (from 84,000 tons in 2004 to 91,000 tons in 2006, of which 56% were chlorinated phosphates) and even greater consumption of these alternative flame retardants could be expected in the last years because of increasing global demand of fire protected materials and products.

The global production volume of TCEP was about 9,000 tons in 1989 and declined to below 4,000 tons by 1997 (IPCS, 1998). Production in EU in 1998 was about 2,000 tons and from 2001 there is no production in EU (European Commission, 2009) since its usage has been replaced with usage of TCPP. The total import in EU was estimated to 1,150 tons pro year.

Total EU production of TCPP from four producers (Supresta, Lanxess, BASF in Germany and Albemarle in UK) in 2000 was 36,000 tons. In the next years production has increased significantly, because of the greater consumption. Total EU production of TDCP in Germany and the UK (Supresta and Albemarle) in 2000 was less than 10,000 tons. There was no import of TDCP into the EU in 2000 (European Commission, 2008b). All six OFR are included in the list of EU High Production Volume Chemicals (HPV) with production/import volumes exceeding 1,000 tons pro year.

Table 2. Fields of application of target OFR.

Compound	Flame retardant (polyurethane foam)	Flame retardant (plasticizer)	Hydraulic fluid, lubricant, motor oil	Anti-foaming agent	Floor polish	Paints, lacquers, adhesives	Textile coating
TCEP	√	√				√	√
TCPP	√	√					√
TDCP	√						√
TBEP		√		√	√		
TnBP		√	√	√		√	
TPP	√		√				

Fields of application of selected OFR are presented in Table 2. OFR are widely used as flame retardants and plasticizers in rubbers, textiles, upholstered furniture, lacquers, plastics, building materials and electronic equipment (Andresen et al., 2004, Reemtsma et al., 2007). Some of these substances, TnBP and TPP, are used as additives in hydraulic fluids, lubricants, transmission and motor oils (WHO, 1991, ATSDR, 1997). TBEP is used in floor polishes, as antifoaming agent and as a plasticizer in rubber and plastics (WHO, 2000). TCEP is mainly used as a flame retardant in the production of polyurethane foam (around 80 %) e.g. as roof insulation for the building industry. The other applications are as plasticizer in furniture, the textile and the building industry as well as in acrylic resins, adhesives and coatings (≈ 20 %) (European Commission, 2009). Since insulation is an effective way of reducing CO_2 emissions, the use of foam insulation in buildings is increasing (Kyoto Protocol), and thus the use of TCEP is also increased.

Most TCPP is used in rigid PUR foam (over 80%) mainly for construction applications. The remaining PUR applications are accounted for flexible foam (over 17%), used in upholstery and bedding for the UK and Irish markets. TCPP tends not to be used in flexible PUR for automotive applications, owing to its volatility and fogging potential.

In year 2000, 26,650 tons of TCPP were used as rigid foam in the production of construction products. Waste from the production of rigid foam is used for adhesive pressing in the production of molded boards for use in kitchen furniture and flooring (European Commission, 2009). In last years, TCPP presented replacement for TCEP in all application fields where it was possible.

TDCP could be used in the same application fields as TCPP, but comparing the price (around twice the price of TCPP), TDCP is only used when a more efficient flame retardant is required to meet specific standards. Consumption of TDCP in the EU was about 10,000 tons in the year 2000. TDCP is mostly used in PUR foams in the automotive industry (about 80 %), with some use in furniture (about 20 %) (European Commission, 2008b).

3.2 OFR - way of acting

Solid materials, such as plastics, do not burn directly: they must be first decomposed by heat (pyrolysis) to release flammable gases (Figure 2). Visible flames appear when these flammable gases burn with the oxygen (O_2) in the air. If solid materials do not break down into gases, then they will only smolder slowly and often self extinguish, particularly if they "char" and form a stable carbonaceous barrier which prevents access of the flame to the underlying material. Materials such as wood burn vigorously, because once ignited the heat breaks down long-chain of molecules into smaller molecules which transpire as gases.

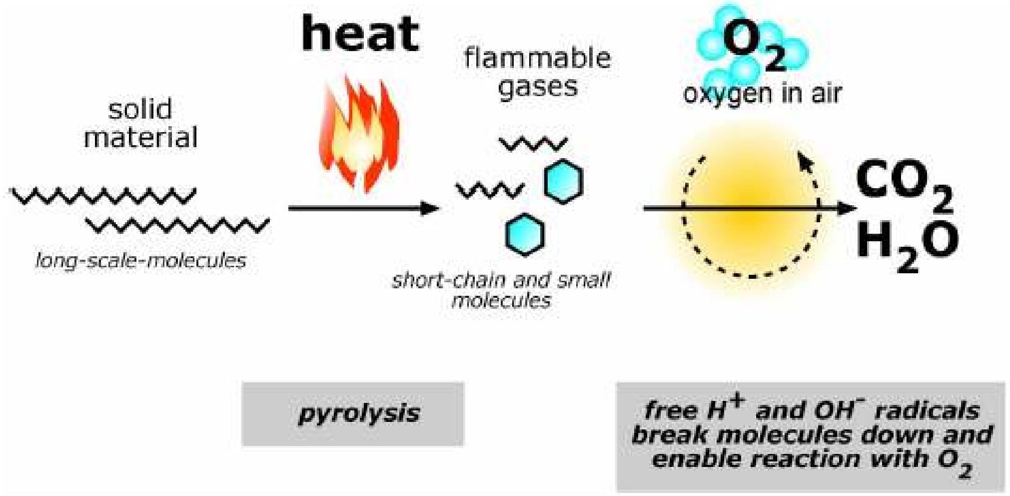


Figure 2. Solid materials-way of burning (source: EFRA, 2006).

The gas flame itself is maintained by the action of high energy "radicals" (H^+ and OH^- in the gas phase) which decompose molecules to give free carbon, which can react with oxygen in air to burn to CO in highly exothermic reaction.

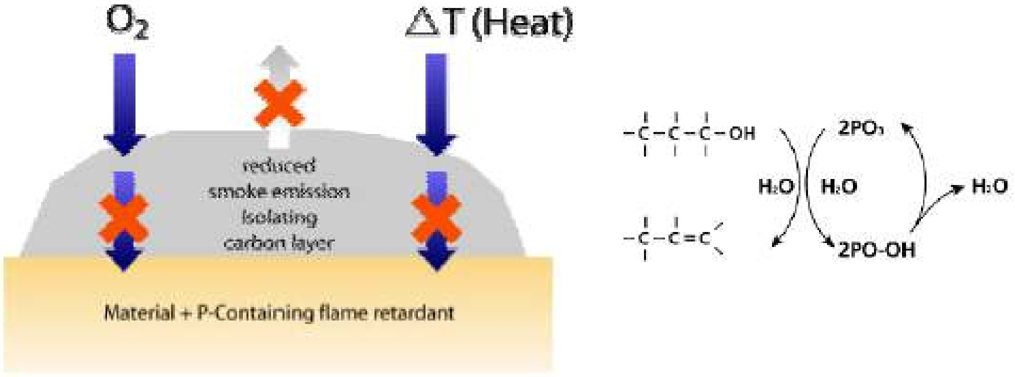


Figure 3. Way of acting of OFR (source: EFRA, 2006).

Phosphorus containing flame retardants take action efficiently in the solid phase of burning materials (Figure 3). When heated, the phosphorus reacts to give a polymeric form of phosphoric acid. Phosphoric acid causes the material to char, forming a glassy layer and inhibiting the "pyrolysis" process (break down and release of flammable gases) which is necessary to feed flames.

By this mode of action the amount of fuel produced is significantly diminished, because char rather than combustible gas is formed. The intumescent char plays particular roles in the flame retardant process. It acts as a two-way barrier, both hindering the passage of the combustible gases and molten polymer towards the flame, and shielding the polymer from the heat of the flame (EFRA, 2006).

3.3 Physico-chemical properties of OFR

OFR are non-flammable, non-explosive and odorless substances. OFR are generally liquids (except of TPP which is in a solid state) in their pure form at 25 °C. The selected OFR have moderate Henry's Law constants ($1.22 \cdot 10^{-6}$ - 0.323 Pa·m³/mol) and vapor pressures ($5.6 \cdot 10^{-6}$ - 0.150 Pa). They could exist in the vapor phase or sorbed to particulate matter (Muir, 1984).
Physico-chemical data of the OFR within this research (water solubility, vapour pressure, log K_{ow}, log K_{oc} and Henry's Law Constant) are presented in Table 3.

Table 3. Selected physico-chemical data of the OFR within this research (European Commission, 2008a, 2008b, 2009, U.S. EPA. 2003).

Compound	Water Solubility at 25 °C (g/L)	Vapour pressure at 25 °C (Pa)	Log K_{ow}	Log K_{oc}	H (Pa·m³/mol)
TCEP	7.409	$1.14 \cdot 10^{-3}$	1.44	2.48	$2.58 \cdot 10^{-3}$
TCPP	1.200	$1.4 \cdot 10^{-3}$	2.68	3.11	$6.04 \cdot 10^{-3}$
TDCP	0.029	$5.6 \cdot 10^{-6}$	3.69	3.96	$2.65 \cdot 10^{-4}$
TBEP	0.027	$1.6 \cdot 10^{-4}$	3.75	5.67	$1.22 \cdot 10^{-6}$
TnBP	0.027	0.150	3.82	3.28	0.323
TPP	0.003	$6.3 \cdot 10^{-5}$	4.59	3.72	$4.03 \cdot 10^{-3}$

TCEP is liquid at the temperature of 20 °C, with melting point at -70 ºC and decomposition at 320 ºC and 1013 Pa. Molecular mass and density of TCEP at 25 °C are 285.49 g/mol and 1.4193 g/cm^3, respectively. The water solubility at 20 °C varies from 5 g/L to 8 g/L in the safety data sheets of the production companies Bayer AG (1991), Hoechst AG (1994), Akzo Nobel (2000) and Courtaulds Chemicals (1996). The water solubility of 7820 mg/L at 20 °C was determined experimentally using the flask method and this value was used for the risk assessment. A value of $1.14 \cdot 10^{-3}$ Pa for vapor pressure at 20 °C was calculated using experimental determination of the vapor pressure at higher temperatures by dynamic method and Clausius-Clapeyron equation (European Commission, 2009). The water solubility at 25 °C of 7409 mg/L was estimated from logarithms of octanol-water partitioning coefficient (log K_{ow}) of 1.44. Soil-sediment water sorption coefficient (log K_{oc}) of 2.48 was estimated from molecular connectivity, while value of Henry's law constant (H) of $2.58 \cdot 10^{-3}$ (Pa·m³/mol) at 25 ºC was obtained from bond method estimation (U.S. EPA, 2003, Verbruggen et al., 2005). Bond contribution values, used to estimate Henry's law constant from chemical structure, have been determined by a least-square analysis of known Henry's law constant values for organic compounds.

TCPP is colorless transparent oily liquid with molecular mass of 327.57 g/mol. Structural formula of TCPP has three asymmetric carbon atoms - chiral centres. The CAS number 13674-84-5 is used for this structure and also for the mixture of isomers as commercially produced. The 1-chloro-2-propyl- can be replaced up to three times by 2-chloro-1-propyl. Therefore three isomers of the main component are possible: bis(1-chloro-2-propyl)-2-chloropropyl phosphate, bis(2-chloropropyl)-1-chloro-2-propyl phosphate and tris(2-chloropropyl) phosphate. Water solubility of TCPP at 25 °C was estimated to be 1200 mg/L (U.S. EPA, 2003, Verbruggen et al., 2005). The preferred value of vapour pressure of $1.4 \cdot 10^{-3}$ Pa at 25 ºC was obtained by the vapour pressure balance method in a modern Good Laboratory Practice (GLP) study (Tremain, 2002) in accordance with Directive 92/69/EC (European Commission, 2008a). Log K_{ow} of 2.68 ± 0.36 was obtained by the HPLC estimation method in a modern GLP study (Cuthbert and Mullee, 2002). Log K_{oc} of 2.48 was estimated from molecular connectivity, while value of Henry's Law Constant ($6.04 \cdot 10^{-3}$ Pa·m³/mol) was obtained from bond method estimation (U.S. EPA, 2003, Verbruggen et al., 2005).

TDCP is a viscous yellow liquid with molecular mass of 430.91 g/mol, relative density of 1.513 and low water solubility of 29 mg/L at 25 ºC (IPCS, 1998, European Commission, 2008b). The preferred value of vapour pressure at 25 °C is $5.6 \cdot 10^{-6}$ Pa, obtained by the vapour pressure balance method in a modern GLP study in accordance with Directive 92/69/EC (Tremain, 2002). The partition coefficient between octanol and water is 3.69 according to the HPLC estimation method (Cuthbert and Mullee, 2002), while log K_{oc} was estimated to be 3.96 according to molecular connectivity method.

TBEP is a light-coloured, high-boiling, non-flammable viscous liquid with a butyl-like odour under normal conditions. It is more soluble in non-polar than in polar solvents with the water solubility of 27 mg/L at 25 ºC. From molecular connectivity method, the highest value of soil-sediment water sorption coefficient (log K_{oc} = 5.67) was estimated for TBEP compared to other studied OFR (U.S. EPA, 2003).

TnBP is a non-flammable, nonexplosive, colourless and odourless liquid. However, it is thermally unstable and begins to decompose at temperatures below its boiling point. TnBP has the highest vapour pressure (0.150 Pa) and Henry's Law Constant value (0.323 $Pa{\cdot}m^3/mol$) compared to the other five studied OFR. TnBP has low water solubility (27 mg/L at 25 ºC). Log K_{ow} and log K_{oc} for TnBP are estimated to be 3.82 and 3.28, respectively (U.S. EPA, 2003, Verbruggen et al., 2005).

TPP is colourless solid with very low water solubility (3 mg/L at 25 ºC) and high log K_{ow} value (4.59). Henry's Law Constant from bond method estimation is calculated to $4.03 \cdot 10^{-3}$ $Pa{\cdot}m^3/mol$.

3.4 Occurrence of OFR in the environment

Individual data on the occurrence of OFR in water and air has increased continuously over the last decade. OFR were detected in river water, lake water, groundwater and rain (Fries and Püttmann, 2003, Regnery and Püttmann, 2009, Martínez-Carballo et al., 2007, Bacaloni et al., 2008, Andresen and Bester, 2006), sediments (Kawagoshi et al., 1999, Lach and Steffen, 1997, Martínez-Carballo et al., 2007), snow (Marklund et al., 2005b, Regnery and Püttmann, 2009), indoor and outdoor air and dust (Saito et al., 2007, Staaf and Ostman, 2005, Ericsson and Colmsjo, 2003, Tollbäck et al, 2009, Green et al., 2008, Ingerowski et al., 2001, Garcia et al., 2007). OFR have also been found in influents and effluents of municipal wastewater treatment plants (Marklund et al., 2005c, Meyer and Bester, 2004), where they are transported via the sewage system from households, industrial sites, and storm water drainage. Concentrations of six studied OFR in different environmental media were presented in Annex (Tables A-F).

Since OFR are physically combined with the polymer matrix they can migrate to the surface of products and be released into the indoor air from furniture, electronic equipment, carpets, and also into the atmosphere from different sources such as buildings and vehicles. Therefore, OFR have been the mostly studied in indoor air (library, private home, office, prison, day care center, computer hall, new car, etc.). TCEP concentrations in indoor air were in range from <0.3 ng/m^3 to 2,037 ng/m^3 in lecture hall in Sweden (Tollbäck et al, 2009, Staaf and Ostman, 2005). High TCEP concentrations were measured in office (730 ng/m^3), laboratory (367 ng/m^3) and day care center (144 ng/m^3) in Sweden (Tollbäck et al, 2009, Carlsson et al., 1997, Marklund et al., 2005a). TDCP, TPP, TnBP and TBEP were measured in low concentration ranges in indoor air in Sweden, 2 -7 ng/m^3, <0.3 – 35.3 ng/m^3, <0.3 – 138 ng/m^3 and <0.2 – 130 ng/m^3, respectively. TCPP was detected in very high concentrations in computer hall (1,080 ng/m^3), laboratory (2,836 ng/m^3) and lecture hall (1,118 ng/m^3) in studies conducted in Sweden. Saito et al. (2007) measured OFR in house and office buildings in Tokio, Japan in very low median concentrations from 0.97 to 6.6 ng/m^3.

Detection of TCEP (1950 ng/g), TCPP (763 ng/g) and TDCP (1320 ng/g) in pine needles in the Sierra Nevada Mountains, United States, suggested 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 (TnBP, TCEP, TCPP, TDCP and TPP) are subjected to long range air transportation (Marklund et al., 2005b). In Svalbard, archipelago in the Arctic, TCEP, TCPP, TDCP and TBEP were measured above the limit of detection (LOD) (Green et al., 2008). In the German part of the North Sea, TCPP dominated in all air samples with individual concentrations up to 1,200 pg/m^3 (Möller et al., 2011). TCPP, TnBP and TBEP were also detected in outdoor air in Tokyo at sampling sites located at verandas or below the eaves of houses and offices with maximum concentrations of 3.1, 1.7 and 1.1 ng/m^3, respectively, whereas TCEP was below the LOD of 0.67 ng/m^3 (Saito et al., 2007).

Due to relatively high values of log K_{oc} and low volatility, it was assumed that most of 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, TPP) have already been detected in urban and rural rainwater and snow samples in Italy and Germany in concentrations between 2 and 743 ng/L (Regnery and Püttmann, 2009; Bacaloni et al., 2008; Fries and Püttmann, 2003). TCPP was determined as the most abundant OFR in rainwater samples collected in Germany and Italy, with the maximum concentrations of 743 and 739 ng/L, respectively. TDCP also occurred in high concentrations (108 – 448 ng/L) in urban and rural rainwater samples in Italy, although in all snow and rainwater samples in Germany TDCP was detected in low concentration ranges from 2 to 24 and 5 to 40 ng/L, respectively.

Marklund et al. (2005b) studied the influence of traffic as a source of OFR in snow samples. They noticed a clear decrease in concentrations, especially for TCPP with increased distance from the road intersection. TnBP and TPP dominated at the airport, where levels of 2.1 to 25 µg/kg and 120-830 ng/kg were found in the snow samples. The main source of TnBP at the airport was traced to aircraft hydraulic fluid, while TPP was identified in lubricants and in waste oil from vehicles, and thus, leakage of transmission and motor oils is a probable source of TPP found at the sampled sites. In previous field experiments it was assumed that precipitation had 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 monitor OFR in bulk snow, meltwater and rainwater samples taken in urban, rural or remote areas.

TBEP, TCPP and TnBP were found in effluents from seven Swedish sewage treatment plants as the most abundant compounds with concentrations ranged between 3,100 and 35,000 ng/L, 1,100 and 30,000 ng/L and 360 and 52,000 ng/L, respectively (Marklund et al., 2005c). Meyer and Bester (2004) studied OFR in two wastewater treatment plants in Germany, where TBEP, TCPP and TnBP were also detected, with maximum levels of 4,000, 2,600 and 1,100 ng/L, respectively. The lower concentrations of TnBP and TBEP in the effluent compared with the influent sample demonstrate a partial biological removal of these organophosphate esters during the cleaning process, while concentrations of chlorinated organophosphate esters were almost in the same range in effluents and influents of wastewater treatment plants (Fries and Püttmann, 2003, Marklund et al., 2005c, Meyer and Bester, 2004).

TBEP and TnBP were also found in the highest concentrations in river samples in Germany with maximum values of 952 and 1,044 ng/L, respectively, showing that the discharge of treated wastewater into rivers is a significant source of river pollution (Fries and Püttmann, 2003). TBEP was also the most prominent compound in Danube, Liesig and Schwechat rivers in Austria with a maximum concentration of 500 ng/L, while the highest concentrations of

TCPP up to 1,300 µg/kg dwt (dry weight) were found in sediments of these rivers. In the two volcanic lakes located in Central Italy, TnBP was the most abundant OFR, with peak of 784 ng/L (Bacaloni et al., 2008). High concentration levels up to 7,395 µg/kg for chlorinated OFR (TCEP, TCPP, TDCP) were found by Kawagoshi et al. (1999) in bottom sediment at a sea-based solid waste disposal site. Lach and Steffen (1997) measured TCEP and TCPP in sediments of the river Ems in Germany in ranges from 7.7 to 160 and 0.6 to 226 µg/kg dwt, respectively.

Migration during bank filtration/underground passage and presence of TnBP, TCEP, TCPP and TBEP in the groundwater have been also reported in some studies (Fries and Püttmann, 2003; Bester et al., 2008, Regnery et al., 2011). In some instances, even higher concentrations of TnBP, TCEP and TBEP were found in ground water samples than in river water samples, caused by infiltration of rainwater into the aquifer or with seepage of high concentrations in river water in the past into ground water which reserves over time.

Only David and Seiber (1999) have analysed TPP in soils at U.S. Air Force Base contaminated with hydraulic fluids. They detected TPP in high concentrations from 2 to 6 µg/g dwt. This is the only study so far on the analysis of OFR in soil.

3.5 Fate of OFR in the environment

Migration of the chlorinated OFR, TCEP, TCPP and TDCP to the surface of the products followed by their release to indoor air causes emissions of OFR into the atmosphere from buildings and vehicles. Total continental emissions for TDCP and TCPP were estimated at 15.33 kg/d and 89.56 kg/d, respectively. Loss of TCEP to air from outdoor and indoor services results in a total release of 1.30 kg/d (European Commission, 2008a, 2008b; OECD, 2004).

Estimated half-lives based on an OH radical concentration of $5 \cdot 10^5$ molecules/mL in air for TCPP and TDCP are 8.6 h and 21.3 h, respectively (European Commission, 2008a, 2008b). In the risk assessment for TCEP, according to its estimated half-life of 17.5 h, photooxidation in air was assumed to represent a major degradation path for TCEP in the environment (European Commission, 2009). The half-life of atmospheric photooxidation of TPP by hydroxyl radicals is estimated to be around 36 h (Environment Agency, 2003). In the atmosphere, TnBP exists as a vapor and will be subject to rapid photodegradation (WHO, 1991).

Due to the atmospheric half-lives, abiotic effects on the atmosphere, such as global warming, ozone depletion and acid rain are likely to be very small for TCEP, TCPP and TDCP (European Commission, 2008a, 2008b, 2009). In the European Union risk assessments of TCPP and TDCP it was concluded that most TCPP and TDCP found in the atmosphere will sorb to particulate matter, which may then be washed out by rainfall due to the relatively low volatility, moderate solubility and high adsorption coefficient of TCPP and TDCP (European Commission, 2008a, 2008b).

Discharge of TCEP into the environment occurs via the wastewater or via the atmosphere. TnBP may enter into the environment by leakage from sites of production or use, as well as by leaching from plastics disposed in landfill sites or aquatic environments. Emission of TBEP is mainly to soil, sediments and surface waters from leachates, plastics on landfills, spillages and effluents. In the environment, TBEP is expected to partition to sediments (WHO, 2000). Entry of TPP into the environment occurs mainly through leakages from hydraulic equipment. The mobility of TPP in soil is not expected because of low vapour pressure and water solubility and high soil sorption coefficient (Anderson et al., 1993).

Henry’s Law constants indicate a preference for TCPP and TDCP for water compared to air, and hence a low rates of volatilisation from surface water to air. TCPP is stable in water at pH 4, 7 and 9 at 25 ºC with half life equal or greater than one year. As output of fugacity models adsorption of TCPP to sediments is estimated to be very low (European Commission, 2008a). However, most of TCPP found in air would precipitate to soil, and the movement between soil and water is very little, because transfer via the air compartment is very slow, for a substance of low volatility (European Commission, 2008a).

In soil and sediment, chlorinated OFR (TCEP, TCPP and TDCP) are considered to be persistent as they have a tendency to adsorb strongly and thus limited availability to microorganisms (Muir, 1984). Nonhalogenated phosphate esters are degraded by microorganisms in activated sludge (WHO, 1991, 2000). Standard biodegradation tests indicated that TnBP, TBEP and TPP are readily biodegradable, but TCPP and TDCP have been shown to be not readily biodegradable (European Commission, 2008a, 2008b, 2009, Environment Agency, 2003, WHO, 2000). TBEP when tested in the OECD 301B essay, achieved 87 % degradation within 28 days (IPCS, 2000). The biodegradation of TnBP is moderate or slow depending on the ratio of TnBP to active biomass. It involves stepwise enzymatic hydrolysis to orthophosphate and n-butanol, which undergoes further degradation (WHO, 1991). TCEP must be considered as non biodegradable (European Commission, 2009ž). TPP has a high potential for bioaccumulation, because of its hydrophobicity. An investigation on primary degradation of TCEP in soil showed a half life of 167 days (European Commission, 2009). Under anaerobic soil conditions, TPP had a half-life of 32 days, while commercial soil produced nearly quantitative recovery of TPP after 101 days (Anderson et al., 1993).

TCEP, as apparent from K_{oc} values, is particularly mobile in soil and has the greatest potential to leach into groundwater. Migrations during bank filtration/underground passage and presence in the groundwater have been reported for TCEP and TCPP (Fries and Püttmann, 2001, 2003, Bester et al., 2008, Regnery et al., 2011). The other OFR (TPP, TnBP, TBEP and TDCP) indicate relatively low leaching potential. Hydrolysis, although slow due to poor solubility and pH dependence, is the most important abiotic fate chemical process for OFR (Boethling and Cooper, 1985).

In the risk assessment for TCEP (European Commission, 2009) it has been concluded that this compound meets the persistent/very persistent (P/vP)- and the toxic (T)-criteria. TCEP has been proposed to be classified as Carcinogenic (Cat. 2). TCPP and TDCP meet the screening criteria as P or potentially vP based on their ultimate mineralization. Chlorinated OFR, TCEP, TCPP and TDCP do not meet the bioaccumulation criterion. Due to the low values of bioconcentration factors (BCF), bioaccumulation is not expected for these compounds (European Commission, 2008a, 2008b, 2009).

4. EXPERIMENTAL PART

4.1 Chemicals

Tris(2-chloroethyl) phosphate (TCEP, 97 %), tris(2-butoxyethyl) phosphate (TBEP, 94 %), tri(n-butyl) phosphate (TnBP, 97 %), triphenyl phosphate (TPP, 99 %), triisopropyl phosphate (TiPP, 99 %) and copper powder were provided from Sigma-Aldrich (Seelze, Germany), while tris(2-chloroisopropyl) phosphate (TCPP, 99.5 %), tris(1,3-dichloro-2-propyl) phosphate (TDCP, 97 %) and deuterated tri(n-butyl) phosphate (TnBP-d27) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). HPLC grade toluene, ethyl acetate, hexane, methanol and acetonitrile were purchased from Promochem (Wesel, Germany).
Ultrapure water was taken from a Sartorius Arium 611VF purification system (Göttingen, Germany).

4.2 Standard solutions

Standard stock solution was prepared by dissolving around 0.01 g of six OFR (TDCP, TPP, TnBP, TBEP, TCPP and TCEP) in 15 L of tap water. Tap water was used because of a four times lower blank value of TnBP in tap water than in ultra pure water taken from a Sartorius Arium 611VF purification system (Göttingen, Germany). High quantity of water was used to dissolve OFR to meet their water solubilities. Tap water was added in 100 mL quantities in flask which was ultrasonicated for 10 minutes and transferred in 15 L basket. Prior usage, basket was rinsed with methanol and dried in oven at 130 °C for 5 h.
Prepared standard stock solution was filled up in 2.5 L brown glass bottles (also precleaned with methanol and dried in oven) and stored in the fridge at 5 °C. Concentrations of stock solutions were 0.86 mg/L for TDCP, 1.37 mg/L for TPP, 1.23 mg/L for TnBP, 0.79 mg/L for TBEP, 0.69 mg/L for TCPP and 1.15 mg/L for TCEP.
TnBP-d27 was dissolved in acetonitrile to prepare a surrogate standard stock solution at a concentration of 10 mg/L. An internal standard stock solution with a concentration of 100 mg/L was prepared by dissolving TiPP in methanol.

4.3 Soil sampling

4.3.1 Sampling procedure

Soil samples were collected from a surface at a depth of 5 - 20 cm. Surface grass root material and top layer of soil were removed with a spade and samples were collected using a spade. The samples were transferred directly into aluminium containers, which were immediately closed. To overcome soil heterogeneities, six sub-samples within an area of 1 m^2 were taken at each sampling site.

4.3.2 Sampling locations and strategy

A first sampling campaign was designed to test the applicability of the analytical method. Soil samples were collected from the university campus located approximately 3 km from the city center of Osnabrück (Germany, about 160 000 inhabitants).

A second sampling campaign was conducted for investigation of spatial distribution of OFR in soil. Soil samples were collected from urban, semi-urban and rural areas between April and November 2010. Sampling sites are listed in Table 4 together with their grid references and mean daily air temperature (measured 2 m above surface) on the sampling day. These data have been taken from the German Weather Service for monitoring stations 10637 (Frankfurt Airport), 10315 (Münster-Osnabrück) and 10200 (Emden airfield). Sampling areas: rural (near village Jemgum), semi-urban (university campus in Osnabrück) and urban (Osnabrück and Frankfurt city centres) are also presented in Figure 4.

Table 4. Grid values and mean daily air temperatures.

Sample ID	Sampling date	North	East	Mean daily air temperature 2 m above surface (°C)
1.1	31.07.2010	50°06'35"	8°40'22"	19.4
1.2	01.08.2010	50°06'35"	8°40'22"	22.1
2.0	01.11.2010	52°16'44"	8°02'51"	7.4
2.1	03.08.2010	52°16'56"	8°01'17"	16.5
3.1	06.04.2010	53°17'00"	7°22'56"	12.5
3.2	06.04.2010	53°17'25"	7°23'58"	12.5
3.3	06.04.2010	53°17'38"	7°23'59"	12.5
3.4	06.04.2010	53°17'03"	7°22'34"	12.5
3.5	06.04.2010	53°17'00"	7°22'27"	12.5

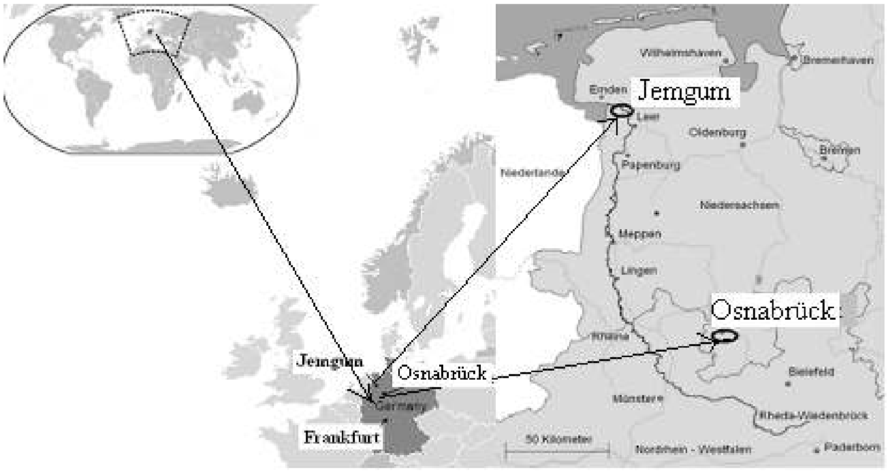


Figure 4. Maps of the sampling areas: rural, semi-urban and urban.

Four sampling areas in Germany were chosen as sampling sites. All sites were grasslands. One of the sampling points was located in the central park, close to the European central bank in Frankfurt (Germany, 672,000 inhabitants). At this location samples were collected before and after rain event (1.1 and 1.2). In Osnabrück two sampling locations were chosen: (2.0) city centre, near the traffic intersection and high building density and (2.1) university campus located approximately 3 km from the city centre of Osnabrück. Frankfurt (1.1 and 1.2) and Osnabrück (2.0) city centres represented the urban category, while university campus in Osnabrück (2.1) represented semi-urban category. The last sampling site (3.1 - 3.5) was located 3 km from the village Jemgum (Germany, 3,600 inhabitants), remote from the traffic jam and could represent rural category.

In order to investigate the influence of deposition processes, a third sampling campaign was performed at one sampling site at twelve different sampling times at different meteorological situations. As a sampling site, 1 m² was selected close to the university campus of Osnabrück (52°16'56.85" N, 8°1'12.51" E) located about 3 km from the city centre. The sampling site was located in the Westerberg district, a semi-urban area of the City of Osnabrück with a population density of 1,873 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.

Table 5 shows the sampling design, sampling date and time, number of sampling events, precipitation quantity between two sampling events (for the first sampling event precipitation on this day), minimum (min) and maximum (max) daily air temperature (measured 2 m above surface) on the sampling day. Data for daily air temperatures were taken from the German Weather Service for monitoring station 10315 (Münster-Osnabrück), 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 4.5.2).

Table 5. Sampling design, precipitation between two sampling dates (L/m^2), min and max daily air temperature (°C).

Sampling design	**Sampling time (date/hour)**	**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

After three days without any wet deposition, soil samples were collected on 29/11/10 (sampling event #1). Prior to sampling, it snowed for about five hours and the soil was completely snow covered. Thus, the OFR concentrations measured in these soil samples represented the initial concentrations. The next sampling dates were after 24 hours (#2) and 7 days (#3), respectively. Since the soil was covered by snow for the whole period, these samples reflected any removal of OFR by biodegradation. After six days, additional soil samples (#4) were collected during snow melt and also 24 h after the snow had melted (#5) to study the input of OFR in soil from the snow melting process. It started to rain two days before the last sampling event. No precipitation occurred between sampling #4 and #5.

The influence of rain on OFR concentrations in soil was studied by collecting soil samples just in time it started to rain (initial concentration - #6) and after 1 h (#7), 24 h (#8) and 48 h (#9), respectively. In addition, soil samples were collected three times during a period without any precipitation (#10, #11, #12) in order to study the impact of dry deposition processes on OFR concentrations in soil samples. Samples were also collected in August 2010 (summer period) from the same sampling site (sample ID – 2.1, Table 4) in order to study seasonal variations between two periods – the summer and the winter period.

4.4 Analysis of OFR in soil samples

The objective of this study was to develop an analytical method for analysing OFR in soil. A combination of Twisselmann extraction and SPME, followed by GC-MS, is presented for the first time to analyse OFR in soil.

4.4.1 Twisselmann extraction and preparation of SPME samples

The soil samples were freeze dried using an ALPHA 1-4 LSC freeze dryer (Christ, Germany). The samples were dried for approximately 24 h until the product temperature reached that of the room temperature. After drying, samples were sieved and the fraction with a particle size < 0.2 mm was taken for analysis. All soil samples were stored at -15 °C until the analysis. The water content calculated by weighing the samples before and after freeze drying ranged from 27.7 to 31.4 % of the total soil weight.

Several parameters during extraction and sample preparation were optimised using the "one variable at a time" (OVAT) methodology to increase OFR recoveries. The soil samples were weighed in thimbles, and aliquots of 10 g were spiked with 100 µL of TnBP-d27 stock solution (addition level 33.3 ng/g) and 1 mL of the OFR stock solution (addition level 22.9 - 45.8 ng/g).

The soil samples were mixed with a laboratory metal spoon and equilibrated for 24 h under a fume hood at room temperature (20 °C ± 0.2 °C). During mixing contact of spoon and spiking solution was strictly avoided.

Extraction was performed for 12 h using a Twisselmann extractor purchased from Gerhardt (Königswinter, Germany). The principle of Twisselmann extraction is similar to Soxhlet extraction. The main advantage of Twisselmann extraction is a solvent temperature near the boiling point. This improves extraction efficiency and reduces the extraction time.

All thimbles, boiling chips and round bottom flasks were precleaned by Twisselmann extraction using an appropriate solvent. A 150 mL of solvent were used for all experiments. Extracts were evaporated to dryness using a rotary evaporator R-114 purchased from Büchi (Flawil, Switzerland). Extracts were redissolved in a mixture of 13 mL of tap water and 1 mL of methanol for 60 min using an ultrasonic bath (Sonorex RK 106, Bandelin eletronic, Berlin, Germany). Methanol was chosen due to its documented high efficiency in extracting organophosphorus compounds from soil (Bouaid et al., 2001). The proportion of tap water was chosen to maintain the percentage of solvent below 10 %, to ensure optimum conditions as reported previously (Hernandez et al., 2000). Extracts were filtered using a 0.2 µm cellulose acetate membrane filter. Seven milliliter aliquots were filled into 10-mL glass headspace vials (Gerstel, Mülheim, Germany). The vials were sealed with magnetic crimp caps equipped with Teflon-faced silicone septa (Gerstel, Mülheim, Germany), spiked with TiPP (addition level 14.5 ng/g) and analysed by SPME/GC-MS. Calibration standards to determine recoveries were prepared in the same way as the samples, but spiked directly prior to SPME.

To determine the laboratory blanks, six soil samples were first precleaned with toluene by Twisselmann extraction. To calibrate the blank samples, six pre-cleaned soil samples were spiked directly prior to SPME with different volumes of the OFR stock solution (addition levels were between 0.68 and 27.46 ng/g).

For comparison purposes, extraction was also performed by ultrasonication of 10 g spiked soil samples instead of Twisselmann extraction. The samples were extracted with 60 mL of toluene for 30 min in an ultrasonic bath at room temperature (20 °C ± 0.2 °C). The extracts were separated from the soil by filtration, and the method was processed as described above.

4.4.2 Solid phase micro extraction/gas chromatography-mass spectrometry

SPME analyses were performed using an MPS2 XL auto sampler (Gerstel, Mülheim, Germany). A 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fibre (Supelco, Seelze, Germany) was exposed directly into the liquid sample. The aqueous solution was agitated in the incubator (incubation time 1 min, temperature 40 °C) at a speed of 250 rpm. The agitator on and off times were 60 s and 1 s, respectively. After extraction, the compounds were thermally desorbed for 300 s in the GC injector. After desorption, the fibre was reconditioned in an externally heated needle heater under a light helium flow at a temperature of 270 °C.

The GC 6890N system (Agilent Technologies, Santa Clara, USA) was equipped with a 30 metre HP-5MS capillary column (Agilent Technologies, Santa Clara, USA) with an I.D. of 250 µm and a film thickness of 0.25 µm. Helium 5.0 served as the carrier gas. The GC oven temperature programe was as follows: initial temperature 50 °C for 2 min, followed by heating at 5 °C/min to 250 °C, and at 15 °C/min from 250 °C to 300 °C and finally held for 1 min at 300 °C.

Data acquisition, processing and instrument control were performed using Chemstation software (Agilent Technologies, Santa Clara, USA). The analytes were detected using an MS5973 inert mass selective detector (Agilent Technologies, Santa Clara, USA) in the electron ionisation positive ion (EI) and selected ion monitoring (SIM) mode. Quantification was performed by calculating the peak area ratio of *m/z* 99 (base peak) for TiPP, *m/z* 103 (base peak) for TnBPd27, *m/z* 57 (base peak) for TBEP, *m/z* 99 (base peak) for TDCP, *m/z* 211 for TnBP, *m/z* 249 (base peak) for TCEP, *m/z* 277 for TCPP (only isomer 1 was considered) and *m/z* 326 (base peak) for TPP. Two additional qualifier ions were selected: *m/z* 125 and 141 for TiPP; *m/z* 231 and 167 for TnBPd27; *m/z* 125 and 199 for TBEP; *m/z* 75 (parent ion) and 191 (parent ion) for TDCP; *m/z* 99 (base peak) and 155 for TnBP; *m/z* 63 and 143 for TCEP; *m/z* 99 (base peak) and 125 for TCPP; and *m/z* 77 and 170 for TPP.

The limit of detection (LOD) was calculated according to DIN 32645 (1994) using equation 1

$$LOD = \frac{SD_y}{m} \cdot t \cdot \sqrt{\frac{1}{N'} + \frac{1}{N}} \tag{1}$$

where SD_y is the absolute standard deviation of the OFR/internal standard peak area ratio, m is the slope of the calibration curve, t is the critical t-value for a "one-tailed" t-test at a probability of p on $N-1$ degrees of freedom; N' is the number of replicate injections per determination ($N' = 1$) and N is the number of individual blank samples (N = 6).

4.4.3 Application of developed method for analysing soil samples

The developed analytical method based on combination of Twisselmann extraction and solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) was applied to detect OFR in soil samples. Quantification of OFR in soil samples was performed using the standard addition method. Two aliquots of 10 g soil were spiked with 100 µL of standard solutions containing TCEP, TCPP, TDCP, TnBP and TBEP with different concentrations in tap water (addition levels 1.37–14.80 ng/g dry weight, dwt). Two replicates were analysed without spiking. Samples were equilibrated for 24 h and extracted for 12 h with 150 mL of toluene in a Twisselmann extractor. Extracts were evaporated to dryness in rotary evaporator and redissolved with 1 mL methanol for 30 min using an ultrasonic bath. Tap water (13 mL) was added to extracts and they were again ultrasonicated for 30 min. Extracts were filtered using a cellulose acetate membrane filter with pore size of 0.2 µm. Seven milliliter aliquots were filled into 10-mL glass headspace vials (Gerstel, Mülheim, Germany), spiked with TnBP-d27 as an internal standard (IS) (addition level 6 ng/g) and analysed by SPME followed by GC-MS. All soil samples were analysed in triplicates.

The total organic carbon (TOC) was measured for all sampling locations in triplicates. 5 mg of freeze dried and sieved soil were analysed by a TOC Analyzer (Vario TOC cube, Elementar, Hanau, Germany).

4.5 Analysing of liquid samples

4.5.1 Snow samples

Snow samples were collected at the soil sampling location, at the university campus in Osnabrück (52°16'56.85" N, 8°1'12.51" E) on 12/12/10 at 9:30h. Samples were collected in 2.5 L brown glass bottles. Prior to sampling, glass bottles were rinsed with ultrapure water and methanol, respectively, and then heated at 110 °C for 5 hours. Samples were melted at room temperature (20 °C) in glass bottles and 7 mL aliquots were filled into 10-mL glass headspace vials (Gerstel, Mülheim, Germany), spiked with triisopropyl phosphate, TiPP (addition level 0.62 µg/L) and analysed by SPME/GC-MS under conditions described in chapter 4.4.2. Calibration curves were obtained by spiking melted snow samples with different concentrations of OFR stock solution (addition levels 0.05 – 4.23 µg/L) and TiPP (addition level 0.62 µg/L) as IS. Three replicates were used for each calibration point.

4.5.2 Rainwater samples

Rainwater samples were collected at the soil sampling location, at the university campus in Osnabrück (52°16'56.85" N, 8°1'12.51" E) at the four different times between 17/01 and 19/01/11 during the third field compaign for investigation the influence of rain on OFR concentrations in soil. Rain was collected in the same sampling times as soil samples to study the influence of rain (see Table 5). Rainwater samples were collected in a Hellmann rainwater gauge which enabled measuring the precipitation quantity in L/m^2 between two soil sampling events. To determine background contamination during sampling, a similar mean amount of ultra pure water taken from a Sartorius Arium 611VF purification system (Göttingen, Germany) as the amount of collected precipitation was put in the rainwater gauge and exposed to the same conditions at the same sampling site as precipitation was collected. An aliquot of 7 mL of each aqueous sample was spiked with IS (TiPP, addition level 0.62 µg/L) in 10-mL glass headspace vials (Gerstel, Mülheim, Germany) and analysed by SPME/GC-MS as reported in chapter 4.4.2. Calibration curves were obtained in the same way as for the snow samples.

5. RESULTS AND DISCUSSION

5.1 Method development

5.1.1 Optimising extraction and sample preparation parameters

The recoveries obtained for each OFR using ethyl acetate, hexane and toluene as extraction solvents were compared. The recoveries for all extraction solvents are shown in Figure 5. For TCPP results were presented for isomer 1. Using ethyl acetate as the solvent, only TCEP and TCPP were detected, with recoveries of 40.7 % and 29.7 %, respectively. This demonstrates that only OFR with higher water solublities such as TCEP and TCPP (Table 3) were extracted using the relative polar ethyl acetate.

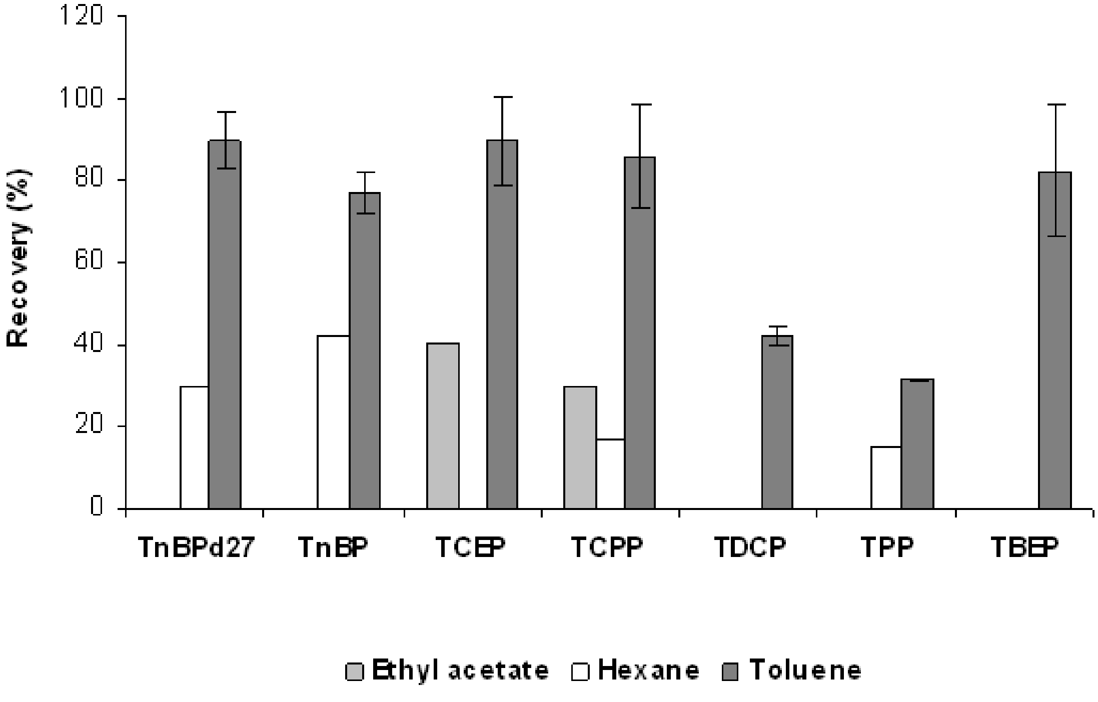


Figure 5. Effect of different solvents for Twisselmann extraction on recoveries obtained for OFR in the soil samples. For toluene, mean values are given with their standard deviations (n = 3).

The results demonstrate that recoveries were heavily dependent on the polarity of the analytes and hence on water solubility. Thus hexane was tested for extraction to increase the extraction of less polar compounds. OFR with lower water solubilities e.g., TDCP, TnBP, TBEP, and TPP, were extracted whereas TCEP was not because of its high polarity. However, recoveries were still low, at between 15.4 % for TPP and 42.0 % for TnBP. The highest recoveries, between 31.5 % (TPP) and 89.6 % (TCEP), were obtained for all OFR when toluene was used for extraction. The highest recoveries, 89.6 % (RSD of 10.9 %) for TCEP and 85.9 % (RSD of 12.7 %) for TCPP, were obtained for the substances with high water solubilities (Table 3). Substances with low water solubilities generated half as low recoveries, 31.5 % for TPP and 42.0 % for TDCP. Also, the recoveries of TCEP, TCPP, TnBP and TBEP were in the range of those previously published for organophosphorus pesticides studied in soils using the SPME method (Bouaid et al., 2001).

Significantly higher recoveries were obtained for toluene than for ethyl acetate and hexane. For this reason, toluene was used for extractions to improve the methodology and to obtain better recovery rates.

The next experiments were conducted by modifying the solvent to dissolve the extracts prior to SPME after evaporating them to dryness. A 14 mL of tap water was added to the extracts, and the results were compared to those for the tap water/methanol (14:1) mixture. The proportion of tap water was chosen to maintain the percentage of solvent below 10 %, as described earlier. Since blank values of OFR were lower for tap water compared to ultrapure water, tap water was preferred. Copper powder was added (150 mg), and the extracts were ultrasonicated for 30 min. The results are shown in Figure 6. For TCPP results were presented for isomer 1.

When only tap water was used, recoveries were about two to seven times lower, except for TPP (since TPP has the lowest water solubility, the slightly higher recovery obtained for tap water compared to the mixture of tap water and methanol may be attributed to variability). Thus, a mixture of 13 mL of tap water and 1 mL of methanol was used for all further analyses.

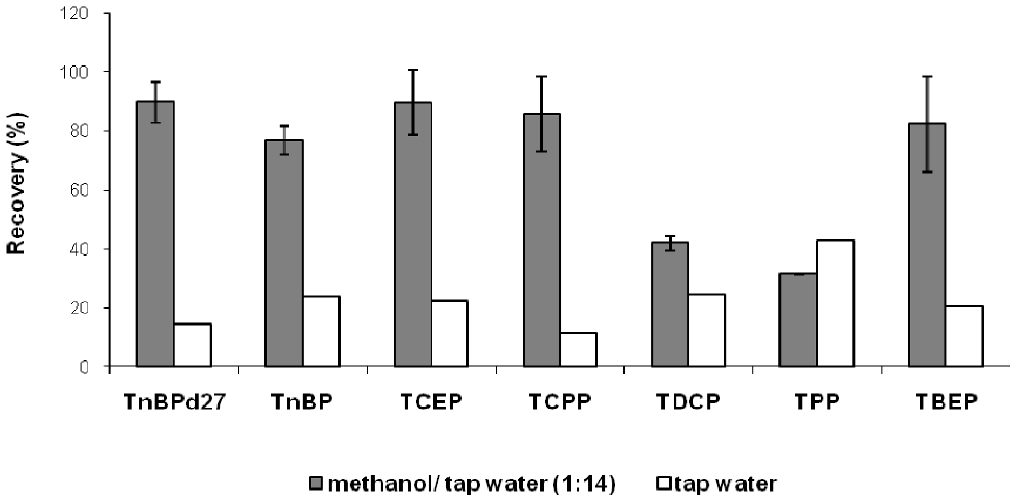


Figure 6. Comparison of recoveries obtained for OFR in the soil samples using tap water or a mixture of methanol/tap water for redissolving the extract. For methanol/tap water, mean values are given with their standard deviations (n = 3).

In all previous analyses, 150 mg of copper powder was added to all samples after extraction to remove sulfur which may disturb the separation of compounds (Riis and Babel, 1999). The results of the present study demonstrate that sulfur did not affect the analyses. However, use of copper powder affected the purity of the samples and apparatus used in the methodology. For this reason, all other samples were processed without adding copper.

The procedure with methanol/tap water (1:14) was repeated, albeit without filtering. By filtering the samples, the milky color was completely removed without affecting recoveries. Thus, all further samples were filtered.

The developed SPME method was tested for OFR analysis in the methanol/tap water (1:14) soil extracts obtained by either ultrasonication or Twisselmann extraction, using toluene as the solvent (Figure 7). For TCPP results were presented for isomer 1.

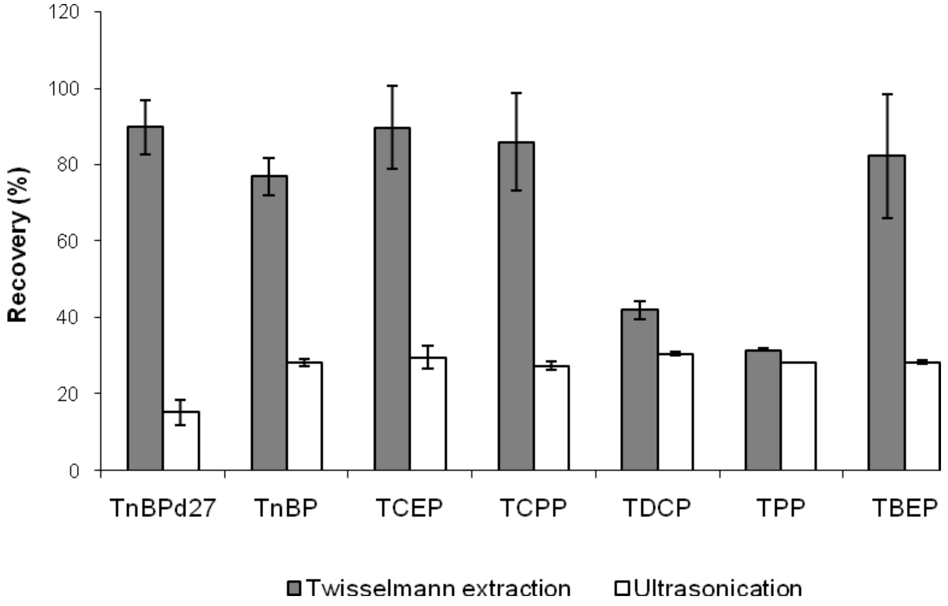


Figure 7. Comparison of results obtained after ultrasonic and Twisselmann extraction of the OFR followed by SPME of the analytes from the methanol/tap water extracts. Mean values are given with their standard deviations (n = 3).

Recoveries obtained by Twisselmann extraction were three to four times higher than those obtained by ultrasonication, except for TDCP and TPP, for which recoveries were similar. The higher recoveries by Twisselmann extraction could be attributed to extraction efficiency due to the longer extraction time and usage of a hot solvent for extraction purposes. However, the variability of recoveries (under 3 %) was lower than observed for Twisselmann extraction. The greater variability by Twisselmann extraction could be attributed to the fact that more materials are involved, such as thimbles, glass, etc., during Twisselmann extraction.

To conclude, the optimum analytical conditions were (i) no use of copper powder, (ii) filtration before SPME, (iii) use of toluene as the solvent for the Twisselmann extraction, and (iv) use of a methanol/tap water (1:14) mixture for redissolving the extract.

A schematic diagram describing developed method for the analysis of OFR in soil samples was presented in Figure 8.

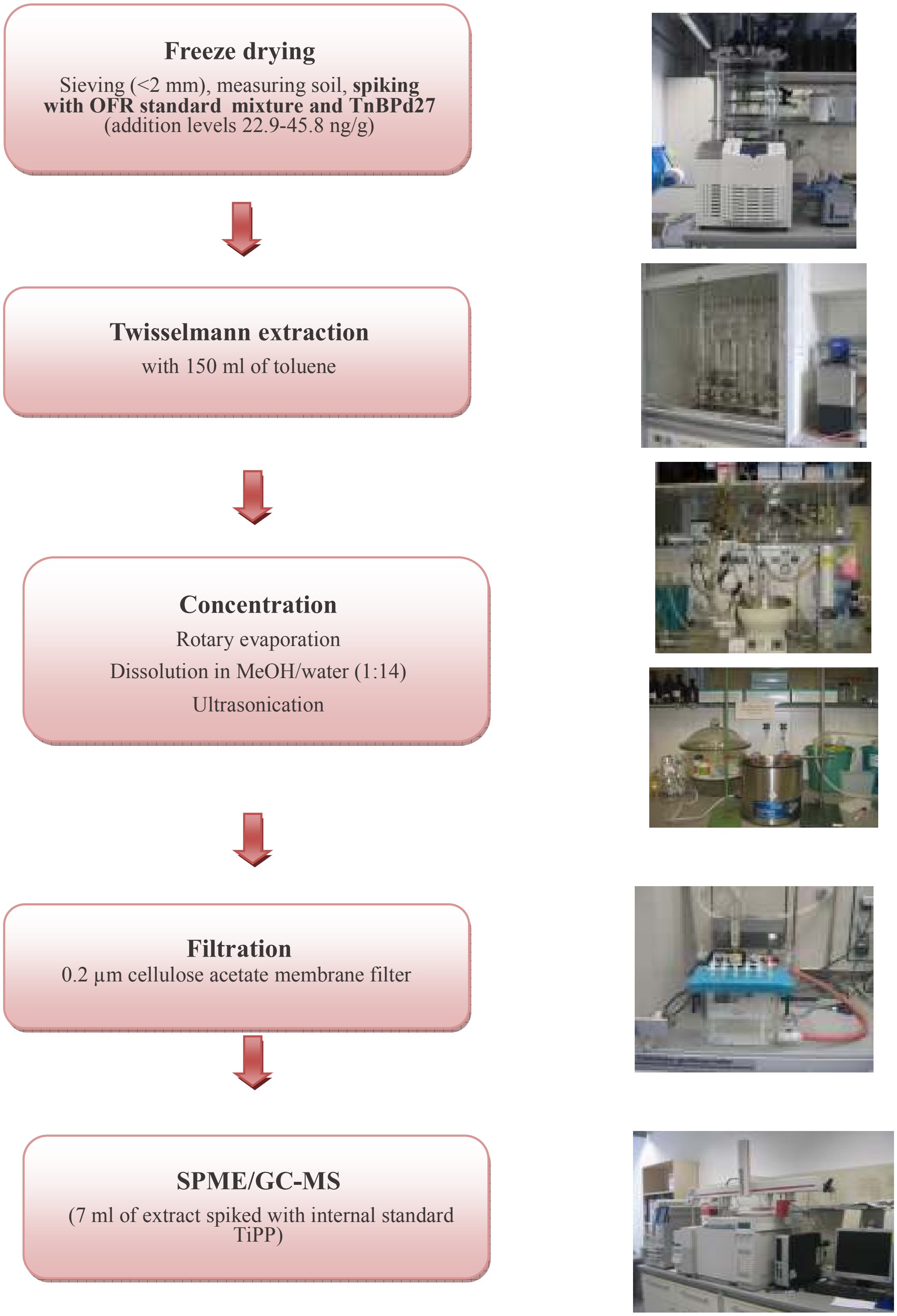


Figure 8. A schematic diagram and pictures represent developed method for the analysis of OFR in soil samples.

5.1.2 Quality Assurance (QA)

The variability of recoveries at optimum sample preparation and extraction conditions was between 0.3 and 16.2 % (n = 3). Calibration curves of all OFR were rather linear, with coefficients of determination (R^2) between 0.964 and 0.996.

The LODs calculated according to eq 1 were 3 ng/g for TnBP and 0.2 ng/g for TBEP. TnBP was already detected as the most abundant compound in indoor air samples (Sanchez et al., 2003) and samples could probably be contaminated during the spiking procedure and exposure to indoor air.

No signals were detected in the chromatograms obtained from the analysis of samples precleaned with toluene for any of the other substances examined. LODs, which were calculated as a signal-to-noise ratio (S/N) of 3/1, were 0.2 ng/g (TCEP), 0.002 ng/g (TCPP), 0.09 ng/g (TDCP), and 0.07 ng/g (TPP), respectively.

5.2 Spatial distribution of OFR in soil samples

A combination of Twisselmann extraction and SPME/GC-MS was developed and successfully applied to analyse OFR in soil samples collected from different sampling locations (urban, semi-urban and rural) in Germany. Mean concentrations (n=3) of TCEP, TCPP and TBEP in soil samples from different areas in Germany and TOC contents of soils are shown in Table 6. For investigation of spatial distribution soil samples were collected between April and November 2010.

Table 6. Concentrations of OFR in soil samples and TOC contents of soils (TOC: total organic carbon, LOQ: limit of quantitation, LOD: limit of detection).

Sample ID	**TCEP (ng/g dwt)**	**TCPP (ng/g dwt)**	**TBEP (ng/g dwt)**	**Mean TOC content (n=3) (% C)**
1.1	13.5	8.33	13	3.7±0.3
1.2	18.2	7.49	4.6	-
2.0	13.0	2.57	2.3	4.9±0.6
2.1	5.0	1.23	<LOQ	2.6±0.3
3.1	1.6	6.29	<LOQ	3.9±0.6
3.2	<LOQ	0.59	2.9	-
3.3	1.3	1.67	<LOD	4.7±0.5
3.4	0.7	1.01	1.1	3.6±0.5
3.5	2.5	2.56	4.5	-

TCPP was detected in all analysed soil samples above LOQ (calculated as three times higher than LOD) of 0.008 ng/g dwt. TDCP could not be detected in soil samples above concentration of 0.09 ng/g dwt (LOD). TnBP concentrations were below LOQ in all soil samples. Since TnBP is also used as a plasticizer, the LOQ of 9 ng/g dwt was relatively high according to a high blank. TBEP was detected in two soil samples below LOQ of 0.6 ng/g dwt.

TPP was detected in one soil sample (sample ID - 2.1) with mean concentration of 3.61 ng/g dwt. The less water-soluble OFR, such as TPP, may be associated with particles and could therefore easily be found in soils, sediments, and sewage sludge samples. However, residues of TPP in soil are likely to decline quickly, based on rapid degradation and mineralization (Anderson et al., 1993), so that detection is no longer possible. This could be why TPP was found in lower concentrations in soil samples compared to the chlorinated OFR. Concentrations of TPP obtained in this study were three orders of magnitude lower than concentrations of TPP found at the U.S. Air Force Base (David and Seiber, 1999) and also significantly lower than maximum permissible concentration (MPC) of 95 ng/g for TPP (Verbruggen et al., 2005).

Concentrations of TCEP, TCPP and TBEP in soil samples from different areas in Germany varied between LOQ and 18.2 ng/g dwt, 0.59 and 8.33 ng/g dwt, LOD and 13 n/g dwt, respectively (Table 6). Mean TCPP concentrations were higher in the Frankfurt city center (1.1, 1.2) compared to the other sampling sites. TCEP concentrations were lower in the rural area (3.1-3.5) compared to the urban and semi-urban sampling sites. For TBEP no site dependent effect on OFR concentrations was obvious at first sight.

Figure 9. presents the mean concentrations of TCEP, TCPP and TBEP in soil samples collected from four studied areas: big city (Frankfurt), small city (Osnabrück), urban background (3 km from Osnabrück city center) and rural background (3 km from village Jemgum). Mean TCEP concentrations decreased from high population and traffic density location to the location with very low traffic and population density (from urban to rural area), while for TCPP and TBEP soil concentrations were even higher in rural area than in the urban area (Osnabrück, Germany). Influence of traffic density on OFR snow concentrations was concluded in the studies of Marklund et al. (2005b).

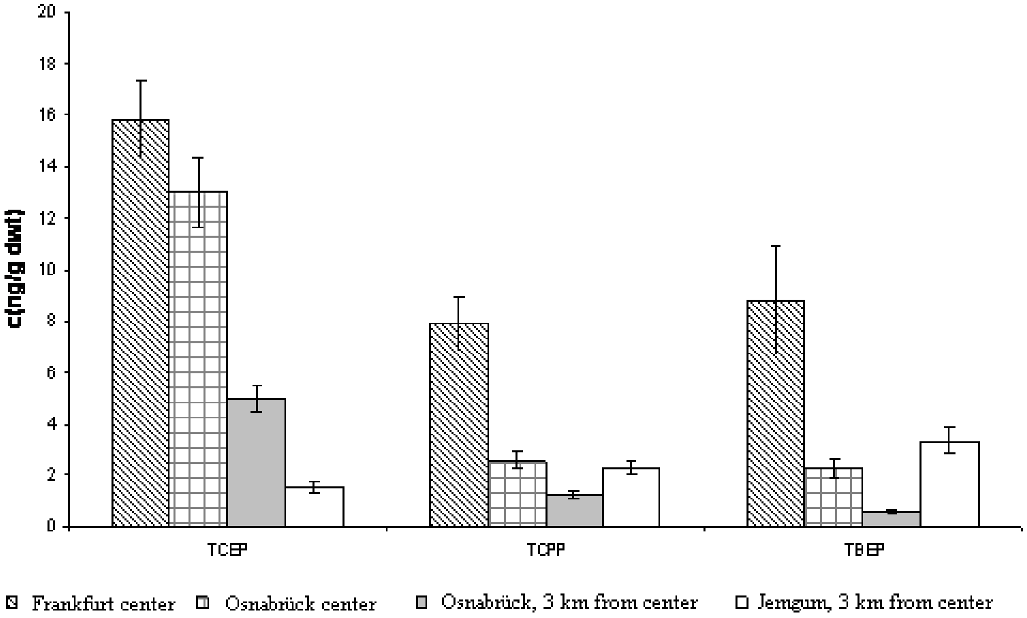


Figure 9. Comparison of concentrations of individual OFR in soil samples collected from different sampling sites in Germany: big city, small city, urban background and rural background (n = 3 - 15).

TCEP was found to be the most abundant in soil in the present study. This might be an indication for an influence of secondary outdoor emission sources on concentrations of OFR in soil. It was reported that TCEP was used in cars whereas TCPP was not because of its potential for fogging (European Commission, 2008a, 2009). In addition, atmospheric deposition by rain could be one of the reasons for higher concentrations of TCEP compared to TCPP due to the higher polarity of TCEP (Table 3). TCEP concentrations were higher in soil samples after rain event compared to concentrations before rain (1.1 vs. 1.2, Table 6). For TCPP and TBEP no conclusion could be drown for results of soil samples collected before and after rain event.

Since the sampling points were selected as they were not affected by irrigation with river water or sewage sludge, contamination from point sources could be excluded for all sampling locations and the influence of atmospheric deposition should be considered as an important source of OFR in soil. These data demonstrated for the first time the occurrence of chlorinated

OFR in soil. Results of this study indicate that atmospheric deposition is an important source of chlorinated OFR in soil.

In the European risk assessments (European Commission, 2008a, 2009) the predicted non effect concentrations (PNEC) for TCEP and TCPP were given at 386 ng/g dwt (*folsomia candida*) and 1700 ng/g soil dwt (*lactuca sativa*), respectively. Measured concentrations for TCEP and TCPP in this study were lower than PNEC. However, pollution of soils with OFR from different sources must be considered when evaluating the fate and risks of OFR in the environment. Thus, more data are needed to distinguish between different atmospheric deposition processes and their influence on soil samples.

5.3 Influence of deposition processes to chlorinated OFR soil concentrations

Due to the relatively low volatility, moderate solubility and high adsorption coefficient of chlorinated OFR (TCPP and TDCP), most chlorinated OFR found in the atmosphere will sorb to particulate matter, which may then be washed out by precipitation (European Commission, 2008a, 2008b). When chlorinated OFR enter to soil and sediment they have a tendency to adsorb strongly and limited availability to microorganisms (Muir, 1984). TCEP, TCPP and TDCP meet the persistent/very persistent (P/vP)-criteria (European Commission, 2008a, 2008b, 2009). TCEP meets also the toxic (T) criterion, and it has been proposed to be classified as Carcinogenic (Cat. 2) (European Commission, 2009). Since it has been shown that chlorinated OFR have negative effects on human health (Matthews et al., 1991, Johnson, 1999), the further studies were focused on the fate of chlorinated OFR. Hence, the influence of deposition processes as a source of chlorinated OFR in soils was systematically investigated.

5.3.1 Influence of snow

TCEP and TCPP were detected in snow samples with similar median concentrations (range) of 286 (236 - 353) ng/L and 233 (226 - 284) ng/L, respectively, while the median concentration of TDCP was much lower, 100 (92 - 128) ng/L. These concentrations were in the same range as concentrations obtained in Middle Germany and at a road intersection in Sweden, but three orders of magnitude lower than those measured at the airport in Umea, Sweden (Regnery and Püttmann, 2009; Marklund et al., 2005; Bacaloni et al., 2008). These findings indicate that snow represents a possible source of OFR in soil.

In soil samples collected from the same location as snow samples in different ages of snow chlorinated OFR concentrations ranged from 5.07 to 23.48 ng/g dwt for TCEP and 6.16 to 19.82 ng/g dwt for TCPP. TDCP was not detected in soil samples because the concentrations in snow and rain were too low. The median concentrations of TCEP and TCPP in soils during sampling events #1, #2, #3, #4 and #5 are shown in Figure 10 (error bars reflect min.-max. values). No significant correlation was observed between the snow deposited and the soil concentrations. In the period of snow deposition (sampling events #2 to #3), a decrease in the

TCEP median concentration was observed, indicating the solution of TCEP in ageing snow due to its high degree of solubility (Meyer et al., 2009b). The decrease in the median TCPP soil concentration was lower than for TCEP probably due to its lower degree of solubility. The biodegradation processes of TCEP and TCPP in soil were estimated to be slow (half-lives of >182 days and 300 days, respectively) (European Commission, 2008a, 2009). Hence degradations of TCEP and TCPP in soil were not expected to be the dominant processes for TCEP and TCPP decreases during the snow deposition period.

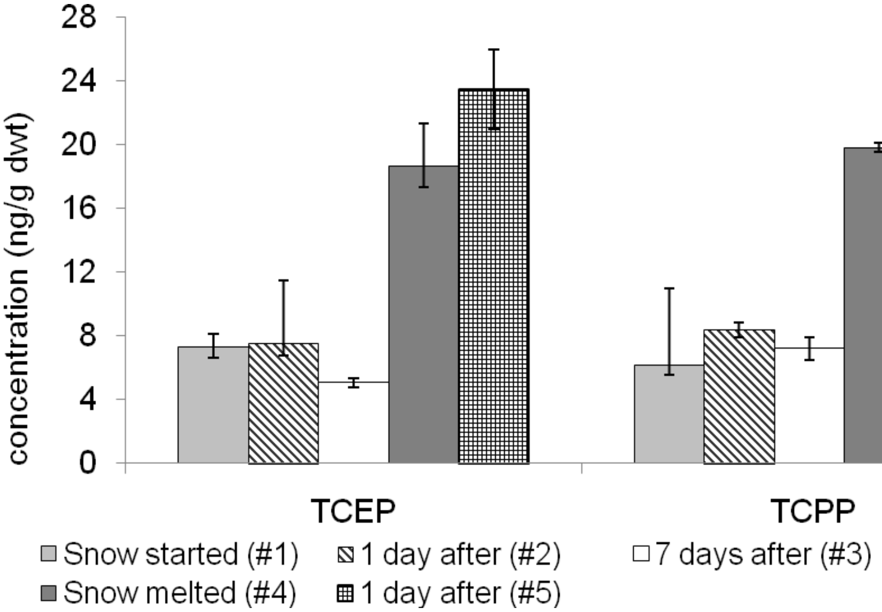


Figure 10. Different scenarios for studying influence of snow on TCEP and TCPP concentrations in soil samples.

Fallen snow undergoes many physical changes, including subliming, compacting, sintering, freezing and melting, depending on the ambient conditions (Wania et al., 1998). Thirteen days after snow had fallen (sampling event #4), the air temperature increased to a daily maximum of 5.4 °C (Table 5), causing the snow to melt. The meltwater generated at the surface percolated downwards due to gravity or capillary forces and took up chemicals present at the snow grain edge. For this reason, amplified concentrations of TCEP and TCPP were detected in soil samples (sampling events #4 and #5). The concentration maxima in water, air and soil caused by snowmelt were also predicted by simulation models (Daly and Wania, 2004; Wania et al., 1998; Meyer and Wania, 2008).

TCEP soil concentration increased from sampling event #4 to #5, while for TCPP a decrease in soil concentration was observed, probably caused by the evaporation of TCPP due to its much higher value of *H* (Verbruggen et al., 2005). The ratios of more water-soluble TCEP to less water-soluble TCPP increased in the soil during the melting period. The opposite behaviour in melting water was observed by Meyer et al. (2009a). The present authors explain this difference by a greater mobility of the more soluble TCEP to lower soil zones or by lateral melt water flow loads compared to that of the less soluble TCPP.

5.3.2 Influence of rain

The median rainwater concentrations of TCEP, TCPP and TDCP were 187, 372 and 46 ng/L, respectively (Table 7). The values of rainwater samples measured in this study were comparable with those in previous studies undertaken in Germany and Italy (Regnery and Püttmann, 2009; Bacaloni et al., 2008; Fries and Püttmann, 2003). The highest concentrations of TCPP were measured in rainwater samples. The reason why the concentrations of TCPP were higher than those of TCEP could be due to the phase-out of TCEP in Europe from the mid 1990s and its substitution by TCPP (European Commission, 2009). Although TCEP usage in products was restricted, its concentrations appeared to be high in the environment, caused by current releases from older products that still contain TCEP or from products imported from other countries where there is no legal restriction of TCEP in products.

Table 7. Median concentrations of OFR (C) with ranges in rainwater and specific loads of OFR (L) deposited by rainwater.

Compound	**C [ng/L]**	**L [ng m^{-2} day^{-1}]**		
		Between 0 and 1 h (#6 - #7)	**Between 1 and 24 h (#7 - #8)**	**Between 24 and 48 h (#8 - #9)**
TDCP	46 (41 - 48)	9	287	231
TCEP	187 (78 - 234)	37	1162	937
TCPP	372 (371 - 385)	74	2307	1860
Total OFR	605 (490 - 667)	120	3756	3028

The specific loads of OFR deposited by rainwater between the different sampling intervals (sampling events #6, #7, #8, #9) are presented in Table 7. Between 1 and 24 h (sampling events #7 and #8), atmospheric washout was higher (about 25 % of OFR concentrations) than in the following 24 h (sampling events #8 and #9). 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. These findings indicate that rain is a possible source of OFR in soils.

The median concentrations of TCEP and TCPP in soil samples were between 5.18 and 7.75 ng/g dwt and 5.66 and 10.06 ng/g dwt, respectively. The median concentrations of TCEP and TCPP in soils during sampling events #6, #7, #8 and #9 are shown in Figure 11 (the error bars reflect min.-max. values). The initial concentration of TCEP was lower than the concentrations of TCPP at sampling event #6, whereas the opposite was the case at sampling event #9. No significant correlation between rainwater amounts and soil concentrations was observed.

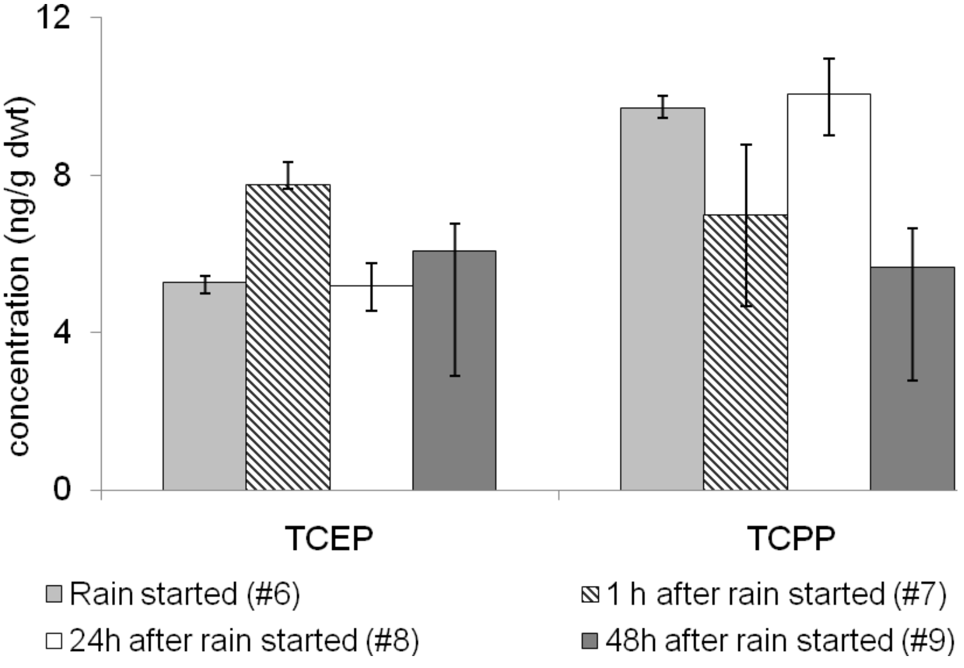


Figure 11. Different scenarios for studying influence of rainwater on TCEP and TCPP concentrations in soil samples.

After comparing TCPP concentrations in soil when rain started (sampling event #6) and 48h after rain started (sampling event #9), even a decrease in TCPP soil concentration was observed during the period of raining (Fig. 11). However, since they were detected in rainwater, atmospheric deposition must occur. Results indicate that the influence of rainwater deposition may be covered by volatilisation or by the migration of both compounds to deeper soil zones with seepage water, based on their volatility and high water solubility, respectively. Both compounds were detected in groundwater influenced predominantly by rainwater infiltration, indicating a vertical transport of TCEP and TCPP in soils (Fries and Püttmann, 2003; Bacaloni et al., 2008). Migration during bank filtration/underground passage and presence in groundwater have also been reported for both compounds (Fries and Püttmann, 2003; Andresen and Bester, 2006, Regnery et al., 2011). The biodegradation processes of TCEP and TCPP in soil were estimated to be slow (half-lives of >182 days for TCEP and 300 days for TCPP) (European Commission 2008a, 2009), thus biodegradation is not expected to be the dominant process for the two compounds in soil samples.

By comparing data after the snow melted in Fig. 10 and data after the rain event in Fig. 11, we can conclude that snow was the more efficient scavenger and transporter of chlorinated OFR into soil, since the soil concentrations were almost two and four times higher for TCPP and TCEP, respectively. The effect of snow melting was shown to be higher for TCEP than for TCPP soil concentrations.

5.3.3 Influence of dry deposition processes

The median concentrations of TCEP and TCPP in soils during sampling events #10, #11 and #12 are shown in Figure 12 (the error bars reflect min.-max. values). No wet precipitation occurred during these sampling events. TCEP soil concentrations decreased within this sampling period from an initial median concentration of 7.67 ng/g dwt at sampling event #10 to 2.08 ng/g dwt at sampling event #12. Since TCEP is considered to be non-biodegradable (half-life in soil > 182 days) (European Commission 2008a), biodegradion could be excluded as the reason for the decrease in soil concentrations. Due to the higher air temperatures at sampling event #10 compared to sampling event #11, higher TCEP air concentrations and lower concentrations in soil could be expected, which was the opposite case in this study.

No significant change of concentrations in soil was observed for TCPP during this period. 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. The atmospheric half-life of TCEP is 17.5 h (<24 h). Assuming a similar emission strength during the sampling events, the decrease in TCEP soil concentrations could be explained by the decreasing air concentrations due to rapid atmospheric photochemical degradation. Simultaneous measurements of OFR concentrations in air are required to clarify the influence of OFR emissions to the atmosphere and their deposition to soil samples.

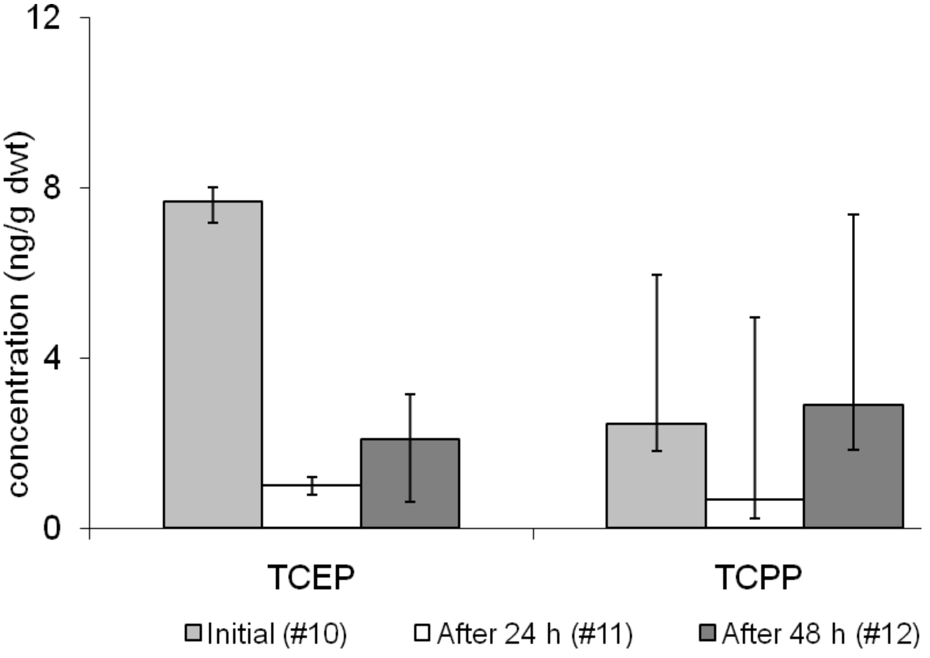


Figure 12. Different scenarios for studying influence of dry deposition on TCEP and TCPP concentrations in soil samples.

5.4 Assessment of air-soil exchange of OFR

5.4.1 Calculated air concentrations

Rainwater concentrations of OFR in ng/L (Table 7) were used for assessment of air concentrations (µg/m^3) at equilibrium conditions by equation (2):

$$C_{air} = C_{rain}/W_{g}\,. \tag{2}$$

W_g represents the scavenging ratio as determined by Pankow et al. (1984):

$$W_g = RT/H, \tag{3}$$

where R is universal gas constant (8.314 J/[mol K]) (Mohr et al., 2008), H is Henry's law constant (in Pa·m³/mol) and T is mean daily temperature (in K). In Table 8, the values of H (Verbruggen et al., 2005) and corresponding values of W_g are shown.

Table 8. Henry's Law constant (H) (Verbruggen et al., 2005), scavenging factors (W_g) and predicted gas phase concentrations (C_{air}) of OFR at equilibrium.

	***H* (Pa·m³/mol)**	**W_g**	**C_{air} (µg/m^3)**
TDCP	$2.65 \cdot 10^{-4}$	$1.7 \cdot 10^{7}$	$4.2 \cdot 10^{-5}$
TCEP	$2.58 \cdot 10^{-3}$	$5.5 \cdot 10^{7}$	$3.4 \cdot 10^{-6}$
TCPP	$6.04 \cdot 10^{-3}$	$3.8 \cdot 10^{6}$	$9.9 \cdot 10^{-4}$

According to eq 3 scavenging ratios of OFR were calculated to predict air concentrations from measured rain concentrations (Table 8). Values of W_g varied between $3.8 \cdot 10^6$ (TCPP) and $5.5 \cdot 10^7$ (TCEP). From C_{rain} between 46 ng/L (TDCP) and 372 ng/L (TCPP), values of C_{air} were between 0.0034 ng/m^3 for TCEP and 0.99 ng/m^3 for TCPP. Similar concentrations of 0.0016 ng/m^3 for TCEP and 0.81 ng/m^3 for TCPP were measured by Marklund et al. (2005) in background air samples from northern Finland. TCEP was not detected in outdoor air in Tokyo (Saito et al., 2007), while maximum TCPP concentration was 3.1 ng/m^3. Calculated air concentrations of chlorinated OFR obtained within this study are in the same range as OFR concentrations obtained in field measurements of outdoor air (Marklund et al., 2005; Saito et al., 2007).

5.4.2 Fugacity Calculations

An approach to air-soil exchange assessment (Harner et al., 2001) explained by Ruzickova et al. (2008) was adopted to investigate the potential for accumulation of OFR in soils. Results of OFR concentrations in soil samples obtained within this study were used for fugacity calculations. Fugacity of OFR in soil (f_s) (in Pa) was calculated according to equation (4)

$$f_s = C_s RT/0.41\Phi_{OM}K_{OA}, \qquad (4)$$

where C_s is concentration of OFR in soil (in mol/m^3), calculated by using density of soil about 1430 kg/m^3 (Brady, 1990) and T is mean daily temperature (K) taken from the German Weather Service for monitoring station 10315 (Münster-Osnabrück). Octanol-air partitioning coefficient (K_{OA}) was calculated by equation (5):

$$K_{OA} = K_{ow} / K_{AW} = K_{ow}RT/ H_{tcor}, \qquad (5)$$

Values of 1.4 for TCEP and 2.6 for TCPP were used for log of octanol-water partitioning coefficient (log K_{ow}) (Wania et al., 1998). K_{AW} represents air-water partitioning coefficient, while H_{tcor} (in Pa m^3/mol) represents the temperature corrected Henry’s law constant calculated using Clausius–Clapeyron equation (Harner et al., 2001)

$$\ln p = - \Delta H/RT + const. \qquad (6)$$

The slope of the function $\ln p = f\,(1/T)$ was used to calculate ΔH and to estimate H_{tcor} from ΔH and H (Verbruggen et al., 2005).

Fugacity of OFR in air (f_a) (in Pa) was calculated by equation (7):

$$f_a = C_{air}RT \qquad (7)$$

where C_{air} is concentration of OFR in outdoor air (in mol/m^3) assessed from scavenging ratios (eq 2).

The fugacity fraction (f_f) which could indicate the key process that controls the levels of OFR present in the soil and air is calculated from f_s and f_a by equation (8)

$$f_f = f_s / (f_s + f_a) \tag{8}$$

Soil-air equilibrium is indicated by a fugacity fraction f_f of 0.5. A value of $f_f < 0.5$ represents net deposition, and a f_f above 0.5 indicates net volatilization. Fugacity fractions between 0.3 and 0.7 could not be considered to differ significantly from equilibrium because of the approximations used in calculations (Harner et al., 2001; Ruzickova et al., 2008).

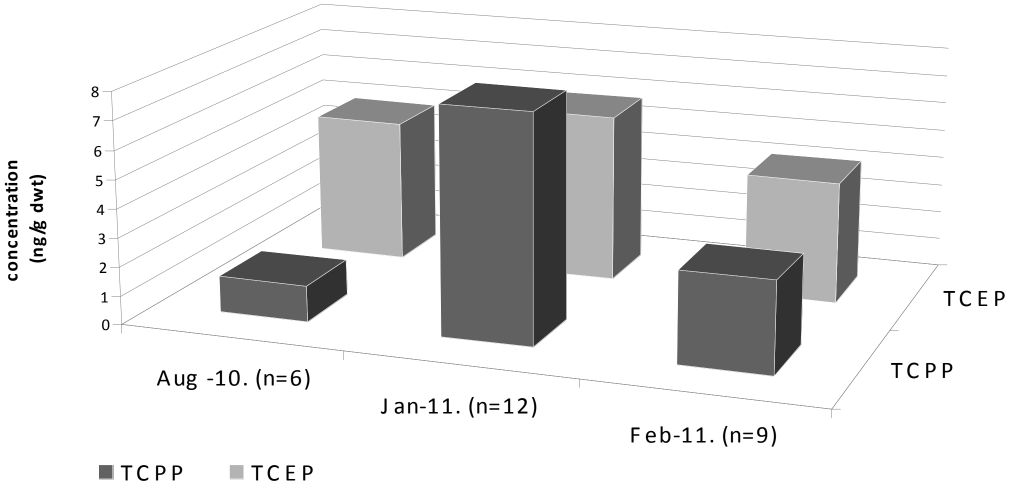
Fugacity calculations indicated net deposition from air to soil since air-soil fugacity fractions were 0.011 to 0.103 for TCPP (Table 9). Net deposition was also confirmed as dominant process for TCEP in air soil exchange (f_f values < 0.073).

Table 9. Fugacity fractions, f_f, for selected OFR, TCEP and TCPP.

Sampling event	*TCEP*	*TCPP*
#1	0.020	0.015
#2	0.011	0.019
#3	0.010	0.024
#4	0.051	0.085
#5	0.025	0.019
#6	0.037	0.103
#7	0.053	0.077
#8	0.025	0.076
#9	0.020	0.030
#10	0.073	0.062
#11	0.005	0.018
#12	0.006	0.011

5.5 Seasonal variations of TCEP and TCPP in soil

Figure 13 shows the monthly averaged OFR levels (6 < n < 12) in soil samples measured at the university campus of Osnabrück, the mean monthly air temperatures 2 m above the surface and the precipitation quantities in the summer and winter period. Higher TCPP volatilisation rates in summer months led to higher amounts of atmospheric TCPP and lower concentrations in soil samples. Thus, TCPP mean soil concentrations were lower in August (1.23 ng/g dwt) than in the winter months (5.89 and 3.13 ng/g dwt) of January and February. The highest soil concentrations for both compounds were observed in January (5.89 ng/g dwt and 7.89 ng/g dwt, respectively). In the next month, the soil concentrations of both compounds decreased to 4.24 ng/g dwt for TCEP and 3.13 ng/g dwt for TCPP. No conclusions could be drawn concerning the influence of precipitation quantities on mean monthly OFR soil concentrations. Since many processes predict the enviromental fate of TCEP and TCPP in soil, more detailed monitoring studies are required to further our knowledge of seasonal OFR soil concentrations, e.g. parallel continuous monitoring of air and soil OFR concentrations, rainwater amount and seepage water. In addition, column experiments are recommended to determine the mobility of chlorinated OFR in the unsaturated-saturated zone.



Aug -10.	**Jan-11.**	**Feb-11.**
16.87 °C	**2.4 °C**	**3.2 °C**
264.6 L/m^2	**83.1 L/m^2**	**31.4 L/m^2**

Figure 13. Monthly averaged OFR concentrations in soil samples.

5.6 Risk assessment of chlorinated OFR

Risk assessment is the process of characterisation the nature and magnitude of health risks to humans (e.g., residents, workers, recreational visitors) and ecological receptors (e.g., birds, fish, wildlife) from chemical contaminants and other stressors, that may be present in the environment (U.S. EPA, 2003). In the risk assessments for chlorinated OFR: TCEP, TCPP and TDCP no data are available for degradation and distribution in soil. There are no data for measured levels of chlorinated OFR in soil samples (European Commission, 2009, 2008a, 2008b).

The predicted environmental concentrations (PEC) in soil samples for TCEP, TCPP and TDCP were given at 39, 2.65 and 1.22 ng/g ww (wet weight), respectively. Based on the PNECsoil of 341, 1500 and 290 ng/g ww, a PEC/PNEC ratios of 0.11, 0.002 and 0.004 were calculated for TCEP, TCPP and TDCP. Thus, it was concluded that there is at present no indication of a risk to the local terrestrial environment.

Releases of chlorinated OFR into the terrestrial compartment could be expected as a result of deposition from the atmosphere and sewage sludge application (European Commission, 2009). The terrestrial environment (soils and vegetation) could be source of indirect exposure of human to OFR via animal’s products such as milk and meat. The other entry pathway of these compounds into human body is passage through soil into ground water and wells as important source of OFR into drinkable water. Thus, the both scenarios could cause elevated daily intake of these compounds for humans.

Although OFR have been already detected in fish tissues and human milk (Marklund et al., 2010, Campone et al., 2010), human exposure to OFR through eating fish or to breastfeeding babies seems to be of minor importance in relation to other potential sources, such as indoor dust inhalation and ingestion. Based on estimated amounts of indoor air inhaled and dust ingested, adults and children in the sampled environments in Sweden would be exposed to up to 5.8 mg/kg/day and 57 mg/kg/day total OFR, respectively (Marklund et al., 2005a).

Main metabolites of OFR were detected in range from <LOD to 27.5 µg/L for bis-(2-chlorethyl)-phosphate and <LOD to 4.1 µg/L for diphenylphosphate in the native urine

samples of 30 persons of the German general population (Schindler et al., 2009). There is also report about acute deaths of dogs due to the ingestion of car seat cushions found to contain large amounts of TCEP, resulting in significant amounts (>2 ppm) of TCEP in stomach contents of dogs (Lehner et al., 2010).

For these reasons it could be very important to take into consideration possible entry sources, behaviour and spatial distribution of OFR in soil in risk assessment reports for chlorinated OFR.

In the European Union risk assessments (European Commission, 2009, 2008a, 2008b) it is concluded that the relatively low volatility and moderate solubility and adsorption coefficient suggest that most TCPP and TDCP found in the atmosphere will adsorb to particulate matter, which may then be washed out by rainfall. In the European Union risk assessment of TCEP, no direct release to soil was identified; no experimental results on the adsorption of TCEP to soil are available. The results of the present field study demonstrate that atmospheric deposition is an important source of OFR in soil, even leading to pollution in the absence of point sources. Although the measured OFR soil concentrations in this study were lower than the predicted non-effect concentrations for TCEP, TCPP and TDCP, the pollution of soils with OFR from diffuse atmospheric input sources must be considered when evaluating the fate and risks of OFR in the environment.

6. CONCLUSIONS AND OUTLOOK

High Production Volume of OFR indicated their ubiquitous presence in nearly all environmental compartments. The development of new analytical method, based on combination of Twisselmann extraction and solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS), in research conducted within this PhD thesis, enabled detection of OFR in soil with high recovery rates. The validated method is suitable for quantifying six selected OFR in soil to assess possible input sources.

Data on the occurrence of OFR in soils collected from different areas (urban, rural, remote) have proven that OFR are ubiquitous in soil environments. Decrease in TCEP concentrations from high population and traffic density location to the location with very low traffic and population density (from urban to rural area), might be an indication for an influence of secondary outdoor emission sources on TCEP concentrations in soil. TCEP was found to be the most abundant compound in soil, since TCEP could enter to soil by the atmospheric wash out and has tendency to adsorb strongly to soil particles and thus has limited availability to microorganisms. TPP concentrations in soil were lower compared to chlorinated OFR concentrations, according to TPP rapid degradation and mineralisation.

According to the absence of any point source of OFR e.g. irrigation with river water or 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. Detection of chlorinated OFR in snow and rainwater samples confirmed the fact that snow and rain could be the possible sources of OFR in soil. Although snow deposition did not raise the chlorinated OFR soil concentrations, snow melting was seen to play a role. Snow melting caused enhanced soil concentrations of TCEP and TCPP, while no significant correlation between precipitation amounts and soil concentrations was observed. The influence of rainwater and dry deposition processes might be covered by migration of TCEP and TCPP to deeper soil zones with seepage water, based on their volatility and high water solubility. During dry weather, soil concentrations of both compounds seemed to be driven mainly by their concentrations in air, which are determined by source emissions strengths and photochemical degradation in the atmosphere.

Fugacity calculations indicated net deposition from air to soil as dominant process in the air-soil exchange. These observations suggest that precipitation could be the dominant deposition process of OFR from air to soil. The detection of the three OFR: TCEP, TCPP and TBEP in soil samples indicates that pollution of soils from diffuse atmospheric sources has to be considered in risk assessments.

PhD thesis addresses a significant need with regards to determining the levels of OFR in soils. The data showed that precipitation (rain and snow), especially in densely populated areas with high traffic volumes, is important as an all-season diffuse source of OFR in soil. Developed method was proved to be an effective for determination of OFR and results in possibility to collect monitoring data for soil samples to conduct a widespread environmental assessment e.g. influence of total organic carbon and water flow to OFR concentrations in different soil types, seasonal variations of OFR in different soil types and zones etc.

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Annex

Table A. Previous measurements of TCEP in the environment.

Study area	Medium	Value	Unit	Reference
House, Japan	Indoor air	1.3 (ND - 136)*	ng/m^3	Saito et al., 2007
Office building, Japan	Indoor air	3.3 (ND - 42.1)	ng/m^3	Saito et al., 2007
Lecture hall, Sweden	Indoor air	<0.3	ng/m^3	Staaf and Ostman, 2005
Computer hall, Sweden	Indoor air	3	ng/m^3	Staaf and Ostman, 2005
Dismantling facility, Sweden	Indoor air	10	ng/m^3	Staaf and Ostman, 2005
Office, Sweden	Indoor air	1.6	ng/m^3	Ericsson and Colmsjo, 2003
Laboratory, Sweden	Indoor air	367	ng/m^3	Tollbäck et al, 2009
Lecture hall, Sweden	Indoor air	2,037	ng/m^3	Tollbäck et al, 2009
Lecture hall, Sweden	Indoor air	47.9	ng/m^3	Sanchez et al., 2002
Day Care center, Sweden	Indoor air	144	ng/m^3	Carlsson et al., 1997
Office, Sweden	Indoor air	11	ng/m^3	Carlsson et al., 1997
Library, Sweden	Indoor air	35.1	ng/m^3	Sanchez et al., 2003
New car, Sweden	Indoor air	109.5	ng/m^3	Sanchez et al., 2003
Private home, Sweden	Indoor air	11.4	ng/m^3	Sanchez et al., 2003
Laboratory, Sweden	Indoor air	20.25	ng/m^3	Sanchez et al., 2003
Living room, Sweden	Indoor air	0.4-3.0	ng/m^3	Marklund et al., 2005a
Prison, Sweden	Indoor air	17	ng/m^3	Marklund et al., 2005a
Office, Sweden	Indoor air	730	ng/m^3	Marklund et al., 2005a
Alnabru, Norway (heavy traffic)	Outdoor air	2.4	ng/m^3	Green et al., 2008
Svalbard, archipelago in the Arctic	Outdoor air	0.27	ng/m^3	Green et al., 2008
Birkenes, Norway	Outdoor air	<0.2	ng/m^3	Green et al., 2008
Finland	Air, background	1.6	pg/m^3	Marklund et al., 2005b
Sierra Nevada Mountains, United States	Pine needles	2.5 – 1,950	ng/g	Aston et al., 1996
Road, Sweden	Snow	7 - 12	ng/kg	Marklund et al., 2005b
Airport, Sweden	Snow	29 - 39	ng/kg	Marklund et al., 2005b
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Snow	19 - 60	ng/L	Regnery and Püttmann, 2009
Bahnbruecke, Germany	Rain water	121	ng/L	Fries and Püttmann, 2003
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Rain water	11 - 196	ng/L	Regnery and Püttmann, 2009
Rome, Martignano Lake, Italy	Rain water	19 - 161	ng/L	Bacaloni et al., 2008
Urban storm water holding tank (SWHT)	Storm water	77 - 104	ng/L	Regnery and Püttmann, 2010
Rhine, Elbe, Main, Oder, Nidda and Schwarzbach Rivers, Germany	River water	17 - 220	ng/L	Fries and Püttmann, 2001
Oder River, Germany	River water	30 – 1,236	ng/L	Fries and Püttmann, 2003
Danube, Liesig and Schwechat Rivers, Austria	River water	13 - 130	ng/L	Martínez-Carballo et al., 2007
Ruhr River, Germany	River water	10 - 130	ng/L	Andresen and Bester, 2006
Oderbruch, Germany	Groundwater	71 - 312	ng/L	Fries and Püttmann, 2003
Oderbruch, Frankfurt, Hessian Ried, Mosel river, Germany	Groundwater	<3 - 141	ng/L	Regnery et al., 2011
Volcanic lakes, Lazio area, Italy	Lake water	4 - 64	ng/L	Bacaloni et al., 2008
Influent, Sewage water, Spain	Wastewater	0.05 - 0.30	ng/L	Rodriguez et al., 2006
Effluent, Sewage water, Spain	Wastewater	0.12 - 0.70	ng/L	Rodriguez et al., 2006
Influent, Wastewater treatment plant, Germany	Wastewater	180 - 260	ng/L	Meyer and Bester, 2004
Effluent, Wastewater treatment plant, Germany	Wastewater	350 - 370	ng/L	Meyer and Bester, 2004
Influent, Wastewater treatment facilities, Sweden	Wastewater	0.09 - 1.0	μg/L	Marklund et al., 2005c
Effluent, Wastewater treatment facilities, Sweden	Wastewater	0.35 - 0.89	μg/L	Marklund et al., 2005c
Osaka North Port Sea-Based Solid Waste Disposal Site	Raw water	0.04 - 87.38	μg/L	Kawagoshi et al., 1999
Wastewater treatment facilities, Sweden	Sludge	6.6 - 110	μg/kg dwt	Marklund et al., 2005c
Dust from private houses and vehicle cabins, Spain	Dust	5.6	μg/g	Garcia et al., 2007
House dust, Germany	Dust	2.23 - 3.75	mg/kg	Ingerowski et al., 2001
Osaka North Port Sea-Based Solid Waste Disposal Site	Sediment	64 – 7,395	μg/kg dwt	Kawagoshi et al., 1999
River Ems, Germany	Sediment	0.5 - 38	μg/kg dwt	Lach and Steffen, 1997
Danube, Liesig and Schwechat river sediments, Austria	Sediment	7.7 - 160	μg/kg dwt	Martínez-Carballo et al., 2007

* median concentration (min - max)

ND – not determined

Table B. Previous measurements of TCPP in the environment.

Study area	Medium	Value	Unit	Reference
House, Japan	Indoor air	1.9 (ND–1,260)	ng/m^3	Saito et al., 2007
Office building, Japan	Indoor air	6.0 (ND–57.6)	ng/m^3	Saito et al., 2007
Lecture hall, Sweden	Indoor air	762 (sum of three isomers)	ng/m^3	Staaf and Ostman, 2005
Computer hall, Sweden	Indoor air	1,080 (sum of three isomers)	ng/m^3	Staaf and Ostman, 2005
Dismantling facility, Sweden	Indoor air	22	ng/m^3	Staaf and Ostman, 2005
Office, Sweden	Indoor air	60.3 (sum of three isomers)	ng/m^3	Ericsson and Colmsjo, 2003
Laboratory, Sweden	Indoor air	2,836 (sum of three isomers)	ng/m^3	Tollbäck et al, 2009
Lecture hall, Sweden	Indoor air	1,118 (sum of three isomers)	ng/m^3	Tollbäck et al, 2009
Lecture hall, Sweden	Indoor air	306 (first isomer)	ng/m^3	Sanchez et al., 2002
Library, Sweden	Indoor air	47.3 (sum of three isomers)	ng/m^3	Sanchez et al., 2003
New car, Sweden	Indoor air	61.4 (sum of three isomers)	ng/m^3	Sanchez et al., 2003
Private home, Sweden	Indoor air	10.0 (sum of three isomers)	ng/m^3	Sanchez et al., 2003
Laboratory, Sweden	Indoor air	112 (sum of three isomers)	ng/m^3	Sanchez et al., 2003
Living room, Sweden	Indoor air	38-210 (sum of three isomers)	ng/m^3	Marklund et al., 2005a
Prison, Sweden	Indoor air	570 (sum of three isomers)	ng/m^3	Marklund et al., 2005a
Office, Sweden	Indoor air	160 (sum of three isomers)	ng/m^3	Marklund et al., 2005a
Alnabru, Norway (heavy traffic)	Outdoor air	1.3	ng/m^3	Green et al., 2008
Svalbard, archipelago in the Arctic	Outdoor air	0.27	ng/m^3	Green et al., 2008
Birkenes, Norway	Outdoor air	<0.2	ng/m^3	Green et al., 2008
Japan	Outdoor air	ND (ND–3.1)	ng/m^3	Saito et al., 2007
Finland	Air, background	810	pg/m^3	Marklund et al., 2005b
Sierra Nevada Mountains, United States	Pine needles	2.5-763	ng/g	Aston et al., 1996
Road, Sweden	Snow	110-170	ng/kg	Marklund et al., 2005b
Airport, Sweden	Snow	100-210	ng/kg	Marklund et al., 2005b
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Snow	20-83 (sum of two isomers)	ng/L	Regnery and Püttmann, 2009
Rome, Martignano Lake, Italy	Rain water	28-739	ng/L	Bacaloni et al., 2008
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Rain water	30-743 (sum of two isomers)	ng/L	Regnery and Püttmann, 2009
Urban storm water holding tank (SWHT)	Storm water	410-1,848 (sum of two isomers)	ng/L	Regnery and Püttmann, 2010
Danube, Liesig and Schwechat Rivers, Austria	River water	33-170	ng/L	Martínez-Carballo et al., 2007
Ruhr River, Germany	River water	50-150	ng/L	Andresen and Bester, 2006
Volcanic lakes, Lazio area, Italy	Lake water	2-62	ng/L	Bacaloni et al., 2008
Oderbruch, Frankfurt, Hessian Ried, Mosel river, Germany	Groundwater	<4-191	ng/L	Regnery et al., 2011
Influent, Wastewater treatment plant, Germany	Wastewater	650-2,500	ng/L	Meyer and Bester, 2004
Effluent, Wastewater treatment plant, Germany	Wastewater	820-2,600	ng/L	Meyer and Bester, 2004
Influent, Wastewater treatment facilities, Sweden	Wastewater	1.1-18	µg/L	Marklund et al., 2005c
Effluent, Wastewater treatment facilities, Sweden	Wastewater	3.1-30	µg/L	Marklund et al., 2005c
Influent, Sewage water, Spain	Wastewater	0.32-0.72	ng/L	Rodriguez et al., 2006
Effluent, Sewage water, Spain	Wastewater	0.31-0.91	ng/L	Rodriguez et al., 2006
Osaka North Port Sea-Based Solid Waste Disposal Site	Raw water	0.03-48.16	µg/L	Kawagoshi et al., 1999
Wastewater treatment facilities, Sweden	Sludge	61-1,900	µg/kg dwt	Marklund et al., 2005c
House dust, U.S.	Dust	572	ng/g	Stapleton et al., 2009
Dust from private houses and vehicle cabins, Spain	Dust	8.4	µg/g	Garcia et al., 2007
House dust, Germany	Dust	1.16-2.35	mg/kg	Ingerowski et al., 2001
Danube, Liesig and Schwechat river sediments, Austria	Sediment	0.61-1,300	µg/kg dwt	Martínez-Carballo et al., 2007
Osaka North Port Sea-Based Solid Waste Disposal Site	Sediment	2-1,181	µg/kg dwt	Kawagoshi et al., 1999
River Ems, Germany	Sediment	0.6-226	µg/kg dwt	Lach and Steffen, 1997

Table C. Previous measurements of TDCP in the environment.

Study area	Medium	Value	Unit	Reference
House, Japan	Indoor air	ND (ND–0.60)	ng/m^3	Saito et al., 2007
Office building, Japan	Indoor air	ND (ND–8.7)	ng/m^3	Saito et al., 2007
Computer hall, Sweden	Indoor air	2	ng/m^3	Staaf and Ostman, 2005
Dismantling facility, Sweden	Indoor air	7	ng/m^3	Staaf and Ostman, 2005
Alnabru, Norway (heavy traffic)	Outdoor air	0.056	ng/m^3	Green et al., 2008
Svalbard, archipelago in the Arctic	Outdoor air	0.19	ng/m^3	Green et al., 2008
Birkenes, Norway	Outdoor air	0.14	ng/m^3	Green et al., 2008
Finland	Air, background	20	pg/m^3	Marklund et al., 2005b
Sierra Nevada Mountains, United States	Pine needles	2.5-1,320	ng/g	Aston et al., 1996
Road, Sweden	Snow	8-230	ng/kg	Marklund et al., 2005b
Airport, Sweden	Snow	5-15	ng/kg	Marklund et al., 2005b
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/Main- Germany	Snow	5-40	ng/L	Regnery and Püttmann, 2009
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/Main- Germany	Rain water	2-24	ng/L	Regnery and Püttmann, 2009
Rome, Martignano Lake, Italy	Rain water	108-448	ng/L	Bacaloni et al., 2008
Urban storm water holding tank (SWHT)	Storm water	11-54	ng/L	Regnery and Püttmann, 2010
Danube, Liesig and Schwechat Rivers, Austria	River water	<3-19	ng/L	Martínez-Carballo et al., 2007
Ruhr River, Germany	River water	10-40	ng/L	Andresen and Bester, 2006
Volcanic lakes, Lazio area, Italy	Lake water	2-1,335	ng/L	Bacaloni et al., 2008
Oderbruch, Frankfurt, Hessian Ried, Mosel river, Germany	Groundwater	<40	ng/L	Regnery et al., 2011
Influent, Wastewater treatment facilities, Sweden	Wastewater	0.210-0.450	µg/L	Marklund et al., 2005c
Effluent, Wastewater treatment facilities, Sweden	Wastewater	0.130-0.340	µg/L	Marklund et al., 2005c
Influent, Wastewater treatment plant, Germany	Wastewater	100-110	ng/L	Meyer and Bester, 2004
Effluent, Wastewater treatment plant, Germany	Wastewater	110-150	ng/L	Meyer and Bester, 2004
Osaka North Port Sea-Based Solid Waste Disposal Site	Raw water	0.6-6.2	µg/L	Kawagoshi et al., 1999
Wastewater treatment facilities, Sweden	Sludge	<3.5-260	µg/kg dwt	Marklund et al., 2005c
House dust, U.S.	Dust	1,890	ng/g	Stapleton et al., 2009
Dust from private houses and vehicle cabins, Spain	Dust	6.1	µg/g	Garcia et al., 2007
Danube, Liesig and Schwechat river sediments, Austria	Sediment	<0.64	µg/kg dwt	Martínez-Carballo et al., 2007
Osaka North Port Sea-Based Solid Waste Disposal Site	Sediment	5-709	µg/kg dwt	Kawagoshi et al., 1999

Table D. Previous measurements of TBEP in the environment.

Study area	Medium	Value	Unit	Reference
House, Japan	Indoor air	1.8 (ND–13.7)	ng/m^3	Saito et al., 2007
Office building, Japan	Indoor air	0.97 (ND–118)	ng/m^3	Saito et al., 2007
Dismantling facility, Sweden	Indoor air	130	ng/m^3	Staaf and Ostman, 2005
Office, Sweden	Indoor air	7.6	ng/m^3	Ericsson and Colmsjo, 2003
Lecture hall, Sweden	Indoor air	3.27	ng/m^3	Sanchez et al., 2002
Day Care center, Sweden	Indoor air	5.9	ng/m^3	Carlsson et al., 1997
Office, Sweden	Indoor air	2.2	ng/m^3	Carlsson et al., 1997
Library, Sweden	Indoor air	0.77	ng/m^3	Sanchez et al., 2003
New car, Sweden	Indoor air	36.4	ng/m^3	Sanchez et al., 2003
Private home, Sweden	Indoor air	42.5	ng/m^3	Sanchez et al., 2003
Laboratory, Sweden	Indoor air	45.8	ng/m^3	Sanchez et al., 2003
Living room, Sweden	Indoor air	<0.4-0.6	ng/m^3	Marklund et al., 2005a
Prison, Sweden	Indoor air	55	ng/m^3	Marklund et al., 2005a
Office, Sweden	Indoor air	<0.2	ng/m^3	Marklund et al., 2005a
Alnabru, Norway (heavy traffic)	Outdoor air	0.22	ng/m^3	Green et al., 2008
Svalbard, archipelago in the Arctic	Outdoor air	0.15	ng/m^3	Green et al., 2008
Birkenes, Norway	Outdoor air	<0.1	ng/m^3	Green et al., 2008
Japan	Outdoor air	ND (ND–1.1)	ng/m^3	Saito et al., 2007
Finland	Air, background	<1.6	pg/m^3	Marklund et al., 2005b
Road, Sweden	Snow	2-12	ng/kg	Marklund et al., 2005b
Airport, Sweden	Snow	7-94	ng/kg	Marklund et al., 2005b
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Snow	4-21	ng/L	Regnery and Püttmann, 2009
Bahnbruecke, Germany	Rain water	394	ng/L	Fries and Püttmann, 2003
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Rain water	3-39	ng/L	Regnery and Püttmann, 2009
Rome, Martignano Lake, Italy	Rain water	38-115	ng/L	Bacaloni et al., 2008
Urban storm water holding tank (SWHT)	Storm water	36-57	ng/L	Regnery and Püttmann, 2010
Rhine, Elbe, Main, Oder, Nidda and Schwarzbach Rivers, Germany	River water	103-663	ng/L	Fries and Püttmann, 2001
Oder River, Germany	River water	121-952	ng/L	Fries and Püttmann, 2003
Danube, Liesig and Schwechat Rivers, Austria	River water	24-500	ng/L	Martínez-Carballo et al., 2007
Ruhr River, Germany	River water	170	ng/L	Andresen and Bester, 2006
Volcanic lakes, Lazio area, Italy	Lake water	8-127	ng/L	Bacaloni et al., 2008
Oderbruch, Germany	Ground water	154-410	ng/L	Fries and Püttmann, 2003
Oderbruch, Frankfurt, Hessian Ried, Mosel river, Germany	Groundwater	<33	ng/L	Regnery et al., 2011
Influent, Wastewater treatment facilities, Sweden	Wastewater	5.2-35	µg/L	Marklund et al., 2005c
Effluent, Wastewater treatment facilities, Sweden	Wastewater	3.1-30	µg/L	Marklund et al., 2005c
Influent, Sewage water, Spain	Waste water	0.99-33.73	ng/L	Rodriguez et al., 2006
Effluent, Sewage water, Spain	Waste water	0.11-9.53	ng/L	Rodriguez et al., 2006
Influent, Wastewater treatment plant, Germany	Wastewater	3,600-4,000	ng/L	Meyer and Bester, 2004
Effluent, Wastewater treatment plant, Germany	Wastewater	400-540	ng/L	Meyer and Bester, 2004
Wastewater treatment facilities, Sweden	Sludge	<5.1-1900	µg/kg dwt	Marklund et al., 2005c
Dust from private houses and vehicle cabins, Spain	Dust	11.4	µg/g	Garcia et al., 2007
Danube, Liesig and Schwechat river sediments, Austria	Sediment	2.4-130	µg/kg dwt	Martínez-Carballo et al., 2007

Table E. Previous measurements of TnBP in the environment.

Study area	Medium	Value	Unit	Reference
House, Japan	Indoor air	4.0 (ND-30.6)	ng/m^3	Saito et al., 2007
Office building, Japan	Indoor air	6.6 (0.46–21.7)	ng/m^3	Saito et al., 2007
Lecture hall, Sweden	Indoor air	5	ng/m^3	Staaf and Ostman, 2005
Computer hall, Sweden	Indoor air	<0.3	ng/m^3	Staaf and Ostman, 2005
dismantling facility, Sweden	Indoor air	24	ng/m^3	Staaf and Ostman, 2005
Office, Sweden	Indoor air	2.5	ng/m^3	Ericsson and Colmsjo, 2003
Lecture hall, Sweden	Indoor air	1.93	ng/m^3	Sanchez et al., 2002
Day Care center, Sweden	Indoor air	13	ng/m^3	Carlsson et al., 1997
Office, Sweden	Indoor air	18	ng/m^3	Carlsson et al., 1997
Library, Sweden	Indoor air	4.10	ng/m^3	Sanchez et al., 2003
New car, Sweden	Indoor air	138	ng/m^3	Sanchez et al., 2003
Private home, Sweden	Indoor air	14.2	ng/m^3	Sanchez et al., 2003
Laboratory, Sweden	Indoor air	11.9	ng/m^3	Sanchez et al., 2003
Living room, Sweden	Indoor air	14-120	ng/m^3	Marklund et al., 2005a
Prison, Sweden	Indoor air	20	ng/m^3	Marklund et al., 2005a
Office, Sweden	Indoor air	8.2	ng/m^3	Marklund et al., 2005a
Alnabru, Norway (heavy traffic)	Outdoor air	1.36	ng/m^3	Green et al., 2008
Svalbard, archipelago in the Arctic	Outdoor air	<0.2	ng/m^3	Green et al., 2008
Birkenes, Norway	Outdoor air	<0.2	ng/m^3	Green et al., 2008
Japan	Outdoor air	ND (ND–1.7)	ng/m^3	Saito et al., 2007
Finland	Air, background	0.28	ng/m^3	Marklund et al., 2005b
Road, Sweden	Snow	11-19	ng/kg	Marklund et al., 2005b
Airport, Sweden	Snow	2.1-25	µg/kg	Marklund et al., 2005b
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Snow	15-192	ng/L	Regnery and Püttmann, 2009
Bahnbruecke, Germany	Rain water	911	ng/L	Fries and Püttmann, 2003
Rome, Martignano Lake, Italy	Rain water	11-48	ng/L	Bacaloni et al., 2008
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Rain water	37-203	ng/L	Regnery and Püttmann, 2009
Urban storm water holding tank (SWHT), Germany	Storm water	57-255	ng/L	Regnery and Püttmann, 2010
Rhine, Elbe, Main, Oder, Nidda and Schwarzbach Rivers, Germany	River water	151-1,510	ng/L	Fries and Püttmann, 2001
Oder River, Germany	River water	69-1,044	ng/L	Fries and Püttmann, 2003
Danube, Liesig and Schwechat Rivers, Austria	River water	20-110	ng/L	Martínez-Carballo et al., 2007
Ruhr River, Germany	River water	40	ng/L	Andresen and Bester, 2006
Volcanic lakes, Lazio area, Italy	Lake water	3-784	ng/L	Bacaloni et al., 2008
Oderbruch, Germany	Ground water	276-1,112	ng/L	Fries and Püttmann, 2003
Oderbruch, Frankfurt, Hessian Ried, Mosel river - Germany	Groundwater	5-90	ng/L	Regnery et al., 2011
Influent, Sewage water, Spain	Waste water	0.06-0.36	ng/L	Rodriguez et al., 2006
Effluent, Sewage water, Spain	Waste water	0.04-0.18	ng/L	Rodriguez et al., 2006
Influent, Wastewater treatment facilities, Sweden	Wastewater	6.6-52	µg/L	Marklund et al., 2005c
Effluent, Wastewater treatment facilities, Sweden	Wastewater	0.36-6.1	µg/L	Marklund et al., 2005c
Influent, Wastewater treatment plant, Germany	Wastewater	260-1,100	ng/L	Meyer and Bester, 2004
Effluent, Wastewater treatment plant, Germany	Wastewater	100-260	ng/L	Meyer and Bester, 2004
Osaka North Port Sea-Based Solid Waste Disposal Site	Raw water	0.2-1.5	µg/L	Kawagoshi et al., 1999
Wastewater treatment facilities, Sweden	Sludge	39-850	µg/kg dwt	Marklund et al., 2005c
Dust from private houses and vehicle cabins, Spain	Dust	0.19	µg/g	Garcia et al., 2007
Osaka North Port Sea-Based Solid Waste Disposal Site	Sediment	2-253	µg/kg dwt	Kawagoshi et al., 1999
Danube, Liesig and Schwechat river sediments, Austria	Sediment	11-50	µg/kg dwt	Martínez-Carballo et al., 2007

Table F. Previous measurements of TPP in the environment.

Study area	Medium	Value	Unit	Reference
House, Japan	Indoor air	ND (ND–5.4)	ng/m^3	Saito et al., 2007
Office building, Japan	Indoor air	ND (ND–0.60)	ng/m^3	Saito et al., 2007
Computer hall, Sweden	Indoor air	1	ng/m^3	Staaf and Ostman, 2005
Dismantling facility, Sweden	Indoor air	17	ng/m^3	Staaf and Ostman, 2005
Office, Sweden	Indoor air	20.1	ng/m^3	Ericsson and Colmsjo, 2003
Laboratory, Sweden	Indoor air	8	ng/m^3	Tollbäck et al, 2009
Lecture hall, Sweden	Indoor air	7	ng/m^3	Tollbäck et al, 2009
Lecture hall, Sweden	Indoor air	3.18	ng/m^3	Sanchez et al., 2002
Day Care center, Sweden	Indoor air	<0.5	ng/m^3	Carlsson et al., 1997
Office, Sweden	Indoor air	0.7	ng/m^3	Carlsson et al., 1997
Library, Sweden	Indoor air	0.494	ng/m^3	Sanchez et al., 2003
New car, Sweden	Indoor air	1.44	ng/m^3	Sanchez et al., 2003
Private home, Sweden	Indoor air	11.7	ng/m^3	Sanchez et al., 2003
Laboratory, Sweden	Indoor air	35.3	ng/m^3	Sanchez et al., 2003
Living room, Sweden	Indoor air	<0.3-8.8	ng/m^3	Marklund et al., 2005a
Prison, Sweden	Indoor air	<0.4	ng/m^3	Marklund et al., 2005a
Office, Sweden	Indoor air	7.1	ng/m^3	Marklund et al., 2005a
Alnabru, Norway (heavy traffic)	Outdoor air	0.88	ng/m^3	Green et al., 2008
Svalbard, archipelago in the Arctic	Outdoor air	<0.05	ng/m^3	Green et al., 2008
Birkenes, Norway	Outdoor air	<0.05	ng/m^3	Green et al., 2008
Finland	Air, background	12	ng/m^3	Marklund et al., 2005b
Road, Sweden	Snow	4-68	ng/kg	Marklund et al., 2005b
Airport, Sweden	Snow	120-830	ng/kg	Marklund et al., 2005b
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Snow	15-192	ng/L	Regnery and Püttmann, 2009
Rome, Martignano Lake, Italy	Rain water	2-19	ng/L	Bacaloni et al., 2008
Kleiner Feldberg Wasserkuppe Bekond Schmuecke Frankfurt/ Main- Germany	Rain water	37-203	ng/L	Regnery and Püttmann, 2009
Danube, Liesig and Schwechat Rivers, Austria	River water	<4.4-10	ng/L	Martínez-Carballo et al., 2007
Ruhr River, Germany	River water	10	ng/L	Andresen and Bester, 2006
Volcanic lakes, Lazio area, Italy	Lake water	2-21	ng/L	Bacaloni et al., 2008
Influent, Wastewater treatment facilities, Sweden	Wastewater	0.076-0.290	µg/L	Marklund et al., 2005c
Effluent, Wastewater treatment facilities, Sweden	Wastewater	0.041-0.13	µg/L	Marklund et al., 2005c
Influent, Wastewater treatment plant, Germany	Wastewater	81-93	ng/L	Meyer and Bester, 2004
Effluent, Wastewater treatment plant, Germany	Wastewater	20-36	ng/L	Meyer and Bester, 2004
Influent, Sewage water, Spain	Wastewater	0.28-0.47	ng/L	Rodriguez et al., 2006
Effluent, Sewage water, Spain	Wastewater	0.22	ng/L	Rodriguez et al., 2006
Osaka North Port Sea-Based Solid Waste Disposal Site	Raw water	<0.1	µg/L	Kawagoshi et al., 1999
Wastewater treatment facilities, Sweden	Sludge	52-220	µg/kg dwt	Marklund et al., 2005c
House dust, U.S.	Dust	7360	ng/g	Stapleton et al., 2009
Dust from private houses and vehicle cabins, Spain	Dust	1.5	µg/g	Garcia et al., 2007
Danube, Liesig and Schwechat river sediments, Austria	Sediment	0.79-1,300	µg/kg dwt	Martínez-Carballo et al., 2007
Osaka North Port Sea-Based Solid Waste Disposal Site	Sediment	9-130	µg/kg dwt	Kawagoshi et al., 1999
U.S. Air force bases	Soil	2-6	µg/g	David and Seiber, 1999

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Mihajlovic, I., Vojinovic Miloradov, M., Fries, E., 2011. Application of Twisselmann Extraction, SPME, and GC-MS to Assess Input Sources for Organophosphate Esters into Soil. Environ Sci Technol, 45 (6), 2264-2269.

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Curriculum vitae

Personal information

Name	Ivana Mihajlović
Birth name	Anđelović
Date of Birth	24.05.1984
Place of Birth	Bor, Serbia
Family status	married, two children

Experience

February 2011 – Present	Research assistant at the Faculty of Technical Sciences, University of Novi Sad, Serbia
March 2010 – February 2011	Practice at the Institute of Environmental System Research, University of Osnabrück, Germany
February 2009 – February 2010	Student research assistant at the Faculty of Technical Sciences, University of Novi Sad, Serbia
August 2008 – December 2008	Physics teacher in primary school in Vrbas, Serbia

Education

April 2008 – April 2009	Master studies at the Faculty for Physical Chemistry, University of Belgrade, Serbia Master thesis: Angular moments in spectroscopy (supervising tutor: Prof. Dr. Miljenko Perić) Graduated physicochemist - master, average mark 10 (out of 10)
October 2003 – March 2008	Diploma studies at the Faculty for Physical Chemistry, University of Belgrade, Serbia Diploma thesis: Solving the relativistic Schrodinger equation for the hydrogen atom (supervising tutor: Prof. Dr. Miljenko Perić) Graduated physicochemist, average mark 9.87 (out of 10)
September 1999 – June 2003	Gymnasium “Bora Stanković” Bor, Serbia, graduated with maximal average mark, 5.0

Declaration of Authorship

I guarantee that PhD thesis entitled:

Dry and wet deposition processes as a source of organophosphate flame retardants (OFR) in soils

was written by myself and that I have used no other sources than those acknowledged.

Direct quotations from and paraphrases of or references to other works are in every case indicated with reference to the source or secondary literature used.

I did not receive any assistance in return for payment by consulting agencies or any other person. No one received any kind of payment for direct or indirect assistance in correlation to the content of the submitted thesis.

The thesis has not been submitted elsewhere for an exam, as thesis or for evaluation in a similar context.

I hereby affirm the above statements to be complete and true to the best of my knowledge.

20.03.2012.

Ivana Mihajlović

Ivana Mihajlović