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Organophosphates in precipitation, lake water, and groundwater from urban and remote areas

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Abstract

Within the present study the occurrence and fate of the organophosphorus flame retardants and plasticizers tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) in precipitation, lake water, surface runoff and groundwater from urban and remote areas in Germany was investigated between June 2007 and October 2009. 255 samples of precipitation, 210 samples of lentic surface water and 72 samples of groundwater were analyzed for the six organophosphates (OPs) by solid phase extraction followed by gas chromatography-mass spectrometry. The research focused on aspects concerning (1) the atmospheric washout of OPs by precipitation, (2) the temporal variation of OP concentrations in precipitation and in lentic surface waters as well as (3) the pollution of groundwater by OPs.

The results of the study emphasize the importance of precipitation as an all-season entry-pathway for OPs in the aquatic environment, particularly in densely populated urban environments with high traffic volume and abundant usage of flame-protected products. No seasonal trends were observed for all analytes in precipitation at the urban sampling site. TCPP dominated in all precipitation and storm water holding tank (SWHT) water samples with maximum levels exceeding 1 µg L^{-1}. An accumulation of OPs deposited in SWHTs was observed with concentrations often exceeding those observed in wet precipitation. Median concentrations of TCPP (880 ng L^{-1}), TDCP (13 ng L^{-1}), and TBEP (77 ng L^{-1}) at the urban SWHT were more than twice as high as those measured at the urban precipitation sampling site (403 ng L^{-1}, 5 ng L^{-1}, 21 ng L^{-1}) located close to the SWHT. OP levels in more remote lakes were often below or close to the limits of quantitation (LOQ). Nevertheless, TCPP was the substance with the highest median concentration in rural volcanic lakes (7–18 ng L^{-1}) indicating an atmospheric transport of the compound. At urban lakes the median OP concentrations were in the range of 23–61 ng L^{-1} (TCEP), 85–126 ng L^{-1} (TCPP), <LOQ–53 ng L^{-1} (TBEP), 8–10 ng L^{-1} (TiBP), and 17–32 ng L^{-1} (TnBP). In laboratory experiments, TBEP, TiBP, and TnBP were photochemically degraded in spiked lake water samples upon exposure to sunlight. In the SWHT a seasonal trend with decreasing concentrations in summer/autumn was evident for TiBP and TnBP but not for the chlorinated OPs. The decreasing concentrations can be explained by in-lake photodegradation.

Results have also shown that the occurrence of OPs in groundwater is depending on the anthropogenic impact during groundwater recharge/natural replenishment. Infiltration of precipitation was found to be no important entry-pathway for OPs into aquifers at rural sites.

Abstract

Highest OP concentrations (>0.1 µg L^{-1}) were determined in groundwater polluted by percolating leachate from contaminated sites or groundwater recharged via bank filtration of OP-loaded recipients. Concentrations of TCEP, TCPP, TiBP and TnBP in groundwater decreased rapidly (89–97%) during bank filtration with increasing distance from the recipient due to adsorption processes and/or biotransformation. Although TCEP and TCPP are stable within the aquifer, they are not suitable as conservative organic tracers in groundwater.

Keywords: Atmospheric transport; bank filtration; degradation; organophosphorus flame retardants; plasticizers; storm water runoff.

Zusammenfassung

Die in der vorliegenden Arbeit untersuchten chlorierten und unchlorierten Organophosphate Tris(2-chlorethyl)phosphat (TCEP), Tris(1-chlor-2-propyl)phosphat (TCPP), Tris(1,3-dichlor-2-propyl)phosphat (TDCP), Tri-iso-butylphosphat (TiBP), Tri-n-butylphosphat (TnBP) und Tris(2-butoxyethyl)phosphat (TBEP) gehören mittlerweile zu den dominierenden Fremdstoffen in Oberflächengewässern. Das Vorkommen dieser Phosphorsäureester in der Umwelt ist ausschließlich anthropogen bedingt. Sie werden einer Vielzahl von Produkten als additive Flammschutzmittel oder Weichmacher zugesetzt und unterliegen der Freisetzung durch Verdampfung sowie Abnutzung, Alterung oder Entsorgung der Produkte. Während die chlorierten Organophosphate TCEP, TCPP und TDCP als Flammschutzmittel vorwiegend in Polyurethan-Schaumstoffen in der Bau-, Möbel- und Fahrzeugindustrie breite Anwendung finden, werden die unchlorierten Organophosphate TBEP, TiBP und TnBP primär als flammhemmende Weichmacher in Kunststoffen, in Hydraulikölen sowie als Entschäumer eingesetzt (*1*). Aufgrund ihrer physikochemischen Eigenschaften (niedrige Henry-Koeffizienten, hohe chemische Stabilität im Wasser) belasten die Substanzen nach ihrer Freisetzung insbesondere die aquatische Umwelt. Die allgemeine Strukturformel der Phosphorsäureester ist in Fig. 0-1 dargestellt. Im Jahr 2004 lag der weltweite Verbrauch an organophosphat-basierten Flammschutzmitteln und Weichmachern bei ca. 207.200 Tonnen pro Jahr. Davon wurden allein in der Europäischen Union (EU) ca. 83.700 Tonnen pro Jahr verwendet (http://www.cefic-efra.com). Aufgrund strengerer Brandschutzbestimmungen sowie der stärkeren Regulierung der Verwendung bromierter Flammschutzmittel wird mit einem weiteren Anstieg des Verbrauchs an chlorierten Organophosphaten gerechnet.

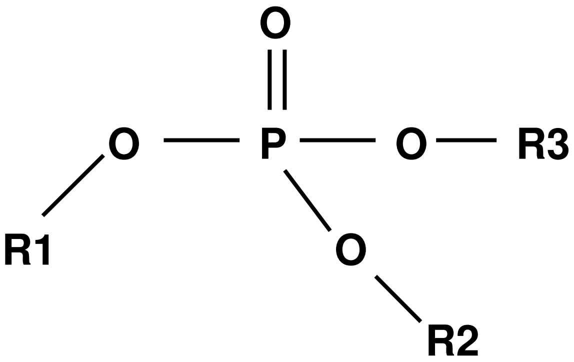


Fig. 0-1. Allgemeine Strukturformel der Phosphorsäureester. R1, R2 und R3 sind entweder gleiche oder verschiedene organische Substituenten. In allen technisch relevanten Produkten ist R1=R2=R3.

Zusammenfassung

Untersuchungen zum Vorkommen und der Persistenz der chlorierten Flammschutzmittel TCEP, TCPP und TDCP in der aquatischen Umwelt sowie deren potenziell gefährliche Wirkung auf aquatische Lebewesen und die menschliche Gesundheit sind in EU Risk Assessment Reports zusammengefasst. Ab Mitte der neunziger Jahre wurde TCEP aufgrund seiner Toxizität für aquatische Organismen sowie seiner Klassifizierung als potenzielles humanes Karzinogen in der EU auf Basis einer freiwilligen Verfügung der Industrie weitgehend durch TCPP substituiert. Von TnBP und TDCP ist ebenfalls eine potenzielle karzinogene Wirkung auf Menschen bekannt, von TCPP wird sie vermutet. Hinsichtlich ihrer Toxizität und ihres Metabolismus ist die Datenlage für einige Organophosphate weiterhin unzureichend (*2*).

Das Auftreten von chlorierten und unchlorierten Organophosphaten wurde in Kläranlagen und Fließgewässern bereits vielfach untersucht. Für die chlorierten Organophosphate ist eine nur sehr geringe biologische Abbaubarkeit bei der Abwasserbehandlung beschrieben. Eine vergleichbare Persistenz ist bei den unchlorierten Organophosphaten nicht gegeben. Durch Adsorption an Aktivkohle können die chlorierten Organophosphate jedoch effizient aus dem Wasser entfernt werden. Bisher wurde das Vorkommen dieser Substanzen in Oberflächengewässern und im Grundwasser hauptsächlich der Einleitung geklärter Abwässer zugeschrieben. Eine in Italien durchgeführte Studie an abgelegenen, hydrographisch geschlossenen Systemen ohne Abwasserbelastung legt aber nahe, dass der Eintrag von Organophosphaten durch nasse und trockene Deposition als weitere Quelle für das Vorkommen dieser Substanzen in Oberflächengewässern in Betracht zu ziehen ist. Ausgehend von den Hauptemittenten Ballungsraum und Straßenverkehr wird ein Transport dieser Substanzen über die Atmosphäre diskutiert (*3,4*).

Vor diesem Hintergrund bestand die Zielsetzung der hier vorliegenden Doktorarbeit in der Klärung der noch offenen Frage, in welchem Ausmaß chlorierte und unchlorierte Organophosphate über die Atmosphäre transportiert und in stehende Oberflächengewässer durch Niederschläge eingetragen werden. Des Weiteren sollte geklärt werden, in welchem Ausmaß der photochemische Abbau der Organophosphate in den Gewässern als Eliminationspfad relevant ist. Zudem sollte überprüft werden, inwieweit Grundwasser bei der natürlichen Grundwasserneubildung bzw. Grundwasseranreicherung durch organophosphat-belastete Niederschläge und Oberflächengewässer beeinflusst wird.

Zur Klärung dieser Fragestellungen wurden von Juni 2007 bis Oktober 2009 insgesamt 255 Regen- und Schneeproben, 210 Proben aus Oberflächengewässern (Regenwasserrückhaltebecken, Seen, Talsperren etc.) und 72 Grundwasserproben aus städtischen sowie abgelegenen Gebieten in Deutschland gesammelt und analysiert. An der städtischen Nieder-

schlagsmessstelle Frankfurt am Main (Rhein-Main-Gebiet) sowie den ländlichen Messstellen Bekond (Mosel) und Taunusobservatorium Kleiner Feldberg (Taunus) wurden ganzjährig Regen- und Schneeproben gesammelt. An den in den Mittelgebirgen Thüringer Wald und Hessische Rhön gelegenen Hintergrundmessstellen Schmuecke und Wasserkuppe fand dagegen nur in den Wintermonaten eine Probenahme von Niederschlag statt. Im Stadtgebiet Frankfurt am Main wurden an einem Regenwasserrückhaltebecken, einem Fluss-Altarm und einem See über den Zeitraum eines Jahres kontinuierlich Proben gesammelt. Im ländlichen Raum (Mosel, Eifel) wurden in regelmäßigen Abständen ein Regenwasserrückhaltebecken sowie drei Seen vulkanischen Ursprungs beprobt. Stichprobenartig wurden zudem Wasserproben an drei Talsperren im Thüringer Wald und einem See in der Hessischen Rhön entnommen. Die analysierten Grundwasserproben stammten vorwiegend aus dem Hessischen Ried, dem Oderbruch (Brandenburg) und vom Gelände der als Altlast eingestuften stillgelegten Mülldeponie Monte Scherbelino (Frankfurt am Main).

Die Analyse der Wasser- und geschmolzenen Schneeproben erfolgte nach Anreicherung der organischen Substanzen durch Festphasenextraktion und anschließender Gaschromatographie-Massenspektroskopie. Das Volumen der jeweiligen Wasserproben variierte zwischen 1 L und 2,5 L. Um ungelöste Bestandteile und organische Schwebstoffe aus den Proben zu entfernen, wurden Proben mit einem hohen Anteil an organischer Matrix mittels Druckfiltration vor der Festphasenextraktion filtriert. Zur Quantifizierung wurde den Extrakten vor Beginn der gaschromatographischen Messung ein interner Standard zugegeben. Die Quantifizierung der gesuchten Substanzen erfolgte in der jeweiligen Massenspur m/z des Hauptions anhand der internen Standardkalibrierung. Die Nachweisgrenzen und Bestimmungsgrenzen (Limit of quantitation, LOQ) der einzelnen Substanzen wurden in Anlehnung an die DIN-Norm 32645 auf Basis mehrfach gemessener Kalibrationskurven mit dem Programm DIN-Test 2000 (Universität Heidelberg) berechnet. Die Nachweisgrenzen der sechs Zielsubstanzen langen zwischen 1 ng L^{-1} und 3 ng L^{-1} und die Bestimmungsgrenzen nach dieser Methode zwischen 3 ng L^{-1} und 8 ng L^{-1}. Die Wiederfindungsraten aller Substanzen lagen im Bereich von 85% bis 99% mit relativen Standardabweichungen zwischen 2,4% und 7,2%. Um zudem Aussagen über schwankende Konzentrationen von chlorierten und unchlorierten Organophosphaten in stehenden Oberflächengewässern über einen längeren Zeitraum treffen zu können, wurden Laborexperimente mit dotierten Reinstwasser- sowie realen Gewässerproben in UV-lichtdurchlässigen transparenten und lichtundurchlässigen schwarzen Teflonflaschen durchgeführt.

Die Ergebnisse der Untersuchungen belegen, dass in urbanen Gebieten, aber auch in abgelegenen Höhenlagen, der Niederschlag ganzjährig als ein wichtiger Eintragspfad von chlorierten und unchlorierten Phosphorsäureestern in Oberflächengewässer angesehen werden muss. Von den untersuchten Organophosphaten wurde TCPP am Häufigsten im städtischen Regen und Regenwasserabfluss (Frankfurt am Main) mit Konzentrationen deutlich über 1 µg L^{-1} nachgewiesen. Generell lagen die in den Regenwasserrückhaltebecken gemessenen Konzentrationen signifikant über den in den Niederschlägen gemessenen Konzentrationen, so dass von einer Aufkonzentrierung der Substanzen in diesen Becken auszugehen ist. So waren die Median-Konzentrationen von TCPP (880 ng L^{-1}), TDCP (13 ng L^{-1}), und TBEP (77 ng L^{-1}) im städtischen Regenwasserrückhaltebecken mehr als doppelt so hoch wie die Median-Konzentrationen, die im Niederschlag an der städtischen Messstelle gemessen wurden (403 ng L^{-1}, 5 ng L^{-1} und 21 ng L^{-1}).

Obwohl einige der Substanzen starken Konzentrationsschwankungen im Niederschlag unterlagen, konnten sowohl für die unchlorierten als auch für die chlorierten Organophosphate keine saisonalen Trends an der städtischen Messstelle beobachtet werden. Schwankende Konzentrationen von TCEP, TCPP und TDCP in den Niederschlagsproben ließen sich nicht mit den meteorologischen Parametern Lufttemperatur und Niederschlagsmenge erklären. Zur Untersuchung der Hintergrundbelastung wurden Regen- und Schneeproben von Messstationen in entlegenen Gebieten (z. B. Schmuecke, Thüringer Wald und Wasserkuppe, Hessische Rhön) einbezogen. Hier wurden drei- bis viermal geringere Phosphorsäureester-Konzentrationen als im Stadtgebiet von Frankfurt am Main gemessen. TiBP und TnBP zeigten in den Sommermonaten in den Regenproben der abgelegenen Messstelle Kleiner Feldberg deutliche Konzentrationsabnahmen gegenüber den Wintermonaten. So waren die Median-Konzentrationen von TiBP (17 ng L^{-1}, 131 ng L^{-1}) und TnBP (25 ng L^{-1}, 133 ng L^{-1}) im Sommer (n = 13) deutlich niedriger als im Winter (n = 16). Die Median-Konzentrationen der chlorierten Flammschutzmittel TCPP (54 ng L^{-1}, 65 ng L^{-1}) und TCEP (33 ng L^{-1}, 46 ng L^{-1}) blieben im Vergleich Sommer/Winter weitgehend unverändert. Daraus lässt sich folgern, dass atmosphärische Photooxidation insbesondere in Sommermonaten mit höherer Globalstrahlung die Konzentration an unchlorierten Organophosphaten während des Transports von urbanen zu abgelegenen Gebieten reduziert. Die Analyse der Schneeproben der vier Hintergrundstationen ergab des Weiteren, dass die Konzentrationen der unchlorierten Phosphorsäureester TiBP und TnBP sowie des chlorierten Phosphorsäureesters TDCP linear mit der Bevölkerungsdichte in der Umgebung der Messstationen anstiegen.

TiBP und TnBP zeigten in den Sommermonaten ebenfalls eine Konzentrationsabnahme im Oberflächenwasser des städtischen Regenwasserrückhaltebeckens. In beiden städtischen Seen konnten für die unchlorierten Organophosphate zwar deutliche Konzentrationsschwankungen, aber keine signifikanten Trends beobachtet werden. Saisonale Trends wurden bei den chlorierten Organophosphaten hingegen nicht beobachtet. Die Ergebnisse der Laborversuche zum photochemischen Abbau der Organophosphate bestätigten die hohe Stabilität von chlorierten Flammschutzmitteln gegenüber natürlicher Strahlung. Lediglich die Konzentrationen der unchlorierten Phosphorsäureester TnBP, TiBP, und TBEP nahmen in den mit realen Gewässerproben gefüllten transparenten Teflonflaschen nach 15-tägiger natürlicher Belichtung mit intensiver Sonneneinstrahlung (Sommer) deutlich ab. Da diese Abnahme auch in mit Hg(II) vergifteten Kontrollen der mit realen Gewässerproben gefüllten, dotierten transparenten Teflonflaschen zu beobachten war, kann auf eine vorrangig photochemische Degradation der unchlorierten Organophosphate geschlossen werden. Die in den beiden urbanen Seen gemessenen Mediane der Organophosphat-Konzentrationen waren im Bereich 23 ng L^{-1} und 61 ng L^{-1} für TCEP, 85 ng L^{-1} und 126 ng L^{-1} für TCPP, <LOQ und 53 ng L^{-1} für TBEP, 8 ng L^{-1} und 10 ng L^{-1} für TiBP sowie 17 ng L^{-1} und 32 ng L^{-1} für TnBP. In den Seen der abgelegenen Gebiete lagen die Konzentrationen der Phosphorsäureester oftmals unterhalb oder nahe der Bestimmungsgrenze. In den drei abgelegenen vulkanischen Seen war TCPP die Substanz, die mit den höchsten Konzentrationen (Mediane zwischen 7 ng L^{-1} und 18 ng L^{-1}) gemessen wurde. TCEP, TCPP und TnBP wurden des Weiteren in den montanen Talsperren nachgewiesen. Da diese Talsperren vorwiegend zur Gewinnung von Trinkwasser genutzt werden, sind sie weitgehend frei von anthropogener Belastung. Ihr Zulauf beschränkt sich auf Niederschlag, Oberflächenabfluss der bewaldeten Umgebung, kleine Gebirgsbäche sowie Grundwasser. Das Vorkommen der Organophosphate in diesen abgelegenen Seen und Talsperren in Mittelgebirgslage bestätigt die Annahme, dass diese Substanzen über die Atmosphäre transportiert und durch nasse und trockene Deposition in die Oberflächengewässer eingetragen werden.

Das Vorkommen von chlorierten und unchlorierten Phosphorsäureestern im Grundwasser ist vom anthropogenen Einfluss während der Grundwasserneubildung bzw. -anreicherung abhängig. In Grundwasserproben von Quellen und tiefen Grundwassermessstellen, die nicht durch Oberflächenwasser beeinflusst werden, konnten die Substanzen in der Regel nicht nachgewiesen werden. Zudem haben die Ergebnisse gezeigt, dass die Infiltration von Niederschlag in ländlichen Gebieten keinen bedeutenden Eintragspfad für Organophosphate in das Grundwasser darstellt. In den Grundwasserproben (n = 10) aus dem Hessischen Ried, die nur durch infiltrierenden Niederschlag beeinflusst sind, wurde TCEP als häufigste Substanz mit einer maximalen Konzentration von 24 ng L^{-1} in weniger als der Hälfte der Proben gemessen. Die Median-Konzentrationen aller analysierter Organophosphate waren in diesen Proben unterhalb der Bestimmungsgrenze. Dennoch ist in städtischen Gebieten aufgrund deutlich stärker belasteter Niederschläge und Oberflächenabflüsse von einem Eintrag dieser Substanzen ins Grundwasser auszugehen. Höchste Konzentrationen an chlorierten und unchlorierten Organophosphaten (>0.1 µg L^{-1}) wurden in Grundwasser, das mit Deponie-Sickerwasser belastet ist sowie in Grundwasser, das durch Uferfiltration beeinflusst ist, gemessen.

Am Transekt Bahnbrücke im Oderbruch nahmen die im Fluss Oder gemessenen Konzentrationen von TCEP (540 ng L^{-1}), TCPP (2353 ng L^{-1}), TiBP (54 ng L^{-1}) und TnBP (99 ng L^{-1}) während der Uferfiltration in das Grundwasser nach dreijähriger Passage im Aquifer um 89% bis 97% ab. Aufgrund ihrer relativ hohen n-Octanol/Wasser-Verteilungskoeffizienten und Feststoff/Wasser-Verteilungskoeffizienten in Böden wird für TDCP und TBEP nur eine geringe Mobilität im Aquifer angenommen. Beide Substanzen wurden, wie auch TiBP und TnBP, nicht in Grundwasser mit einem höheren Grundwasseralter (>6 Jahre) nachgewiesen. Die Stabilität von TCEP und TCPP im Grundwasserleiter unter anaeroben Bedingungen wird dadurch bestätigt, dass die Substanzen selbst in Proben von Messstellen mit einem Grundwasseralter zwischen 20 und 45 Jahren mit Konzentrationen im Bereich 4–9 ng L^{-1} gemessen wurden. Dabei ist zu berücksichtigen, dass zu damaliger Zeit deutlich geringere Mengen der beiden Substanzen verwendet und in die Umwelt eingetragen wurden. Generell wurden von allen untersuchten Targetsubstanzen TCEP und TCPP am Häufigsten in den Grundwasserproben nachgewiesen. Die beiden chlorierten Flammschutzmittel wurden zuvor als potenzielle konservative organische Tracer im Grundwasser vorgeschlagen (*5*). Die Ergebnisse der Untersuchungen am Oderbruch haben gezeigt, dass diese Substanzen hierfür nicht geeignet sind, da ihre starke Konzentrationsabnahme zu Beginn der Uferfiltration vermutlich durch Adsorption und/oder biologische oder chemische Transformation in der hyporheischen Zone und nicht ausschließlich durch Verdünnung im Grundwasserleiter bedingt ist. Zurzeit liegen jedoch noch keine quantitativen Daten zum Abbau von chlorierten und unchlorierten Organophosphaten in Böden und Grundwasser vor. Die Konzentrationen der stärker wasserlöslichen organischen Spurenstoffe Triglyme und Tetraglyme (beides Polyether) nahmen hingegen, wie auch die Konzentrationen der anorganischen Ionen Cl^{-} und Na^{+}, im Grundwasser linear mit wachsender Entfernung zum Fluss ab und implizieren ein konservatives Verhalten während der Uferfiltration.

Da viele der komplexen Prozesse, die für den Rückhalt von organischen Spurenstoffen im Wasser bei der Uferfiltration verantwortlich sind, noch nicht vollständig untersucht sind, besteht weiterhin Forschungsbedarf, um den Abbau/Rückhalt der chlorierten und unchlorierten Phosphorsäureester im Grundwasser besser beurteilen zu können. Des Weiteren werden mehr Monitoring-Daten benötigt, um den Anteil der durch trockene und nasse Deposition eingetragenen Phosphorsäureester an der aktuell beobachteten Belastung von Oberflächengewässern mit Organophosphaten quantifizieren zu können. Die vorliegenden Daten lassen aber bereits erkennen, dass dieser Anteil in Ballungsgebieten erheblich sein kann.

Abbreviations

c	Concentration
CAS	Chemical Abstracts Services registry number
DIN	German Institute of Standardizations
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EFRA	European Flame Retardants Association
EI	Electron impact
ESIS	European substances information system
EU	European Union
GC	Gas chromatography
HLUG	Hessian Agency for the Environment and Geology
HPLC	High performance liquid chromatography
HPV	High Production Volume Chemical
IS	Internal standard
IUCLID	International uniform chemical information database
K-factor	Correction factor
LOD	Limit of detection
Log K_{oc}	Solids/water partition coefficient for soils
Log K_{ow}	n-Octanol/water partition coefficient
LOQ	Limit of quantitation
m/z	Mass to weight ratio
MS	Mass spectrometry
OPs	Organophosphates
POP	Persistent organic pollutant
PVC	Polyvinyl chloride
R	Coefficient of correlation
R^2	Coefficient of determination
R-factor	Response factor
RSD	Relative standard deviation
SDVB	Styrene-divinylbenzene polymer
SIM	Selected ion monitoring
SPE	Solid phase extraction
SPIN	Database for substances in preparations in Nordic countries
SVOC	Semi-volatile organic compound

Abbreviations

SWHT	Storm water holding tank
TBEP	Tris(2-butoxyethyl) phosphate
TCEP	Tris(2-chloroethyl) phosphate
TCPP	Tris(2-chloro-1-methylethyl) phosphate
TDCP	Tris(1,3-dichloro-2-propyl) phosphate
TiBP	Tri-iso-butyl phosphate
TIC	Total Ion chromatogram
TnBP	Tri-n-butyl phosphate
TOC	Total organic carbon
TPeP	Tripentyl phosphate
UV	Ultraviolet
v/v	Volume by volume
w/w	Weight by weight
W_s	Water solubility
ZALF	Leibniz-Centre for Agricultural Landscape Research

1 Introduction

1.1 Environmental impact of organophosphates

The focus on environmental issues caused by so-called “emerging” or “re-emerging" pollutants such as pharmaceuticals, personal care products, steroid hormones, flame retardants, and plasticizers increased significantly during the past decades. These chemicals are continuously released into the environment as a result of anthropogenic activity and are typically characterized by high production volumes, high polarity, and low biodegradability. Although they are largely used since a long time to make human life more comfortable and secure, information about their long-term ecotoxicological risks and environmental fates in different matrices are poorly documented. For most of these chemicals it is almost impossible to recapture them once emitted to the environment. Therefore potential risks to human health and the environment arise when they persist, e. g., in the aquatic ecosystem. These low concentrated but potentially harmful trace organic compounds often enter the aquatic environment via discharges to the domestic sewer systems. A wide range of them is not readily removed during wastewater treatment and can therefore reach associated receiving surface waters. Within this context, contamination of groundwater with trace organic pollutants during bank filtration of affected surface water or artificial recharge of treated wastewater has become of great concern.

Organophosphorus flame retardants and plasticizers are one group of re-emerging pollutants in the environment for which significant data gaps are existing with respect to their environmental fate and potential adverse effects to the ecosystem and human health (*6,7*). Various direct, e. g., leakage, and diffuse sources, e. g., road traffic and urban settlements, of organophosphates (OPs) in the environment have been discussed in previous studies (*3,4*). Anthropogenic activities including emissions from vehicles and buildings, abrasion of tires, and leakage of hydraulic fluids and motor/transmission oils from vehicles are considered as potential OP sources. The OPs have previously been detected in several indoor (*8-11*) and outdoor (*3,4,6,12*) environments as well as human urine (*13,14*). In indoor environments, OPs were found in dust (*8,11*) and indoor air (*15-17*) at mg kg^{-1} levels and ng m^{-3} or µg m^{-3} levels, respectively. They have also been detected in different environmental matrices such as surface water (*4,18,19*), groundwater (*20,21*), wastewater (*22,23*), leachate (*24*), precipitation (*25,26*), particulate matter (*27*), pine needles (*28*), and sediments (*29,30*). In the aquatic environment, OP concentrations varied between a few ng L^{-1} and several µg L^{-1}. Hence, the acceptable OP concentration level of 0.1 µg L^{-1} in water proposed by the Federal

Environmental Agency of Germany (*31*) was often exceeded even in treated wastewater and thereof impacted surface waters.

1.2 Target substances

Organophosphorus flame retardants and plasticizers are derivatives of phosphoric acid, composed of either similar or varied organic materials that can contain either non-halogenated or halogenated alkyl groups or aryl groups. The chlorinated trialkyl phosphates tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCP) as well as the non-chlorinated ones tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) are mainly applied as flame retarding additives to materials such as plastics, textiles, construction foams, timber, e. g., in cars, furniture, electronics, etc. (Table 1-1).

Table 1-1. Application purposes and CAS registry numbers of the target compounds.

Compound	**Acronym**	**CAS registry No.**	**Usage**
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	flame retardant (polyurethane foam) [a]
Tris(2-chloro-1-methylethyl) phosphate	TCPP	13674-84-5	flame retardant (polyurethane foam) [b]
Tris(1,3-dichloro-2-propyl) phosphate	TDCP	13674-87-8	flame retardant (polyurethane foam), textiles [c]
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3	flame retardant plasticizer, floor polish, anti-foaming agent [d]
Tri-n-butyl phosphate	TnBP	126-73-8	aircraft hydraulic fluids, anti-foaming agent, plasticizer, lacquers, paints [e]
Tri-iso-butyl phosphate	TiBP	126-71-6	aircraft hydraulic fluids, anti-foaming agent, plasticizer, lacquers, paints [f]

[a] (*32*)
[b] (*33*)
[c] (*34*)
[d] (*35*)
[e] (*36*)
[f] http://techcenter.lanxess.com/fcc/emea/de/products/datasheet/TiBP_d.pdf (accessed 03.12.2009).

These OPs suppress flaming (oxidation of gaseous products) and glowing (solid phase combustion) during combustion of polymers due to the formation of phosphoric acids. The phosphoric acids can form a coating that retards oxidative degradation. Halogens (e. g., chloride, bromide) in halogenated trialkyl phosphates provide additional flame reduction by trapping free-radicals and thus suppressing the combustion chain reaction. The fire resistance and thermal stability of trialkyl phosphates is also important for their use as hydraulic fluids and lubricants. In general, TCEP, TCPP, and TDCP are prepared commercially by reaction of ethylene oxide or propylene oxide with phosphorus oxychloride (*37*). TBEP, TiBP, and TnBP are produced by reacting phosphorus oxychloride and butyl glycol or butyl alcohol, respectively (*35,36*). These compounds are widely used industrial chemicals with an estimated global annual consumption of 186,000 t yr^{-1} in 2001. In the European Union (EU), their consumption raised from 58,000 t yr^{-1} in 1995 to 91,000 t yr^{-1} in 2006 (http://www.cefic-efra.com). According to an increasing global demand of fire protected materials and products, the production volume of chlorinated and non-chlorinated organophosphates is expected to further increase worldwide (*29*). All six organophosphates are included in the list of EU High Production Volume Chemicals (HPVs) with production/import volumes exceeding 1,000 t yr^{-1}. Due to the partly insufficient knowledge about their risk potential, TCEP (second priority list), TCPP, and TDCP (both fourth priority list) are also subject to EU risk assessment processes. As these compounds are not chemically bound to the polymer matrix when used as plastic additives, dissolution of retardants from the surfaces of treated products and volatilization into the environment can occur. Removal through abrasion and disposal is also possible. In general, organophosphate levels of about 5% to 15% (w/w) of the finished product, e. g. foam, are required to achieve appropriate flame retarding effects (*31*). Approximately 40% of a flame retardant (e. g., TCPP) used in a finished product is available for release (*33*).

TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP are non-flammable, non-explosive, odorless, and colorless liquids. Due to their physicochemical properties, they can be classified as semi-volatile polar organic compounds (*10*) with water being a preferred environmental compartment of distribution (*38*). The water solubility of the phosphate triesters is in the range of 18.1 mg L^{-1} for TDCP and 7820 mg L^{-1} for TCEP (Fig. 1-1). In natural waters containing for instance 50 mg L^{-1} of suspended sediment with an organic carbon content of 10%, more than 90% of the present OPs are expected to be in the aqueous phase (*37,39*). Nevertheless, the n-octanol/water partition coefficient values (log K_{ow}) are moderate to high (1.7–4.0) and indicate a relatively high affinity of OPs to airborne particles. Their adsorption behavior in soils is described as being proportional to the soil organic carbon content (*33*). High log K_{oc} values (soil/sediment water sorption coefficient) for TDCP (4.09) and TBEP (5.67) suggest low leaching potential in soils relative to many organophosphate pesticides (*37*). The calculated Henry's law constants of the analyzed organophosphates ($1.22 * 10^{-4}$ –0.323 Pa m^{-3} mol^{-1}) indicate low rates of volatilization from the aquatic phase to air. Relative to volatilization from water, the release of organophosphates from products is more likely because of their moderate vapor pressure. Their vapor pressures at 25 °C range from 1.71 Pa for TiBP to $5.6 * 10^{-6}$ Pa for TDCP.

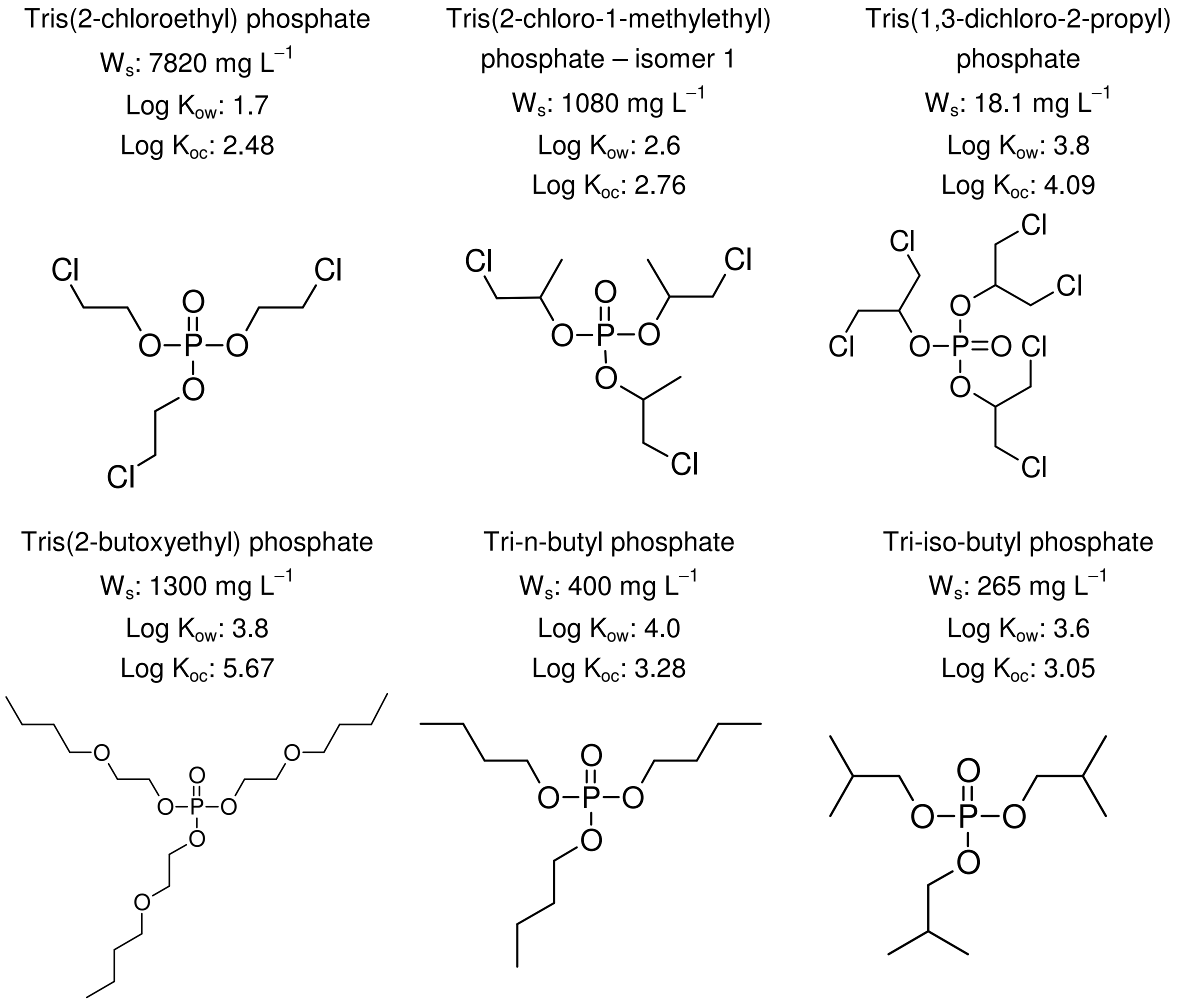


Fig. 1-1. Structure and physicochemical characteristics of the organophosphate triesters (W$_s$ = water solubility, log K$_{ow}$ = n-octanol/water partition coefficient, log K$_{oc}$ = soil/sediment water sorption coefficient) (*38*).

OPs are generally resistant to direct photolysis in water du to the absence of significant absorbance of light with wavelengths longer than 290 nm. Additionally, hydrolysis in neutral or acidic waters (pH 5–7) is negligible (*37,40*). Furthermore, the chlorinated OPs (TCEP, TCPP, and TDCP) are characterized by low biodegradability. In general, the potential for biodegradation of alkyl phosphates decreases with the length of the alkyl chains. The main path for biodegradation of phosphate esters is supposed to comprise a stepwise microbially catalyzed hydrolysis of the ester bonds, with phosphoric acid di- and mono-esters as degradation products (*41,42*). Atmospheric photooxidation with estimated half-lives <24 h is suggested to be another degradation pathway for chlorinated ($t_{½}$ = 8.6–21.3 h) and non-chlorinated ($t_{½}$ = <1–4 h) organophosphates in the environment (*32-34*).

The chemical structure of organophosphorus flame retardants and plasticizers is similar to that of organophosphorus insecticides. These insecticides are designed to affect the nervous system of insects. In the human nervous system, TCEP, TBEP, and TnBP may inhibit the enzyme acetylcholinesterase, which is necessary to terminate nerve signals. Nevertheless, the acute toxicity of OPs towards aquatic organisms varies among the compounds as well as between the species, although their potential effects at environmental concentrations are mostly unknown (*7*). Due to its toxic effects to aquatic organisms and its classification in the EU as "potential human carcinogen", TCEP was mainly substituted by TCPP in Europe since mid 1990s (*31*). TCPP is expected to be non-toxic to aquatic organisms at concentrations less or equal than 1 mg L^{-1} (*33*). However, data gaps referring to its carcinogenicity still exist (*2*). TDCP has been classified as dangerous for aquatic organisms because of its toxicity (*34*). TBEP and TiBP are not classified at EU level, whereas TnBP is labeled as a carcinogenic substance in the online European chemical substance information system (ESIS). In risk assessments, TCEP, TCPP, and TDCP do not fulfill the PBT criteria, i.e., persistence, bioaccumulation, and toxicity, as there is no indication of bioaccumulation. After dermal or oral resorption OPs are spontaneously or enzymatically hydrolyzed in blood and urine to form the corresponding dialkyl phosphates as main metabolites (*13*).

1.3 Research questions

So far, treated and untreated wastewater discharges are presumed to be the main entry-pathway for OPs to surface waters and impacted groundwater (*1*). However, organophosphorus flame retardants and plasticizers have recently been detected in rainwater and closed hydrographic systems (*4*), even in the absence of industrial activities, anthropogenic influences, and wastewater discharges. Transport of OPs to remote areas via the atmosphere after emission from urban settlements and road traffic has been proposed (*3*). Nevertheless, monitoring data supporting these observations are scarce though most of these studies are limited to few spot samplings at a limited number of sampling sites. Up to now, no long-term systematic study of the occurrence of OPs in precipitation at a variety of sampling sites under different anthropogenic impact has been conducted.

Results from previous studies indicated that non-chlorinated OPs are less stable in aquatic and atmospheric environments than chlorinated flame retardants (*1,24*). Some OPs were primarily biodegraded when exposed to natural microbial river populations (*41*). In laboratory experiments, a second order photodegradation reaction of OPs was observed in UV-irradiated solutions containing hydrogen peroxide (*40*). However, it is not clear, if OP concentrations in lentic surface waters are affected by photochemical decomposition under natural sunlight. Furthermore, adsorption, dilution, and biological/chemical transformation processes of OPs have so far only been studied with respect to the attenuation of OPs in sewage treatment plants (*43,44*) but are not yet sufficiently understood for groundwater, surface water and in systems with interaction of groundwater and surface water. Infiltration experiments with wastewater for groundwater recharge indicated little TCEP attenuation causing a high potential of the compound to reach groundwater (*21,45*). Particularly in urban areas, groundwater contaminated with chlorinated OPs might cause problems for drinking water production.

Significant knowledge gaps concerning the distribution, stability, adsorption, and transformation of chlorinated and non-chlorinated OPs in the environmental compartments water and atmosphere become evident. The main research questions of the present doctoral thesis are in summary:

1) **Atmospheric washout of OPs by precipitation:** Does precipitation represent an all-season source and entry-pathway of OPs into the aquatic environment? Is atmospheric transport from urban to remote areas relevant for OP distribution?

2) **Temporal variation of OP concentrations:** Can fluctuations of OP concentrations in precipitation and lentic surface waters (e. g., lakes, oxbow lakes, storm water holding tanks) be observed as seasonal trends and are they caused by degradation processes?

3) **Groundwater polluted by OPs:** How far is groundwater influenced by infiltrating precipitation and OP-loaded surface water during bank filtration? Do OPs generally persist in the aquifer and are chlorinated OPs suitable as conservative tracers?

2 Research papers

I Analytical method for the determination of organophosphates in water by solid phase extraction and gas chromatography-mass spectrometry

Abstract

The six organophosphates (OPs) tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) were identified and quantified in different aqueous samples, i.e., precipitation, lake water, and groundwater. A rapid and effective method for the determination of phosphoric acid triesters in water samples is described and evaluated. Samples were analyzed for the six OPs by gas chromatography-mass spectrometry after pressure filtration and solid phase extraction. The limits of detection ranged from 1 ng L^{-1} to 3 ng L^{-1} in the water samples. Recoveries of the analytes in spiked ultrapure water and lake water samples ranged from 85% to 99% and 72% to 99%, respectively.

Introduction

First reports of the environmental occurrence and fate of organophosphates (OPs) employed as flame retardants and plasticizers date back to the late 1970s (*41*) and 1980s (*46-48*). During the 1960s and 1970s the use of flame retardants increased greatly because of improved fire safety demands in commercial products made from synthetic polymers (*37*). OPs such as tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) are derivatives of phosphoric acid containing either non-halogenated or halogenated alkyl groups. Currently these flame retarding compounds are high production volume chemicals (HPV) with an annual global consumption of 296,000 t yr^{-1} (2004), thereof almost 83,700 t yr^{-1} in Western Europe (http://www.cefic-efra.com). Tri-chloroalkyl phosphates are mainly applied as flame retardants in polyurethane foam in domestic, public, and automotive applications (*32-34*). Non-chlorinated alkyl phosphates are often employed as plasticizers, but also as anti-foaming agents, flame retardants, and additives in paints, lacquers, hydraulic fluids or floor polish (*35,36*). TnBP is also an important solvent for the extraction in nuclear fuel processing (*49*). The purposes of application of the analyzed OPs are summarized in Table 1-1 (chapter 1.2). Fig. 1-1 (chapter 1.2) gives an overview of their structural formulae, water solubility, and n-octanol/water partition coefficients.

Organophosphorus flame retardants are not chemically bound to the polymer when used as plastic additives. Therefore volatilization and leaching from materials and products into indoor and outdoor environments to significant levels have to be considered. According to the literature, OPs can be regarded as widely spread substances of anthropogenic origin in the environment (*1,6*). So far, OPs have been detected in treated and untreated wastewater (*50,51*), wastewater-impacted surface water (*18,52*), groundwater affected by surface water (*20*), rain (*25,26*), snow (*3*), aerosols (*27*), and pine needles (*28*). Furthermore, OPs were detected in indoor air (*16,17*), house dust (*8,11*), and the interior of vehicles, e. g. fogging condensate (*9,10,53*). For some OPs a wide range of adverse biological effects have been reported. Consequently, TCEP, TCPP, and TDCP are subject to the European Union risk assessment processes (*32-34*).

Within this study, an analytical method for qualitative and quantitative determination of OPs in water samples published by Fries and Püttmann (*54*) is improved and evaluated to investigate the target compounds TCEP, TCPP, TDCP, TBEP, TnBP, and TiBP in precipitation, lake water, and groundwater samples from urban and remote areas. The applied analytical method is based on solid phase extraction (SPE) followed by gas chromatography-mass spectrometry (GC-MS) of the extracts.

Experimental

Chemicals. TCPP (a mixture of three isomers) and TDCP were kindly supplied by Akzo Nobel (Amersfoort, The Netherlands). TCEP, TiBP, TnBP, TBEP and the internal standard squalane were obtained from Sigma Aldrich (Steinheim, Germany). Surrogate standard tripentyl phosphate (TPeP) was obtained from TCI Europe (Zwijndrecht, Belgium). Acetonitrile (ultrapure HPLC grade) was obtained from J. T. Baker (Deventer, The Netherlands) and was used as received. All other organic solvents were analytical grade (Merck, Darmstadt, Germany) and were distilled before use. Ultrapure water was produced from de-ionized water using an Astacus ultrapure water purification system (MembraPure, Bodenheim, Germany). Individual and composite stock solutions (1 µg μL^{-1}) of target compounds were prepared in methanol/acetonitrile (1/1 v/v) and stock solutions (1 µg μL^{-1}) of the internal standard (IS) squalane and surrogate standard TPeP were prepared in hexane and stored in the dark at 5 °C for a maximum of 1 month. Working standard solutions were obtained by appropriate dilution of stock solutions.

Sampling. A detailed description of all sampling sites is provided in research papers II–VI in chapter 2. Sampling of rain and snow was carried out from November 2007 to April 2009 (n = 255). Lentic surface waters such as lakes, storm water holding tanks (SWHT), and reservoirs were sampled during June 2007 and October 2009 (n = 210). Groundwater samples were collected in 2009 (n = 72).

Pressure filtration. Samples were extracted by SPE. To avoid plugging of SPE cartridges, all rain, melted snow, and surface water samples were subjected to pressure filtration before extraction, to remove insoluble components and suspended particulate matter. Groundwater samples and OP solutions of ultrapure water and lake water prepared for the laboratory degradation experiments were not filtered before extraction.

A stainless steel pressure holder (2.12 L capacity; Sartorius, Goettingen, Germany) with a 142 mm diameter borosilicate glass fiber filter (filter pore size <1 µm; type A/E, Pall, Dreieich, Germany) was used at an operating pressure of 1.5 bar (nitrogen). To avoid blank problems all glass fiber filters were heated in an oven for more than 2 h at 400 °C before being enclosed in aluminum foil. The 2.12 L capacity of the stainless steel holder enabled the total sample volume to be incorporated in the barrel, thus minimizing contamination from ambient laboratory air. TPeP was used as a surrogate internal standard and was spiked onto the top of the glass fiber filter (2 µL of a 1 µg μL^{-1} standard) before filtration. After filtration of each sample the filtration equipment was decomposed and thoroughly cleaned with ultrapure water.

To exclude the risk of significant losses of analytes (e. g., particle bound OPs) during filtration, filtered (n = 5) and non-filtered (n = 5) samples (1 L) of a 10 L rain sample from Frankfurt/Main and a 10 L water sample from SWHT Kalbach were analyzed and compared regarding their OP concentrations.

Solid phase extraction (SPE). SPE was carried out using Bond Elut PPL cartridges (1 mL; Varian, Darmstadt, Germany). Cartridges comprised a functionalized styrene-divinylbenzene (SDVB) polymer as non-polar sorbent (100 mg). The high surface area (640 m^2 g^{-1}) of Bond Elut PPL was most suitable for the extraction of polar and medium polar species from large volumes of water samples. Up to 20 cartridges were mounted on a VacElut 20 cartridge processing station and were sequentially conditioned with 1 mL methanol by means of gravitation and 1 mL methanol/acetonitrile (1/1 v/v) using a vacuum of 800 mbar. Subsequently, cartridges were filled with 1 mL ultrapure water. They were connected to the samples via Teflon adapters and Teflon tubes filled with ultrapure water. Samples (1–2.5 L) were then passed through the cartridges using a vacuum of 700–800 mbar. A flow rate of 300 mL h^{-1} was not exceeded. Bottle openings were closed by stoppers equipped with activated charcoal filter tubes (Type Niosh; Dräger, Luebeck, Germany) to minimize contact of the water surface with organic compounds in ambient laboratory air during the extraction process. After extraction (cartridges must not run dry) the SPE cartridges were dried in a nitrogen stream and then Elutd three times with 333 µL methanol/acetonitrile (1/1 v/v). These extracts were again dried in a nitrogen stream and dissolved in 100 µL acetonitrile. Subsequently, squalane (4 µL of a 1 µg μL^{-1} standard) was added to each sample as an internal quantitation standard.

Gas chromatography-mass spectrometry. From June 2007 to July 2008 quantitative analyses were performed using a Fisons gas chromatograph GC 8000 coupled to a Fisons MD 800 mass spectrometer (Thermo Fisher, Dreieich, Germany). Acquired data were processed using Fisons MassLab software (version 1.3). The gas chromatograph was equipped with a SLB^{TM}-5ms capillary column (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness; Supelco, Bellefonte, PA). Helium (≥99.999%) was used as carrier gas at a constant pressure of 70 kPa. The initial column oven temperature (80 °C) was increased at 4 °C min^{-1} to a final temperature of 300 °C, which was maintained for 25 min. Sample injection (1 µL) was accomplished using a Fisons AS 800 autosampler in the splitless mode (1 min splitless time) at an injector temperature of 240 °C. The mass spectrometer was operated in electron impact (EI) mode with 70 eV ionization energy and full scan spectra were collected in the range m/z 50–600.

Since August 2008 samples were analyzed by a Trace GC Ultra gas chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich, Germany) using the same type of capillary column (SLB^{TM}-5ms; 30 m length, 0.25 mm internal diameter, 0.25 µm film thickness) and the same oven temperature program as in the Fisons GC-MS system: 80 °C (held for 1 min), at 4 °C min^{-1} to 300 °C (held for 25 min). Helium (≥99.999%) was used as carrier gas at a constant flow of 1.1 mL min^{-1}. Sample injections (1 µL) were made in splitless mode (1 min splitless time) using a Thermo Scientific AS 3000 autosampler. Injector temperature was set at 240 °C. The GC-MS transfer line temperature was maintained at 280 °C and the ion source temperature was held at 220 °C. The mass spectrometer was operated in EI mode (70 eV). EI spectra were recorded in full scan mode (m/z 50–600). Excalibur software (Thermo Fisher Scientific, version 2.0.7) was used to process the acquired data. All mass spectra were compared with spectra in the Wiley AccessPak spectral library, 8th edition (Palisade, Ithaca, NY).

Quantitation with internal standard. Identification of target compounds was achieved by mass spectra (Wiley AccessPak spectral library) and retention times of standards. Analytes were quantified by the internal standard method (*54*). Analyte concentrations in water samples were calculated by measuring the peak areas of each compound relative to the peak area of the IS. Squalane was used as IS for quantitation, whereas surrogate standard TPeP acted as qualifier.

The ratio between the peak area of an analyte and the peak area of the IS (both measured in total ion chromatogram TIC) was described as response factor R. Quantitation of the analytes was performed in selected ion monitoring (SIM) mode. Therefore, another correction factor K was necessary to specify the relation between the peak area of a compound in the TIC and its peak area in the mass trace. To determine the analyte specific R- and K-factors, analyte standards (2 µL of a 1 µg µL^{-1} standard) and IS squalane (2 µL of a 1 µg µL^{-1} standard) were diluted in 100 µL acetonitrile and injected into the GC-MS system. Afterwards the resulting peak areas of the six target compounds were compared with the peak area of the IS squalane. Correction (1) and response (2) factors for the target compounds were estimated according to the following equations

$$K = \frac{A_{TIC}}{A_{m/z}} \qquad (1)$$

$$R = \frac{A_{TIC}}{m_A} \times \frac{m_{IS}}{A_{IS}} \qquad (2)$$

where A_{TIC} is the peak area of the analyte in TIC, $A_{m/z}$ is the peak area of the analyte in mass trace m/z, A_{IS} is the peak area of the IS in TIC, m_A is the mass of the analyte, and m_{IS} is the mass of the IS. Both factors were determined for the GC-MS system at any sample sequence. Ions used for quantitation in SIM mode were m/z 63 (TCEP), m/z 75 (TDCP), m/z 99 (TCPP, TnBP, TiBP), and m/z 125 (TBEP).

On the basis of these R- and K-factors, analyte concentrations (c_i) in water samples were calculated according to equation (3)

$$c_i = \frac{A_i}{A_{IS}} \times \frac{m_{IS}}{V_{sample}} \times \frac{1}{R} \times K \qquad (3)$$

where A_i is the peak area of the analyte in mass trace m/z, A_{IS} is the peak area of the IS in TIC, m_{IS} is the mass of the IS (e. g., 4 µg), V_{sample} is the volume of the water sample (e. g., 2.5 L), R is the response factor, and K is the correction factor.

Technical TCPP is mainly composed of three isomers at a ratio of approximately 9:3:1. Another isomer 4 named tris(2-chloro-1-propyl) phosphate is only present in trace levels (<1% w/w). The main isomers are tris(2-chloro-1-methylethyl) phosphate (isomer 1, 50–85% w/w), bis(1-chloro-2-propyl)-2-chloropropyl phosphate (isomer 2, 15–40% w/w), and bis(2-chloropropyl)-1-chloro-2-propyl phosphate (isomer 3, <15% w/w) (*33*). The quantitation of TCPP was performed by summation of isomer 1 and isomer 2.

Quality assurance. To prevent the introduction of contaminant OPs during sampling, all laboratory equipment was glass, stainless steel, or Teflon. Prior to sampling, glass bottles were rinsed with ultrapure water and methanol, respectively, and then heated to 110 °C for a minimum of 6 h. Blanks for analyses were ultrapure water placed in glass bottles and treated in the same way as field samples, to test for sample contamination during transport and processing. Validation of the analytical procedure was achieved by the method of standard addition of TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP to ultrapure water and lake water samples (Lake Holzmaar, Eifel, Germany). Three lake water samples (not containing the analytes) and six ultrapure water samples of 1 L volume were spiked with 2 µg of each target compound prior to extraction to calculate OP recovery rates.

The limit of detection (LOD) was estimated for each substance in accordance to DIN norm 32645 using the computer program DINTest 2000 (Schmitt and Herbold, University of Heidelberg), on the basis of measured calibration curves. Ultrapure water samples (1 L) spiked with different standard mixtures of target compounds were extracted by SPE. Concentration levels were 1 ng L^{-1}, 2 ng L^{-1}, 5 ng L^{-1}, 20 ng L^{-1}, 50 ng L^{-1}, 200 ng L^{-1}, and 1000 ng L^{-1}. Seven-point calibration curves were generated using three replicates of each concentration. Corresponding to DIN 32645, the limit of quantitation (LOQ) for the analytes was estimated as three times their LOD.

Results and discussion

MS fragmentation and quantitation parameters. The fragmentation of the OPs under EI-MS analysis is dominated by three successive McLafferty rearrangements with consecutive losses of the alkyl substituents resulting in protonated phosphoric acid (m/z 99) as final cation (*55-57*). For all six analytes, no molecular ions were observed in the mass spectra under the applied EI ionization. Fragmentation of TnBP and TiBP molecular ions was characterized by losses of the three butyl groups resulting in ions m/z 211, m/z 155, and base peak m/z 99. The mass spectrum of TnBP is shown in Fig. I-1a. Clusters of product ions separated by two mass units from each other were obtained in the mass spectra of chlorinated OPs due to the different isotope masses and ratios of chlorine (Cl^{35} and Cl^{37}). Relatively intense ions at m/z 249, m/z 251, and m/z 253 for TCEP were attributed to the loss of chlorine from the molecular ion (Fig. I-1b). During the McLafferty rearrangement of TCEP, the positive charge of the protonated molecule can be transferred to one of the alkyl groups. This alkyl group was observed as alkyl cation (m/z 63) after splitting of the C – O bond. In case of TCPP and TDCP, characteristic ion clusters attributed to losses of CH_2Cl from their molecular ions appeared at m/z 277, m/z 279, m/z 281 and m/z 379, m/z 381, m/z 383, respectively.

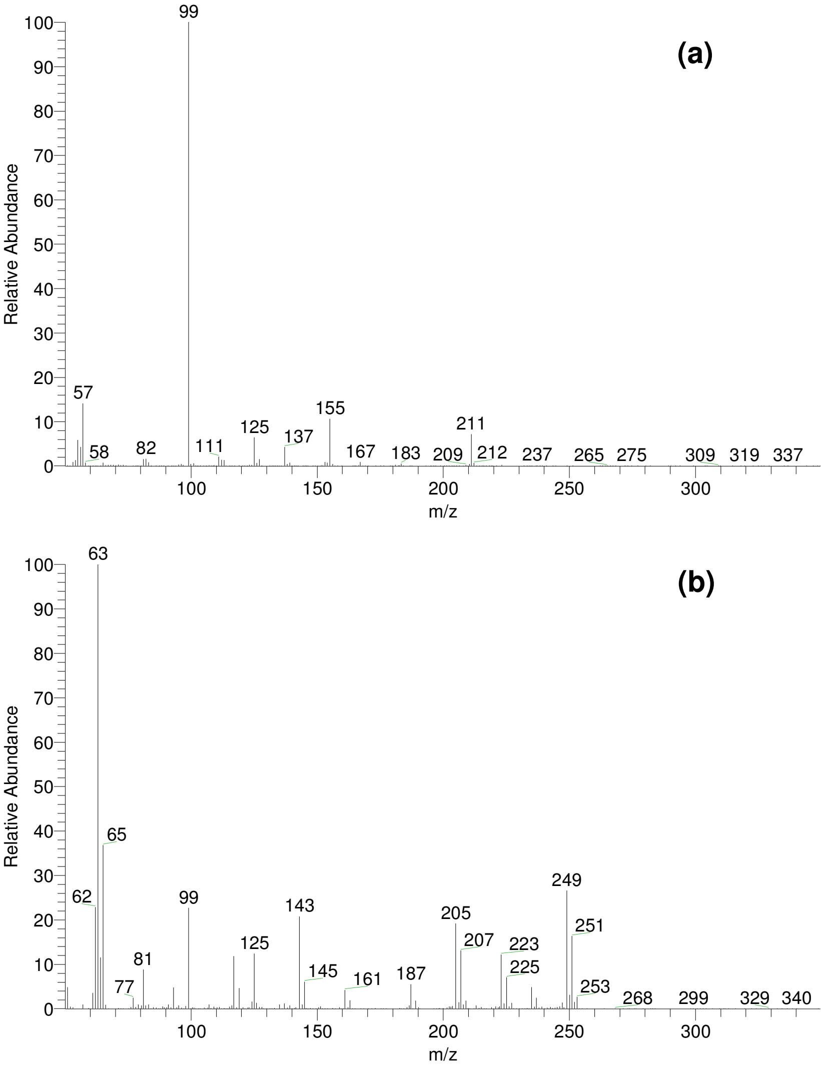


Fig. I-1. Mass Spectra of (a) TnBP and (b) TCEP obtained by EI-MS analysis in positive ion mode.

Ions used for quantitation and the values of the R- and K-factors are listed in Table I-1. R-factors of the analytes ranged between 0.33 for TBEP and 1.08 for TiBP.

Table I-1. Molecular weights (*38*) and quantitation parameters of analytes.

Compound	**Molecular weight (g mol^{-1})**	**Quantifier ions m/z**	**Qualifier ions m/z**	**Response factor** [a)]	**Correction factor** [a)]
TCEP	285.5	63	143, 249	0.46	6.31
TCPP	327.6	99	125, 157, 201	0.36	8.34
TDCP	430.9	75	99, 191, 381	0.46	8.16
TBEP	398.5	125	85, 199, 299	0.33	18.44
TnBP	266.3	99	155, 211	0.66	2.01
TiBP	266.3	99	155, 211	1.08	2.04

[a)] Response and correction factors were determined at any GC-MS sample sequence.

Both R- and K-factors can vary slightly during longer sample sequences. Therefore, two standard mixtures (Fig. I-2) were analyzed in the beginning and end of one GC-MS series of measurements. Concentrations of the target analytes in water samples were afterwards calculated with the mean values of the determined R- and K-factors. Furthermore, both factors were determined at any GC-MS sample sequence.

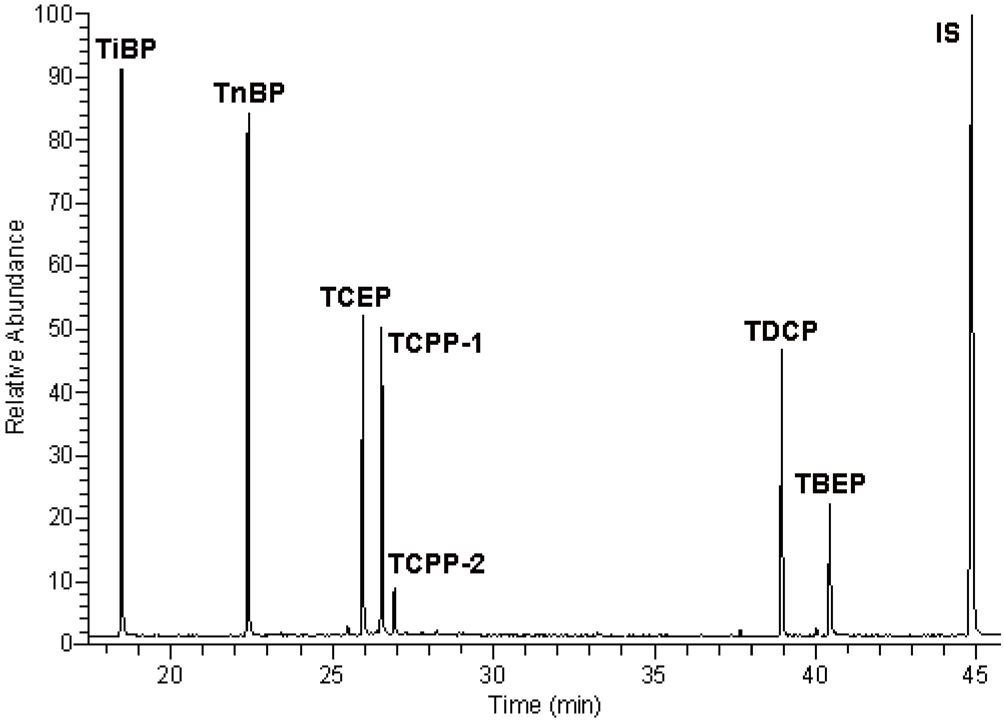


Fig. I-2. Total ion chromatogram (TIC) of an OP standard mixture plus internal standard (IS) squalane.

Quantitation with internal standard squalane has been approved in previous studies (*19,54*). Due to its low polarity, a removal of squalane from the Bond Elut PPL sorbent during elution with methanol/acetonitrile (1/1 v/v) can be excluded. So even if squalane is present in natural water samples, it will not occur in the extracts after SPE (*54*). Furthermore, squalane was used as internal standard since this compound is not superimposed by other constituents of rain and surface water.

Recoveries. The results of the filtration experiment are presented in Table I-2. For both rain and water samples the relative standard deviation (RSD) between the mean OP concentration of the filtered and non-filtered samples were clearly below 10% for all OPs. The water solubility of the six OPs is moderate to high (*58*). Therefore, most of the OPs are expected to be dissolved in the water phase (*39*). The results of the present filtration experiment and the results of Kawagoshi et al. (*39*) confirmed that potential losses of OPs during filtration with glass fiber filters (pore size 1 µm) can be neglected. However, the filtration step is necessary to provide acceptable enrichment rates of OPs in marginally polluted water samples since SPE cartridge plugging occurs if non-filtered water samples exceed the volume of 0.5–1 L.

Table I-2. Mean OP concentrations (ng L^{-1}) and relative standard deviations (RSD) of filtered and non-filtered precipitation (Frankfurt/Main) and surface water (SWHT Kalbach) samples.

Compound	**Precipitation**			**SWHT**		
mean c (ng L^{-1})	filtered n = 5	non-filtered n = 5	RSD (%)	filtered n = 5	non-filtered n = 4	RSD (%)
TCEP	64	63	0.7	101	104	2.2
TCPP [a)]	441	444	0.5	1911	1848	2.7
TDCP	121	126	3.0	51	54	3.4
TBEP	29	29	1.6	57	55	1.7
TiBP	216	225	3.0	63	60	3.0
TnBP	118	121	2.1	255	229	7.7

[a)] Sum of two isomers; tris(2-chloro-1-methylethyl) phosphate, CAS 13674-84-5; bis(1-chloro-2-propyl)-2-chloropropyl phosphate, CAS 76025-08-06.

Table I-3 summarizes the attained results from the extractions of spiked ultrapure water and lake water samples. SPE recovery rates in ultrapure water (n = 6) ranged from 85% to 99% for all analyzed OPs with RSDs between 2.4% and 7.2%. Recoveries from 72% to 99%, with RSDs also below 10%, were obtained for all compounds in the three spiked lake water samples. Concerning the real water samples (e. g., rain, snow, surface water, groundwater), no adjustments were made for differences in recoveries of individual OPs during SPE.

Table I-3. Recovery rates and relative standard deviations (RSD) of the target compounds in ultrapure water and lake water samples.

Compound	**Recovery ± RSD (%) (n = 6, ultrapure water)**	**Recovery ± RSD (%) (n = 3, lake water)**
TCEP	95±2.7	99±3.5
TCPP [a)]	91±5.5	81±8.0
TDCP	99±2.4	92±0.5
TBEP	93±7.2	88±4.1
TnBP	89±4.6	82±9.2
TiBP	85±6.2	72±9.9

[a)] Sum of two isomers.

Previous laboratory experiments have shown the stability of OPs in water for at least two weeks in the absence of light and oxygen. All water samples were stored in brown glass bottles for no more than 7 days at 5 °C until being analyzed in the laboratory. Losses of target compounds resulting from sample alteration following collection were considered to be negligible.

Calibration and limits of detection. The LODs for the six OPs were determined using a significance level of 1% and an error of 33.3%. Using the Fisons GC-MS system, the LODs for TCEP (2 ng L^{-1}), TCPP (1 ng L^{-1}), TDCP (1 ng L^{-1}), TBEP (3 ng L^{-1}), TnBP (1 ng L^{-1}), and TiBP (2 ng L^{-1}) were somewhat higher than those obtained for the Thermo Scientific GC-MS system (LOD of 1 ng L^{-1} for each of the six substances). The LOQ was estimated as three times the LOD according to DIN 32645 and ranged between 3 ng L^{-1} (TCEP) and 4 ng L^{-1} (TBEP) for the Thermo Scientific GC-MS system and 3 ng L^{-1} (TCPP) and 8 ng L^{-1} (TBEP) for the Fisons GC-MS system. Fig. I-3 shows the calibration curves (mean, n = 3) of all OPs using Thermo Scientific GC-MS system. Correlation coefficients for all analytes were R^2 = 0.999.

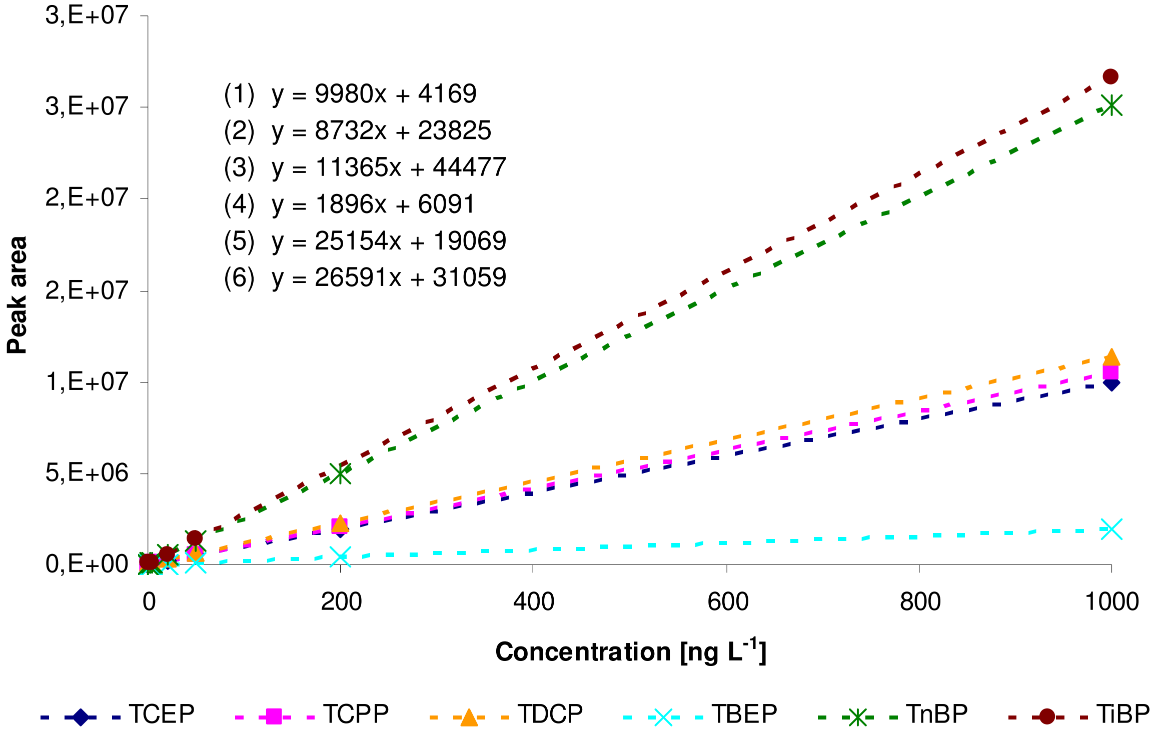


Fig. I-3. Calibration curves (mean, n = 3) of TCEP (1), TCPP (2), TDCP (3), TBEP (4), TnBP (5), and TiBP (6) using Thermo Scientific GC-MS system.

Blanks. Mean blank values in ultrapure water samples analyzed in March 2009 (n = 11) were 14 ng L^{-1} for TDCP, 6 ng L^{-1} for TBEP, and 1 ng L^{-1} for TiBP, whereas TCEP, TCPP and TnBP have not been detected in the blanks. Procedural blanks were periodically performed for each sampling set in order to avoid false positives during analysis of real water samples. The concentrations of OPs in blank samples were subtracted from concentrations of analytes in the rain, snow, and surface water samples. Furthermore, tap water samples collected at monitoring stations Wasserkuppe, Schmuecke, and Frankfurt am Main were regularly analyzed in addition to the blanks, and were found to contain no detectable concentrations of the six OPs.

Procedural blanks often showed the presence of TDCP and TBEP at mean concentrations up to 14 ng L^{-1} and 6 ng L^{-1}, respectively. The exact source of the contamination could not be identified. As the flame retardant TDCP is mainly used in flexible polyurethane foams in automotive applications, TDCP contamination could be associated with transport of the samples. In case of TBEP, the biannual used floor polish for the PVC flooring of the corridors was considered as possible contamination source. Blank values for TCEP, TCPP, TnBP, and TiBP were in general below 2 ng L^{-1} or even not detectable. Previous laboratory experiments have shown a high blank value for TiBP if paper filters (pre-cleaned with dichloromethane) were used for filtration of water samples. TiBP is apparently applied as an additive (e. g., wetting agent) during production of these paper filters. Hence, a contamination of water samples with TiBP or other OPs during filtration was prevented by use of glass fiber filters, heated in an oven for more than 2 h at 400 °C before filtration step.

Application to real samples. The analytical method was used to determine the six OPs in precipitation, surface water, and groundwater samples from several sampling sites under different anthropogenic impact. Fig. I-4 illustrates a TIC and the corresponding mass chromatogram (m/z 63, 75, 99, 125) of a SWHT sample extract from Frankfurt/Main including the IS squalane. All results of the study carried out between June 2007 and October 2009 are reported and discussed in detail in research papers II–VI in chapter 2.

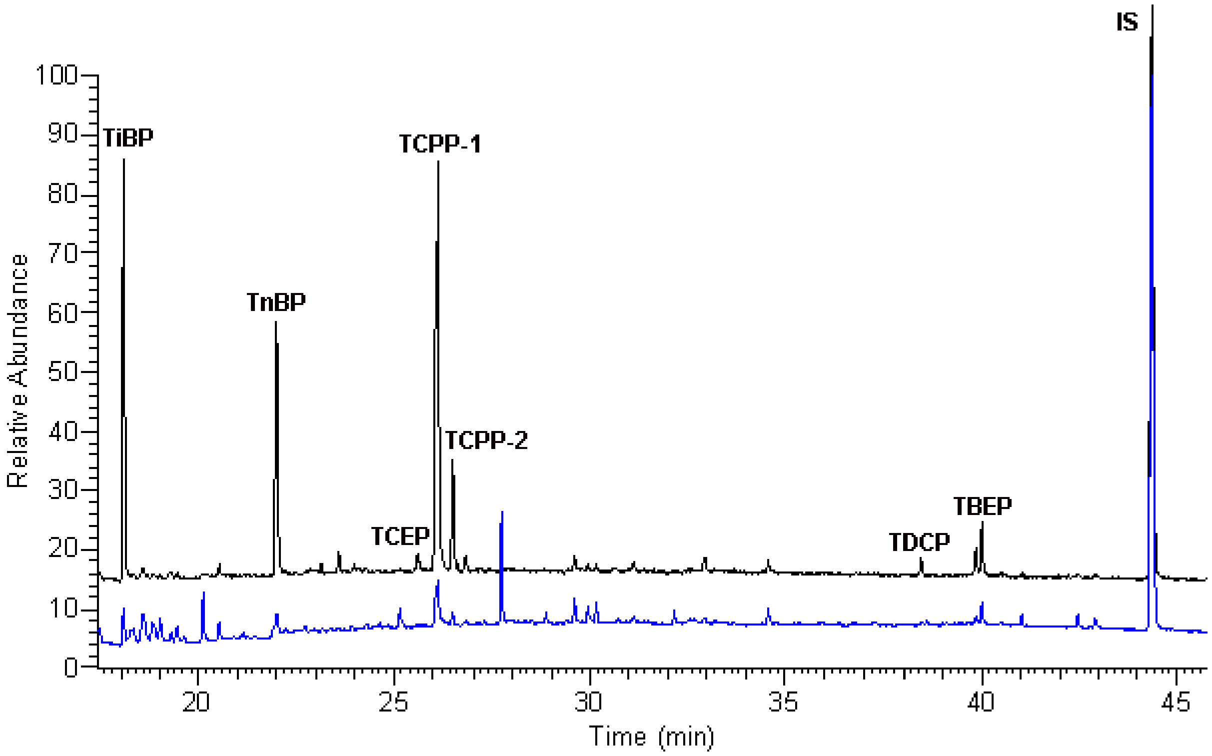


Fig. I-4. TIC (blue) and mass chromatogram (m/z 63, 75, 99, 125; black) of a surface runoff extract from Frankfurt/Main. All target analytes were identified in the mass chromatogram (IS = internal standard squalane).

Conclusion

In the present investigation, SPE followed by GC-MS after pressure filtration was shown to be a suitable method for the determination of OPs in natural water samples. In particular the filtration step was necessary to yield acceptable enrichment rates of OPs in marginal polluted water samples since SPE cartridge plugging occurred if non-filtered water samples exceeded the volume of 0.5–1 L. The optimized method provided good precision, a wide range of linearity, and low ng L^{-1} LOD levels for all six OPs in water samples of 1–2.5 L volume. TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP were found in precipitation, lake water, and groundwater samples from urban and remote areas in Germany. Hence, the occurrence of OPs in the aquatic environment apparently is almost ubiquitous.

II Organophosphorus flame retardants and plasticizers in rain and snow samples from middle Germany

Abstract

The role of precipitation as an important source of, and entry-pathway for, organophosphates (OPs) into the aquatic environment was investigated. Rainwater and snow samples (53 and 43, respectively) collected between November 2007 and April 2008 from urban and remote areas of middle Germany were analyzed for OPs by gas chromatography-mass spectrometry (GC-MS) after solid phase extraction (SPE). The analytes tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) were detected in almost all rain and snow samples. TCPP was the most abundant chlorinated alkyl phosphate ester in urban rainwater, with concentrations ranging from 46–2659 ng L^{-1}. In general, concentrations of OPs in urban rainwater were 3–4 times higher than those at background monitoring stations (e.g., Schmuecke, Thuringian Forest). Variable concentrations of chlorinated flame retardants were found in precipitation, but their occurrence was not correlated with air temperature. The results of the study indicate that volatilization of OPs from objects protected by flame retardants, including vehicles and buildings, causes these compounds to reach the aquatic environment via washout from the atmosphere, despite their reported short atmospheric half-lives (<24 h).

Introduction

Organophosphates (OPs) are derivatives of phosphoric acid, composed of either similar or various organic materials that can contain either non-halogenated or halogenated alkyl groups or aryl groups (*38*). The sources of environmental OPs are exclusively anthropogenic as these compounds do not occur naturally. The occurrence of OPs including tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) in aquatic environments as a result of anthropogenic activity has been verified in recent studies. OPs have also been detected in treated and untreated wastewater (*23,59*), wastewater-impacted surface waters (*18,52*), and groundwater affected by surface water (*21,60*). In untreated wastewater, but also in treated wastewater and surface water impacted by wastewater, the concentrations of OPs often exceed the acceptable concentration (0.1 $\mu g\ L^{-1}$) proposed by the Federal Environmental Agency of Germany (*31*). The broad application of OPs in many products, as flame retardants, plasticizers, antifoaming agents, and additives, is attributable to their favorable physicochemical characteristics. These compounds are non-flammable; non-explosive; odorless; colorless; resistant to temperature, light and water; and have plasticizing effects.

Chlorinated alkyl phosphate esters are included as flame retardants in polyurethane foam in domestic, public, and automotive applications. Other applications are use in unsaturated polyester resins (building industry), acrylic resins, adhesives, and coatings (*61*). When used as plastic additives, flame retardants are typically mixed into the polymer concurrently with other ingredients, but they are not chemically bound to the polymer matrix. Therefore, migration to the surface and release into the environment by volatilization can occur. Retention of retardants in polymers is particularly dependent on retardant vapor pressure. Dissolution of retardants from the surfaces of treated products and removal through abrasion are possible. In general, flame retardants constitute about 2–15% (w/w) of the finished product (e.g., foam); such levels are required to achieve appropriate flame retardant effects (*62*).

Primary and secondary emissions of various flame retardants from building materials in indoor environments have been analyzed (*16,17*) because of the potentially negative effects of these compounds and their reaction products on indoor air quality. Primary emissions are defined as the physical release of substances from new products, whereas secondary emissions are releases of substances following chemical reactions in the product or of the product with ambient indoor air (*17*). Area-specific emission rates of TCPP from assembly foams and other building materials were determined in test chambers by Kemmlein et al. (*63*).

In 2006 the use in western Europe of chlorinated and non-chlorinated organophosphate flame retardants was estimated by the European Flame Retardants Association (EFRA) to be 91,000 t yr^{-1} (http://www.cefic-efra.com). Several studies have pointed to persistence of chlorinated OPs in the environment (*1*). Moreover, a wide range of adverse biological effects have been reported for some OPs, and TCEP, TCPP, and TDCP are subject to an European Union risk assessment process under an Existing Substances Regulation (EEC 793/93). TCEP is registered on the second priority list, whereas TCPP and TDCP are on the fourth priority list. These three OPs are also included in the list of EU High Production Volume Chemicals (HPV), together with the non-chlorinated OPs TBEP, TiBP, and TnBP. The physicochemical properties of the substances analyzed in this study, including Henry's law constants and vapor pressures at ambient temperature are summarized in Table II-1. Because of their physicochemical properties, chlorinated flame retardants can be classified as semi-volatile organic compounds (SVOCs), with water being their main mode of distribution in the environment. Furthermore, TCEP, TCPP, and TDCP are characterized by low biodegradability during conventional wastewater treatment (*50*). Adsorption onto activated carbon has been shown to be efficient for removal of these compounds from water (*64,65*). The predicted behavior of TCPP during conventional wastewater treatment indicates a partitioning of 97.9% to the water column and 2.1% to sludge. Substances with an organic carbon/water partition coefficient (K_{oc}) higher than that of TCPP (K_{oc} = 174 L kg^{-1}) may adsorb more strongly to sludge (*33*). Volatilization of OPs from the water phase into air is negligible because of low Henry coefficients (Table II-1).

For the above reasons, treated and untreated wastewater discharges are presumed to be the main entry-pathway for OPs to surface waters and impacted groundwater (*1*). However, OP flame retardants have recently been detected in rainwater and closed hydrographic systems, even in the absence of industrial activities, anthropogenic influences, and wastewater discharges (*4*). In small volcanic lakes and other closed hydrographic systems, precipitation, runoff processes, and local anthropogenic sources are the only possible sources of contamination. Transport of OPs to remote areas via the atmosphere after emission from urban settlements and road traffic has been proposed (*3*). Several OPs have been detected following spot sampling of rain (*20,25,26*), snow (*3*), aerosols (*27*), and pine needles (*28*) in remote areas. However, no long-term systematic study of the occurrence of OPs in rainwater and freshly fallen snow at a variety of sampling sites has been conducted.

Table II-1. Physicochemical data of the analyzed OPs in this study (*32-34,38,58*).

Compound	Abbreviation	CAS registry No.	n-Octanol/ water partition coeff. (log K_{ow})	Henry's law constant at 25 °C (Pa m^{-3} mol^{-1})	Vapor pressure at 25 °C (Pa)	Photo-degradation atmosphere (5 × 10^5 OH mol^{-1})
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	1.7	2.58×10^{-3}	1.14×10^{-3}	t ½ = 17.5 h
Tris(2-chloro isopropyl) phosphate	TCPP	13674-84-5	2.6	6.04×10^{-3}	1.4×10^{-3}	t ½ = 8.6 h
Tris(1,3-dichloro-2-propyl) phosphate	TDCP	13674-87-8	3.8	2.65×10^{-4}	5.6×10^{-6}	t ½ = 21.3 h
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3	3.8	1.22×10^{-6}	1.64×10^{-4}	t ½ = 3 h
Tri-n-butyl phosphate	TnBP	126-73-8	4.0	0.323	0.465	t ½ = <1 h
Tri-iso-butyl phosphate	TiBP	126-71-6	3.6	0.323	1.71	t ½ = 4.3 h

The aim of this study was to investigate precipitation as an important source and entry-pathway of OPs into the aquatic environment. The influence of air temperature on fluctuations in OP precipitation concentrations was also investigated. Rainwater (53 samples) and snow (43 samples) from urban and remote areas were collected between November 2007 and April 2008, and analyzed for the occurrence of TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP using solid phase extraction (SPE) followed by gas chromatography-mass spectrometry (GC-MS).

Experimental

Chemicals. TCPP (a mixture of three isomers) and TDCP were kindly supplied by Akzo Nobel (Amersfoort, The Netherlands). TCEP, TiBP, TnBP, TBEP, and the internal standard squalane were obtained from Sigma Aldrich (Steinheim, Germany). Surrogate standard tripentyl phosphate (TPeP) was obtained from TCI Europe (Zwijndrecht, Belgium). Acetonitrile (ultrapure HPLC grade) was obtained from J. T. Baker (Deventer, The Netherlands) and was used as received. All other organic solvents were analytical grade (Merck, Darmstadt, Germany) and were distilled before use. Ultrapure water was produced from de-ionized water using an Astacus ultrapure water purification system (MembraPure, Bodenheim, Germany). Individual stock solutions (1 µg μL^{-1}) of target compounds were prepared in methanol/acetonitrile (1/1 v/v) and stock solutions (1 µg μL^{-1}) of the internal standards squalane and TPeP were prepared in hexane.

Sampling. Five locations in middle Germany were chosen as sampling sites for collection of rain and snow (Fig. II-1). These sites are listed in Table II-2 together with their grid references. Rain samples were collected from November 2007 to April 2008 using a stainless steel sampler located on top of the Geosciences Center of Frankfurt University (Riedberg campus). This sampling site is located in the north of Frankfurt am Main which is at the moment one of the largest areas of construction in the Rhine-Main urban region. Precipitation was also collected in two stainless steel boxes (area 1 m^2, height 20 cm) placed at monitoring stations on Mount Schmuecke (December 2007–April 2008) and Mount Wasserkuppe (January–March 2008). The Schmuecke ambient air quality monitoring station (Federal Environmental Agency) is representative of low mountain range areas in Germany, and is situated on a mountain ridge in Thuringian Forest, at a height of 937 m above sea level. The Wasserkuppe weather station (German Weather Service) is located southwest of Schmuecke in the Hessian Rhoen mountain range, at a height of 950 m above sea level.

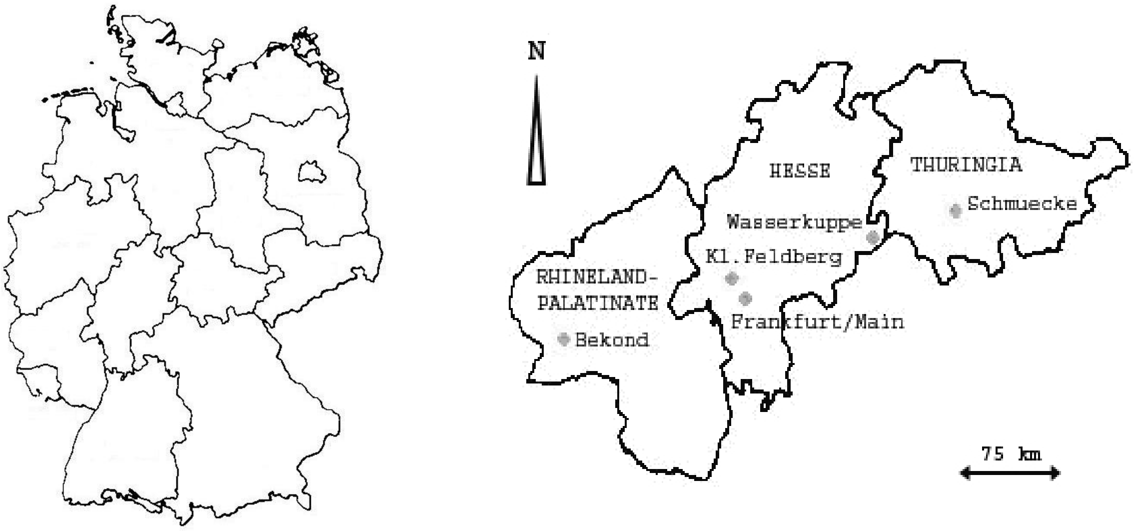


Fig. II-1. Location of the sampling stations.

Precipitation was collected in large glass or stainless steel funnels at two other sampling sites, the Taunus University Observatory on Mount Kleiner Feldberg and the small village of Bekond on the Mosel River, during the period from December 2007 to April 2008. With the exception of Frankfurt am Main, all sampling sites are located in sparsely populated areas and can be regarded as background monitoring stations. Because of its closeness to Frankfurt am Main, the sampling location at Kleiner Feldberg is influenced by urban emissions, depending on meteorological conditions. Mean daily air temperatures and rainfall for all monitoring stations were obtained from the German Weather Service.

Table II-2. Grid values of the monitoring stations (north, east, altitude).

	North	East	Altitude
Bekond	49 50570	6 48240	210 m
Kleiner Feldberg	50 13210	8 26530	810 m
Frankfurt am Main	50 10250	8 38030	128 m
Wasserkuppe	50 29520	9 56340	915 m
Schmuecke	50 39160	10 46080	937 m

Sampling was carried out in winter with the objective of obtaining freshly fallen snow, particularly at higher altitude stations. Sampled snow (age ≤1 day) was immediately melted and transferred to 1–2.5 L brown glass bottles. After each sampling the stainless steel boxes were rinsed thoroughly with ultrapure water. Sample volumes varied according to rainfall. For low rainfall situations, samples from a maximum of three consecutive days were accumulated in one bottle and analyzed as a composite sample. All water samples were stored in brown glass bottles for up to 7 days at 5 °C until analyzed in the laboratory. Previous laboratory experiments have shown the stability of OPs in water for at least two weeks in the absence of light and oxygen. Therefore, losses of target compounds resulting from sample alteration following collection were considered to be negligible.

To prevent the introduction of contaminant OPs during sampling, all laboratory equipment was glass, stainless steel, or Teflon. Prior to sampling, glass bottles were rinsed with ultrapure water and methanol, respectively, and then heated to 110 °C for a minimum of 6 h. Blanks for analyses were ultrapure water placed in glass bottles and treated in the same way as field samples, to test for sample contamination during transportation.

Sample preparation. Samples were extracted by SPE. To avoid plugging of cartridges, all rain and snow samples were subjected to pressure filtration before extraction, to remove insoluble components and suspended particulate matter. A stainless steel pressure holder (2.12 L capacity; Sartorius, Goettingen, Germany) and a 142 mm diameter borosilicate glass fiber filter (filter pore size 1 µm; type A/E, Pall, Dreieich, Germany) were used at an operating pressure of 1.5 bar (nitrogen). To avoid blank problems all glass fiber filters were heated in an oven for more than 2 h at 400 °C before being enclosed in aluminum foil. The 2.12 L capacity enabled total sample volume to be incorporated in the barrel, thus minimizing contamination from ambient laboratory air. TPeP was used as a surrogate internal standard and was spiked onto the top of the glass fiber filter (2 µL of a 1 µg μL^{-1} standard) before filtration. After filtration of each sample the filtration equipment was decomposed and thoroughly cleaned with ultrapure water.

SPE was carried out using Bond Elut PPL cartridges (1 mL; Varian, Darmstadt, Germany). Cartridges were sequentially conditioned with 1 mL methanol, 1 mL methanol/acetonitrile (1/1 v/v), and 1 mL ultrapure water. Samples (1–2.5 L) were then passed through the cartridges using a vacuum of 800 mbar. Bottle openings were closed by stoppers equipped with activated charcoal filter tubes (Type Niosh; Dräger, Luebeck, Germany) to minimize contact of the water surface with organic compounds in ambient laboratory air during the extraction process. After extraction the SPE cartridges were dried in a nitrogen stream and then Elutd three times with 333 µL methanol/acetonitrile (1/1 v/v). These extracts were again dried in a nitrogen stream and dissolved in 100 µL acetonitrile. Subsequently, 4 µg of squalane was added to each sample as an internal quantitation standard.

Instrumentation. Quantitative analyses were performed using a Fisons gas chromatograph GC 8000 coupled to a Fisons MD 800 mass spectrometer (Thermo Fisher, Dreieich, Germany). Acquired data were processed using Fisons MassLab software (version 1.3). The GC was equipped with a SLB^{TM}-5ms capillary column (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness; Supelco, Bellefonte, PA). Helium (≥99.999%) was used as carrier gas at a constant pressure of 70 kPa. The initial column oven temperature (80 °C) was increased at 4 °C min^{-1} to a final temperature of 300 °C, which was maintained for 25 min. Sample injection (1 µL) was accomplished using a Fisons AS 800 autosampler in the splitless mode (1 min splitless time) at an injector temperature of 240 °C. The mass spectrometer was operated in electron impact mode with 70 eV ionization energy, and full scan spectra were collected in the range m/z 50–600.

Quantitation and limit of detection. Identification of target compounds was achieved by mass spectra analysis and retention times of standards. All mass spectra were compared with spectra in the Wiley AccessPak spectral library, 8th edition (Palisade, Ithaca, NY). Analytes were quantified by the internal standard method (*54*), whereas response and correction factors for target compounds were determined at any GC-MS series of measurements. Ions used for quantitation in selected ion monitoring (SIM) mode were m/z 63 (TCEP), m/z 75 (TDCP), m/z 99 (TCPP, TnBP, TiBP) and m/z 125 (TBEP). The limit of detection (LOD) in this method was estimated for each substance using the computer program DINTest 2000 (Schmitt and Herbold, University of Heidelberg), on the basis of measured calibration curves. The LODs for TCEP (2 ng L^{-1}), TCPP (1 ng L^{-1}), TDCP (1 ng L^{-1}), TBEP (3 ng L^{-1}), TnBP (1 ng L^{-1}), and TiBP (2 ng L^{-1}) were determined using a significance level of 1% and an error of 33.3%.

Results and discussion

SPE recovery rates ranged from 85% to 99% (n = 6) for all analyzed OPs. The concentrations of OPs in blank samples were subtracted from concentrations of analytes in the rain/snow samples, but no adjustments were made for differences in recoveries of individual OPs during SPE. The mean blank values (n = 5) were 3 ng L^{-1} for TCEP, 6 ng L^{-1} for TCPP, 7 ng L^{-1} for TDCP, 3 ng L^{-1} for TBEP, 2 ng L^{-1} for TnBP, and 3 ng L^{-1} for TiBP. Tap water samples collected at monitoring stations Wasserkuppe, Schmuecke, and Frankfurt am Main were analyzed in addition to the blanks, and were found to contain no detectable concentrations of the six OPs.

Concentrations of organophosphates. The analytes TCEP, TCPP, TDCP, TBEP, TnBP, and TiBP were detected in almost all analyzed snow and rain samples. In some samples the concentrations of TDCP and TBEP were below the LODs. The median and maximum concentrations are shown in Table II-3. Because of the skewed concentration distributions, the results are presented as median values. In winter 2007/2008 it was possible to collect only one snow sample at Frankfurt am Main. The significance and validity of concentrations of OPs in this sample may not be representative. In general, concentrations of OPs in urban rainwater were significantly higher than those from the background monitoring stations Schmuecke, Wasserkuppe, Bekond, and Kleiner Feldberg. Higher OP concentrations in urban precipitation were expected, based on results of earlier studies (*3,4*), and suggest that emissions from urban settlements and road traffic are the dominant sources of OPs in the atmosphere.

TCPP was the most abundant chlorinated OP in urban rainwater, with concentrations ranging from 46–2659 ng L^{-1}. The median TCPP level (743 ng L^{-1}) in rainwater from Frankfurt am Main was only about 2.5 times lower than the median concentrations of TCPP (1575 ng L^{-1} and 1607 ng L^{-1}, respectively) in the influent and effluent of two municipal wastewater treatment plants in the Frankfurt area (*23*). Furthermore, the median TCPP concentrations at the five sampling sites showed linear relationships with population density (coefficient of determination, $R^2 = 0.996$) and the proportion of settlement plus transportation area to total area ($R^2 = 0.988$). In snow samples of the four background monitoring stations, median concentrations of TiBP ($R^2 = 0.962$) and TnBP ($R^2 = 0.910$) also showed linear relationships with population density. No other analyzed substances showed a relationship to these two parameters.

Table II-3. Median concentrations of OPs (ng L^{-1}) in snow and rain samples [a].

	Kleiner Feldberg		**Wasserkuppe**		**Bekond**		**Schmuecke**		**Frankfurt/M.**
Compound	**Snow**	**Rain**	**Snow**	**Rain**	**Snow**	**Rain**	**Snow**	**Rain**	**Rain**
[ng L^{-1}]	n = 8	n = 4	n = 12	n = 3	n = 5	n = 9	n = 17	n = 11	n = 26
TCEP	42	196	60	11	22	12	19	14	73
	(61)	(390)	(488)	(70)	(127)	(41)	(102)	(45)	(338)
TCPP [b]	83	236	73	86	20	387	47	30	743
	(177)	(1154)	(385)	(123)	(154)	(1101)	(132)	(77)	(2659)
TDCP	40	24	5	2	17	9	12	17	7
	(113)	(31)	(23)	(2)	(83)	(53)	(52)	(25)	(32)
TBEP	17	39	6	3	21	7	4	5	25
	(242)	(208)	(137)	(5)	(205)	(40)	(139)	(9)	(162)
TnBP	192	133	64	57	15	45	43	37	203
	(458)	(253)	(228)	(163)	(25)	(110)	(117)	(182)	(818)
TiBP	196	123	100	97	39	42	66	52	244
	(424)	(221)	(351)	(233)	(67)	(160)	(185)	(367)	(1410)

[a] Maximum concentrations are given in parenthesis.

[b] Sum of two isomers; tris(2-chloroisopropyl) phosphate, CAS 13674-84-5; bis(1-chloro-2-propyl)-2-chloropropyl phosphate, CAS 76025-08-06.

In Italy, Bacaloni et al. (*4*) recorded TCPP levels of 739 ng L^{-1} and 633 ng L^{-1} in two urban rainwater samples, and 28 ng L^{-1} in a rural rainwater sample. The comparative levels of TiBP (30 ng L^{-1}, 39 ng L^{-1}, and 6 ng L^{-1}) and TnBP (48 ng L^{-1}, 44 ng L^{-1}, and 11 ng L^{-1}) in these samples were lower than values obtained in the present study, whereas the concentrations of TDCP (448 ng L^{-1}, 360 ng L^{-1}, and 108 ng L^{-1}) were much higher. The rainwater samples in the cited study were collected in May and June (summer), when photochemical decomposition of TnBP and TiBP would be expected to be faster than in winter. It has been reported that non-chlorinated OPs are less stable in aquatic and atmospheric environments than chlorinated flame retardants (see Table II-1) (*1,24*). In addition, differences in the concentrations of individual OPs in rainwater from Germany and Italy may be due to differences in application, or the products synthesized or used in these countries.

The concentrations of TCEP detected in snow and rainwater samples were quite high despite the supposed phase-out of TCEP in Europe since the mid 1990s (*1,32,66*). As shown in Table II-3, the highest concentrations of TCEP were found in snow samples from the Wasserkuppe monitoring station (488 ng L^{-1} and 414 ng L^{-1}) and rainwater samples from Kleiner Feldberg (390 ng L^{-1}) and Frankfurt am Main (338 ng L^{-1}). Based on these observations the data for TCEP concentrations in snow and rain samples obtained from the Schmuecke sampling site were plotted against ambient air temperature (Fig. II-2). For TCEP a higher peak concentration was found in freshly fallen snow (102 ng L^{-1}) than in rainwater

(45 ng L^{-1}), but a consistent relationship between TCEP concentrations in snow or rain and ambient temperature was not evident.

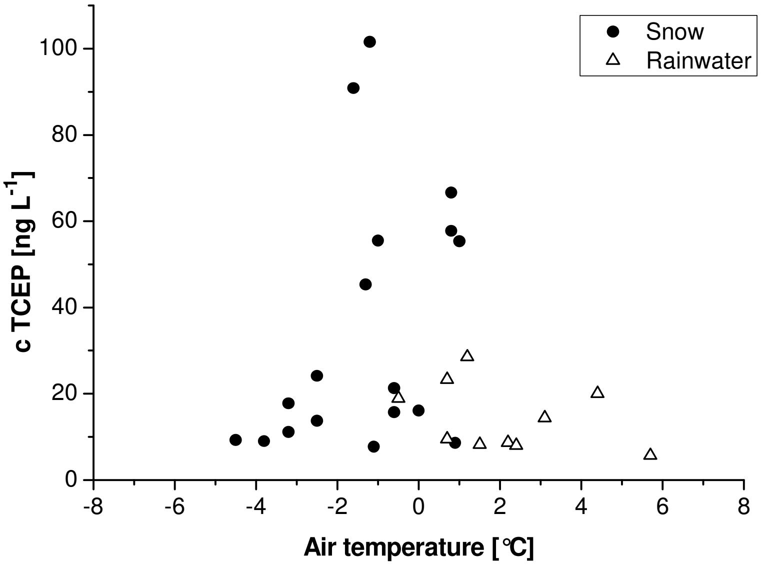
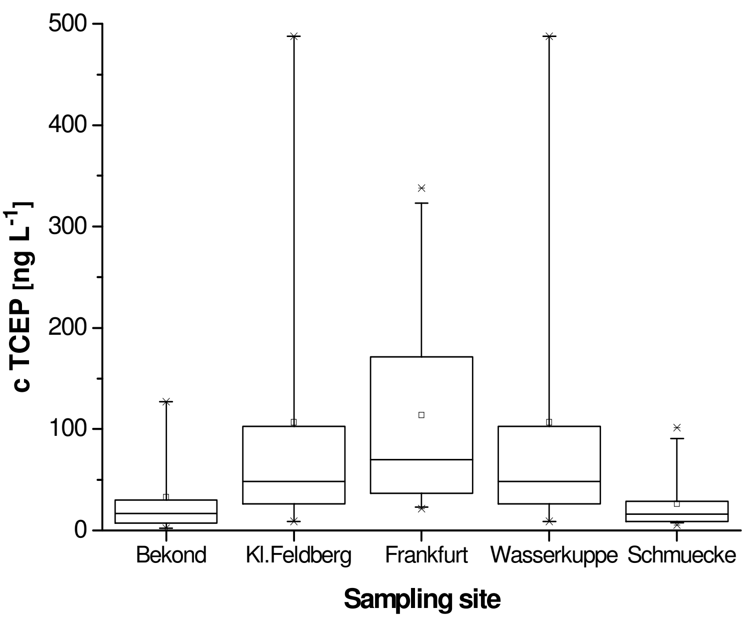


Fig. II-2. TCEP concentrations in snow and rainwater at Schmuecke monitoring station.

By comparison, Laniewski et al. (*26*) reported TCEP levels ranging from 1–21 ng L^{-1} in rainwater and snow samples from remote areas of Ireland, Poland, and Sweden (winter 1996/1997). Concentrations of 121 ng L^{-1} and 87 ng L^{-1} were reported in a rainwater sample from Germany (*20*) and a wet deposition sample from Sweden (*3*), respectively. As with TCEP, concentrations of no other OP analyzed in this study were correlated with ambient air temperature, despite concentration variability in precipitation samples.

Fig. II-3 shows box plots for TCEP and TCPP concentrations in precipitation samples from all sampling sites. The concentrations were quite high and ranged from the LOD (<2 ng L^{-1}) to 488 ng L^{-1} for TCEP, and from the LOD (<1 ng L^{-1}) to 2659 ng L^{-1} for TCPP. Highest TCPP values were found in samples from sites in urban settlements, Frankfurt am Main and Bekond. In contrast, the mean values of TCEP at the Wasserkuppe (96 ng L^{-1}) and Kleiner Feldberg (96 ng L^{-1}) sampling sites were close to the mean TCEP concentration at Frankfurt am Main (109 ng L^{-1}).



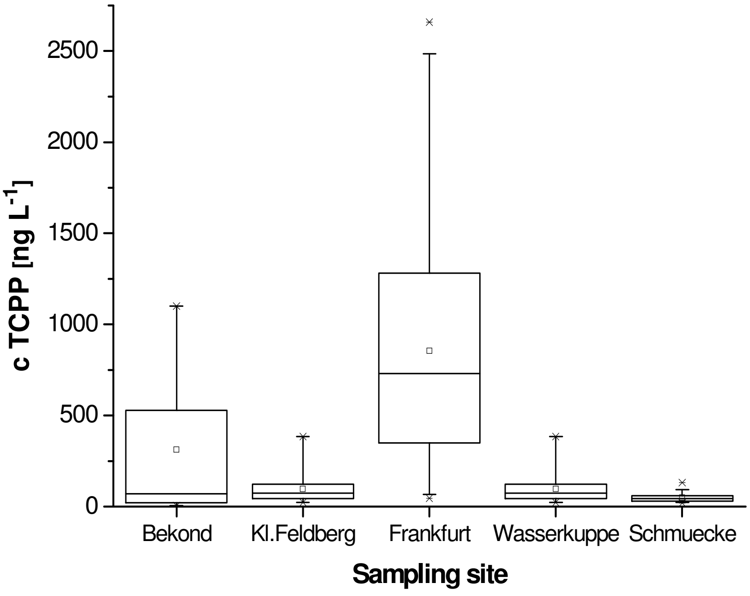


Fig. II-3. Box plots of TCEP and TCPP concentrations in precipitation samples from all sampling sites (November 2007 to April 2008).

Fig. II-4 shows the annual mean wind direction distributions for four sampling sites, obtained from official German weather stations. Wasserkuppe and Schmuecke are situated in the plume from the Rhine-Main area, as the dominant wind direction in middle Germany is west–southwest (Fig. II-4). The concentrations of TCEP, TCPP, TnBP, and TiBP decreased in an east–northeast direction from Wasserkuppe to Schmuecke, with increasing distance from the Rhine-Main urban area. These observations suggest that these substances are released into the air and are transported until either washed out or decomposed by photooxidation.

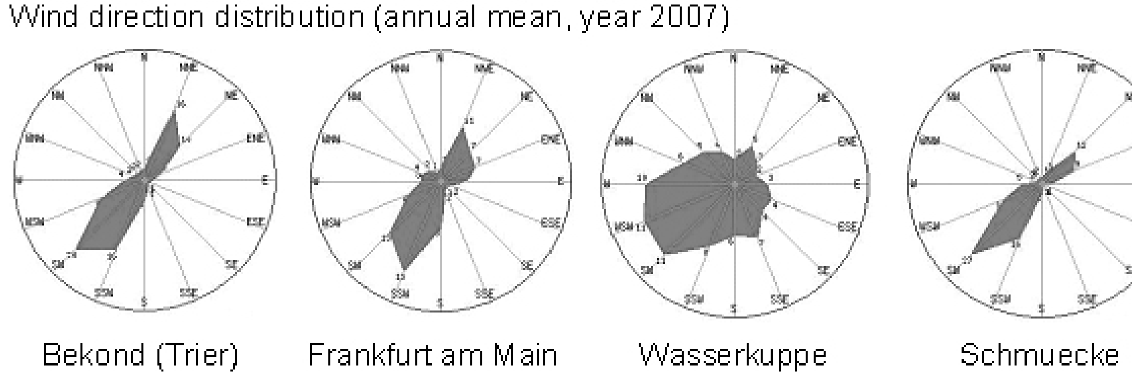


Fig. II-4. Wind roses from sampling sites (http://www.windfinder.com, 2008-07-01).

Possible sources of OPs in the atmosphere. The various direct (e.g., leakage) and diffuse sources (road traffic, urban settlements) of OPs in the atmosphere have been discussed elsewhere (*3,4*). Anthropogenic activities including emissions from vehicles and buildings, abrasion of tires, and leakage of hydraulic fluids and motor/transmission oils from vehicles are considered as potential OP sources. Three possible pathways for entry of OPs into the atmosphere are discussed below.

1. Volatilization from water systems

The tendency of a substance to partition between air and water, defined by the Henry's law constant, is the ratio of the equilibrium concentration of the substance between these two phases. Therefore, a low Henry's law constant indicates a tendency to remain in the aqueous phase, whereas a large Henry's law value indicates a more volatile compound. The calculated Henry's law constants of TCEP (2.58×10^{-3} Pa m^{-3} mol^{-1}), TCPP (6.04×10^{-3} Pa m^{-3} mol^{-1}), and TDCP (2.65×10^{-4} Pa m^{-3} mol^{-1}) indicate low rates of volatilization from the aquatic phase to the air (*33,34*). In addition, volatilization of TBEP (Henry's law constant = 1.22×10^{-6} Pa m^{-3} mol^{-1}) from surface waters to the atmosphere is not an important removal process. For TiBP and TnBP (Henry's law constant for both = 0.323 Pa m^{-3} mol^{-1}), it is also unlikely that volatilization from surface water will occur to any significant extent.

2. Release from vehicles and buildings

Relative to volatilization from water, the release of OPs from products such as vehicles and heat insulation of buildings is more likely because of their moderate vapor pressure. The vapor pressures of the analyzed substances at 25 °C ranged from 1.71 Pa for TiBP to 5.6 ×

10^{-6} Pa for TDCP (see Table II-1). Loock et al. (*53*) and Wensing et al. (*10*) analyzed the thermally-conditioned OP emissions from polymer materials used in passenger compartments of automobiles. SVOCs in particular can condense after the emission in the passenger compartment as, for example, film deposits (e.g., fogging condensate) on the inside of the windshield. Flame retardants can diffuse from car interiors to the ambient air and the environment via the ventilation system, or be released by cleaning procedures. In test chamber studies Kemmlein et al. (*67*) determined area-specific emission rates of OPs for several building materials including insulation boards, assembly foam (PUR foam), and upholstery foam. The area-specific emission rates for TCPP from PUR foam were in the range 50–140 µg m^{-2} h^{-1}, depending on foam age and surface structure.

Analysis of fogging condensate and air from vehicle interiors showed that flame retardants TCPP and TDCP were the dominant substances emitted (*9,10,53,68*), especially in new cars. Under driving conditions and during standing at room temperature the concentrations of TCPP and TDCP were below the indoor guideline value RW I (5 µg m^{-3}) suggested for some OPs by Sagunski and Roßkamp (*69*). However, as a result of increasing vapor pressure, the proportions of OPs in condensate and internal vehicle air increased when the temperature was raised. During hot summer days it is not unusual for the interior temperature of cars parked in sunshine to reach over 50 °C, and therefore concentrations of OPs (especially in new vehicles) can be similar to those of test stands under heated-up conditions (*9,10*). Depending on the settings of the ventilation system, the air exchange rate in driving vehicles can be up to 240 h^{-1} (*70*), resulting in emissions being continuously released into the environment from these vehicles. The qualitative analyses of Marklund (*68*) indicated varying distribution patterns of OPs in vehicles. Levels of TCEP, TCPP, TDCP, and TBEP depended strongly on the materials used by each car manufacturer.

The draft EU risk assessments for TCPP and TDCP suggest that TCPP, in particular, is not used in automotive applications, which would result in vehicle traffic no longer being a source of environmental TCPP (*33*). However, this is not consistent with the findings of Marklund (*68*).

3. Volatilization from soils

Monitoring of successive condensations/volatilizations of chlorinated OPs between air and terrestrial surfaces in relation to seasonal temperature changes at mid latitudes (the "grasshopper" mechanism known for persistent organic pollutants – POPs) (*71*) has not been undertaken. The results of modeling of environmental distribution of TCPP indicate that little movement occurs between soil, water, and air (*33*). In general, transfer between soil and water via air is very slow for substances of low volatility. The distribution modeling for TnBP indicates that 100% of this substance entering soil will be retained (*72*). TBEP is also predicted to adsorb to soil because of its low vapor pressure and high estimated soil sorption coefficient (K_{oc} = 2300). Therefore, only slight soil mobility is assumed (*35*).

The present study has shown that release of OPs by volatilization from products protected by flame retardants is the dominant process explaining their occurrence in precipitation.

Atmospheric transport and photodegradation. The global distribution mechanisms (known as the global distillation effect) and cold condensation have been studied, particularly for POPs, with respect to polar and high altitude ecosystems. It is assumed that a temperature decrease during atmospheric transport of these compounds will increase their tendency to condense and accumulate in cold environments (*71*). Long-range air transportation and deposition processes for various POPs have been studied and calculations have been made (*73*), but OPs have not yet been included in monitoring studies in Arctic regions (*6*). Data for remote areas such as high altitude lakes are not available. In risk assessments TCEP, TCPP and TDCP do not fulfill the PBT criteria (persistence, bioaccumulation, and toxicity), as there is no indication of bioaccumulation. The calculated half-lives for atmospheric reaction of chlorinated OPs with hydroxyl radicals are of 17.5 h (TCEP), 8.6 h (TCPP), and 21.3 h (TDCP). The calculated half-lives for the non-chlorinated OPs (TBEP, TiBP, and TnBP) are considerably lower (Table II-1). No experimental studies on photodegradation of OPs adsorbed to atmospheric particles have been undertaken (*32-34*).

Brown and Wania (*74*) use a minimum hydroxyl radical atmospheric oxidation half-life of two days as the criterion for long-range air transportation. According to their atmospheric half-life times, chlorinated OPs are not sufficiently persistent in the atmosphere to be classified as POP substances, but their calculated photooxidation half-lives in air are nevertheless sufficient for short-range or medium-range atmospheric transportation.

In general, TCPP occurs at higher concentrations than TCEP. At the urban sampling site Frankfurt am Main, the median concentration of TCPP was approximately 10-fold higher than that of TCEP (Table II-3). Greater release of TCPP at urban sites relative to TCEP was expected as TCPP has been used as a substitute for TCEP in Europe since the mid 1990s. However, in comparison to TCEP, there was greater variation in TCPP concentration in precipitation samples from urban sampling sites (see Fig. II-3). This can be explained by the shorter atmospheric half-life of TCPP during transport, or by a higher potential of TCPP to adsorb to airborne particles, which may then be removed by rainfall (*33*). The relatively high soil sorption and n-octanol/water partition coefficients of TDCP, TBEP, TiBP, and TnBP (log K_{ow} values between 3.6 and 4.0, Table II-1) confirm their potential to adsorb to airborne particles when released to the atmosphere. TCEP (log K_{ow} 1.7) and TCPP (log K_{ow} 2.6) had lower log K_{ow} values, and TCEP in particular will bind less to particles than more lipophilic compounds.

Impact of precipitation as a source of OPs in surface waters. The data show that precipitation (rain and snow) is important as a source of OPs in surface waters, although treated and untreated wastewaters still remain the main entry-pathway for OPs. For this reason, OP-loaded precipitation might influence water protection areas, groundwater, or drinking water wells that are not affected by wastewater discharges.

The results of model scenarios in the EU risk assessment indicate that most TCPP in air will be precipitated to soil and water. This assumption can probably be applied to other OPs. However, the conclusion of the TCPP risk assessment study concerning atmospheric distribution is inconsistent with the data obtained in the present study. The risk assessment concluded as follows: "Given the low levels of releases, the relatively low volatility and moderate solubility and adsorption coefficient of TCPP, together with its short predicted atmospheric half-life for degradation by hydroxyl radicals, it is not expected that exposure via the atmosphere will be significant (*33*)."

Approximately 40% of the TCPP in a finished product is available for release (*33*). In the EU risk assessment the total continental European emission discharges of TCPP to air were determined to be 89.56 kg d^{-1}, and the total regional emission discharges of TCPP to air were 134.85 kg d^{-1} (*33*). These values were calculated with the program 'European Union System for the Evaluation of Substances' (EUSES 2.0). "The standard model parameters for the regional scale are set to mimic a typical densely populated area in the EU of 40,000 km^2 with 20 million inhabitants. By default, it is assumed that 100% of European production and use of the chemical takes place within this area. The continental scale is parameterized to mimic 'Western Europe' as the sum of the EU Member States (area 3.56 million km^2) (*75*)." The environmental release rates include release of TCPP from production, formulation, use, and end-of-life disposal. However, the specified release rates for TCPP in wastewater (24.09 kg d^{-1} continental, 18.70 kg d^{-1} regional) and surface water (6.02 kg d^{-1} continental, 4.68 kg d^{-1} regional) are considerably lower (*33*). Because of the comparatively low production/consumption of TCEP and TDCP in the EU, their total emission discharges to air were determined to be 1.01 t yr^{-1} for TCEP (regional and continental release) (*32*), and 2.49 kg d^{-1}

(regional) and 15.33 kg d^{-1} (continental) for TDCP (*34*). Consequently, the role of precipitation as an entry-pathway for chlorinated OPs into surface waters should not be disregarded.

Concluding remarks

The results of the present study show that the highest concentrations of OPs in precipitation occur in densely populated areas with high traffic volumes. Atmospheric distribution models for the chlorinated flame retardants TCEP, TCPP, and TDCP are not available. Even if photooxidation is a degradation pathway with estimated half-life times <24 h for non-chlorinated and chlorinated OPs in the environment, the chlorinated substances are sufficiently stable for short- and medium-range atmospheric transportation. Furthermore, neither predicted degradation data for particle-adsorbed OPs in the atmosphere nor experimental photodegradation studies are available. Nevertheless, the increasing use of flame-protected thermal insulation materials (based on polyurethane) in external walls of buildings will lead to increasing emissions of OPs into the atmosphere, particularly in developed areas.

III Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff

Abstract

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

Introduction

The environmental occurrence of organophosphates (OPs), employed as flame retardants, plasticizers, antifoaming agents, and additives in many products and materials, is exclusively man-made as these compounds do not occur naturally. They are triesters of phosphoric acid and comprise non-halogenated or halogenated alkyl groups as well as aryl groups (*38*). The chlorinated compounds tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP) are preferentially applied as flame retardants whereas the non-chlorinated esters tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) are used as plasticizers, antifoaming agents and additives in many applications (*1*). All these OPs are listed as European Union (EU) High Production Volume Chemicals (HPVs) with production/import volumes exceeding 1,000 t per year and are considered as emerging contaminants in the environment (*6*). Due to their physicochemical properties, the chlorinated flame retardants TCEP, TCPP, and TDCP and the non-chlorinated plasticizers TBEP, TiBP, and TnBP can be classified as semi-volatile organic compounds (*10*) with water being a preferred environmental compartment of distribution (*38*). Several studies have pointed to a wide range of adverse biological effects for some OPs (*1*); therefore TCEP, TCPP, and TDCP are subject of the EU risk assessment process (*32-34*). Furthermore, the resistance of chlorinated flame retardants to biodegradation and conventional potable water and wastewater treatments is well documented (*50,76*).

Transport of OPs via the atmosphere after emission from urban settlements and road traffic has been discussed previously (*3,4,77*). When used as plastic additives, migration to the surface and release into the environment by volatilization, abrasion, and dissolution can occur, as these ingredients are not chemically bound to the polymer matrix. According to the field of application, flame retardants constitute about 5–14% (w/w) of the finished product, e.g., polyurethane insulation or assembly foams (*31*). For instance, approximately 40% of TCPP used in a finished product is available for release (*33*). As a result of increasing vapor pressure, higher proportions of released OPs in indoor and outdoor environments are expected when ambient temperature is rising (*8-10,78*).

The atmospheric washout of OPs by precipitation or dry deposition and local contamination sources such as treated and untreated wastewater discharges, are presumed to be the main entry-pathways for OPs into the aquatic environment (*4,77*). However, so far the available amount of data is to low for an estimation of the proportion by which the possible sources of OPs contribute to the currently observed surface water pollution. Moreover, data on the seasonal fluctuations and trends of OP concentrations in precipitation are required for the assessment of the influence of photodegradation on the OP concentrations in precipitation.

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

Materials and methods

Chemicals. TCEP, TiBP, TnBP, TBEP, and squalane (internal standard) were purchased from Sigma Aldrich (Steinheim, Germany). TCPP (a mixture of three isomers) and TDCP were supplied by Akzo Nobel (Amersfoort, The Netherlands). Acetonitrile (ultrapure HPLC grade) was obtained from J. T. Baker (Deventer, The Netherlands). All other organic solvents were purchased from Merck (Darmstadt, Germany) at analytical grade and were distilled before use. Ultrapure water was generated with an Astacus ultrapure water purification system from MembraPure (Bodenheim, Germany). Individual stock solutions of each compound were prepared in methanol/acetonitrile (1/1 v/v) at 1 µg μL^{-1} concentration. Hexane was used to prepare the stock solution (1 µg μL^{-1}) of the internal standard squalane. Working standard solutions were obtained by appropriate dilution of stock solutions.

Sampling locations. The three locations chosen for sampling of precipitation are located in middle Germany. Sampling sites and sampling procedures are described in detail in research paper II (see chapter 2) and reference Regnery and Püttmann (*77*). All-season precipitation sampling took place at the urban sampling site Frankfurt am Main (November 2007–April 2009; 90 samples), the small village Bekond nearby Mosel River (December 2007–March 2009; 48 samples) and the Taunus University Observatory on Mount Kleiner Feldberg (November 2007–January 2009; 29 samples). Precipitation was collected using a stainless steel sampler on top of the Geosciences Center of Frankfurt University (Riedberg campus) and large glass or stainless steel funnels at the two other sampling sites. The SWHT Kalbach (N° 50 10570; E° 8 38060) next to the precipitation sampling site in the north of the urban center of Frankfurt am Main, is a technical installation for the collection of surface drainage of public streets, lanes, and squares as well as private properties. The SWHT is not affected by local contamination sources such as sewage inflow. It has a total surface area of about 35,000 m^2 and consists of two basins: a small settling pond in the inlet area and a greater pond with a throttle structure controlling the runoff into a small creek. The basins are connected to each other via overflow pipes. The water depth averages between 1.5–2.0 m. To avoid contact between surface water and groundwater, the basin bottom was sealed off using calcinations (http://www.umweltamt.stadt-frankfurt.de). Sampling of the SWHT Kalbach was carried out biweekly from May 2008 to April 2009. Water samples of 2 L volume were collected just below the water surface at each of the basins. Additional, few spot samples of surface water (2 L) were collected from a small SWHT (N° 49 51420; E° 6 47430) next to the precipitation sampling site Bekond. The basin is located in a public park and dewaters a small area zoned for economic activities.

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

Analytical methods. The analytes were extracted and enriched from the water, rain, and melted snow samples by use of solid phase extraction (SPE). Prior to SPE all water samples were subjected to pressure filtration with a 142 mm diameter borosilicate glass fiber filter (filter pore size 1 µm; type A/E, Pall, Dreieich, Germany) to avoid cartridge plugging during SPE. After filtration the samples (1–2.5 L) were extracted by a styrene-divinylbenzene polymeric SPE cartridge (Bond Elut PPL, 1 mL; Varian Darmstadt, Germany), Elutd with 1 mL methanol/acetonitrile (1/1 v/v), and analyzed by GC-MS in full scan mode. Quantitation was carried out using squalane as internal calibration standard. See reference (*77*) and research paper I (chapter 2) for a detailed specification of the applied analytical method.

From November 2007 to July 2008 quantitative analyses were performed using a Fisons gas chromatograph GC 8000 coupled to a Fisons MD 800 mass spectrometer (Thermo Fisher, Dreieich, Germany) as described in reference (*77*). Since August 2008 samples were analyzed by a Trace GC Ultra gas chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich, Germany). Method and instrument parameters remained constant. Acquired data were processed using Excalibur software (Thermo Fisher Scientific, version 2.0.7). The limit of detection (LOD) for each of the six substances was estimated on the basis of measured calibration curves in accordance with DIN 32645 (DINTest, University of Heidelberg, $\alpha = 1\%$). The LODs for TCEP (2 ng L^{-1}), TCPP (1 ng L^{-1}), TDCP (1 ng L^{-1}), TBEP (3 ng L^{-1}), TnBP (1 ng L^{-1}), and TiBP (2 ng L^{-1}) using the Fisons GC-MS system were somewhat higher than those obtained for the Thermo Scientific GC-MS system (LOD of 1 ng L^{-1} for each of the six substances). The limit of quantitation (LOQ) was estimated as three times the LOD according to DIN 32645 and ranged between 3 ng L^{-1} (TCEP) and 4 ng L^{-1}

(TBEP) for the Thermo Scientific GC-MS system and 3 ng L^{-1} (TCPP) and 8 ng L^{-1} (TBEP) for the Fisons GC-MS system.

All laboratory equipment used in this study consisted of glass, stainless steel, or Teflon and was regularly controlled to be OP-free. Glass bottles were rinsed with ultrapure water and methanol, respectively, and finally heated to 110 °C over night before using for sampling. The glass fiber filters were heated for more than 2 hours at 400 °C. Blanks for analyses were ultrapure water and tap water treated in the same way as field samples, to test for sample contamination during transportation and preparation. To avoid losses of target compounds, all samples were stored in brown glass bottles at 5 °C until they were extracted within 7 days after sampling. The mean blank values (ultrapure water, n = 11) for TDCP (14 ng L^{-1}), TBEP (6 ng L^{-1}), and TiBP (1 ng L^{-1}) were subtracted from concentrations of analytes in the water samples. The blanks were found to contain no detectable amounts of TCEP, TCPP, and TnBP. For all analyzed OPs no adjustments were made in regard to SPE recovery rates (85–99%, n = 6). To exclude the risk of significant losses of analytes (e. g., particle bound OPs) during filtration, filtered (n = 5) and non-filtered (n = 5) samples (1 L) of a 10 L rain sample from Frankfurt/Main and a 10 L water sample from SWHT Kalbach were analyzed and compared regarding their OP concentrations.

Results and discussion

The results of the filtration experiment are already presented in Table I-2 (chapter 2, research paper I). For both rain and water samples the relative standard deviation (RSD) between the mean OP concentration of the filtered and non-filtered samples were clearly below 10% for all OPs. Therefore, possible losses of analytes during filtration were regarded as negligible. All water samples within this study were filtered to avoid cartridge plugging during SPE.

All-season precipitation and storm water runoff. Concentration levels of the six OPs found in all analyzed precipitation and storm water runoff samples at Frankfurt/Main, Bekond and Kleiner Feldberg are reported in Table III-1. Due to the skewed distributions of OP levels, the median, minimum, and maximum values are presented. TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP were detected at all selected precipitation monitoring stations and SWHTs. However, the concentrations of TDCP and TBEP were below LOD in several precipitation samples, both at urban and rural sampling sites. In general, concentrations of OPs in urban rainwater were significantly higher than those from the rural monitoring stations. Based on results of former studies, higher OP concentrations in urban precipitation compared to rural precipitation are expectable (*3,4,77*). These investigations suggest that emissions from urban settlements and road traffic are main sources for OPs in the atmosphere.

Table III-1. Concentrations of OPs (ng L^{-1}) in precipitation and storm water holding tank (SWHT) samples [a)].

	Frankfurt/Main		**Bekond**		**Kl. Feldberg**
[ng L^{-1}]	**Precipitation** n = 90	**SWHT** n = 42	**Precipitation** n = 48	**SWHT** n = 10	**Precipitation** n = 29
TCEP	71 (10-485)	77 (33-275)	12 (<LOD-127)	78 (23-131)	40 (11-390)
TCPP[b)]	403 (32-3562)	880 (16-5791)	134 (5-1214)	410 (197-4847)	57 (<LOD-1154)
TDCP	5 (<LOD-532)	13 (<LOD-73)	7 (<LOD-87)	11 (<LOD-36)	16 (<LOD-497)
TBEP	21 (<LOD-505)	77 (<LOD-1616)	<LOD (<LOD-205)	36 (<LOD-77)	17 (<LOD-242)
TiBP	106 (<LOD-1410)	117 (2-1478)	14 (<LOD-160)	359 (32-826)	41 (<LOD-424)
TnBP	108 (<LOD-1679)	57 (4-417)	16 (<LOD-110)	138 (13-347)	64 (<LOD-458)

[a)] Median (minimum-maximum).

[b)] Sum of two isomers; tris(2-chloro-1-methylethyl) phosphate, CAS 13674-84-5; bis(1-chloro-2-propyl)-2-chloropropyl phosphate, CAS 76025-08-06.

The box plots with TCEP, TCPP, TiBP, and TnBP concentrations from the all-season precipitation samplings are shown in Fig. III-1. TCPP was the most abundant chlorinated OP in precipitation, with maximum concentrations exceeding 1 µg L^{-1} at all sampling sites. Highest TCPP values were found in samples from the urban sampling site Frankfurt/Main (3562 ng L^{-1}). The all-season median TCPP value at Frankfurt/Main (403 ng L^{-1}, n = 90) is lower than the median value investigated at the same sampling site in an earlier study (743 ng L^{-1}, n = 26) (*77*). As shown in Table III-1 and Fig. III-1A, the highest concentrations of TCEP in rainwater were found at Frankfurt/Main (485 ng L^{-1}) and Kleiner Feldberg (390 ng L^{-1}). TCEP is still present at such high concentration levels, although TCEP has been substituted by TCPP in Europe since the mid 1990s as a voluntary agreement of industry. TCEP has been detected in all of the analyzed precipitation samples from Frankfurt/Main and Kleiner Feldberg. On the contrary, the TCEP levels of 14 rain and snow samples from Bekond (n = 48) were below LOD. These 14 rain and snow samples were mostly collected during wintertime (November–February). Obviously, higher TCEP volatilization rates in summer months have led to higher amounts of atmospheric TCEP available for wet deposition at rural sampling site Bekond.

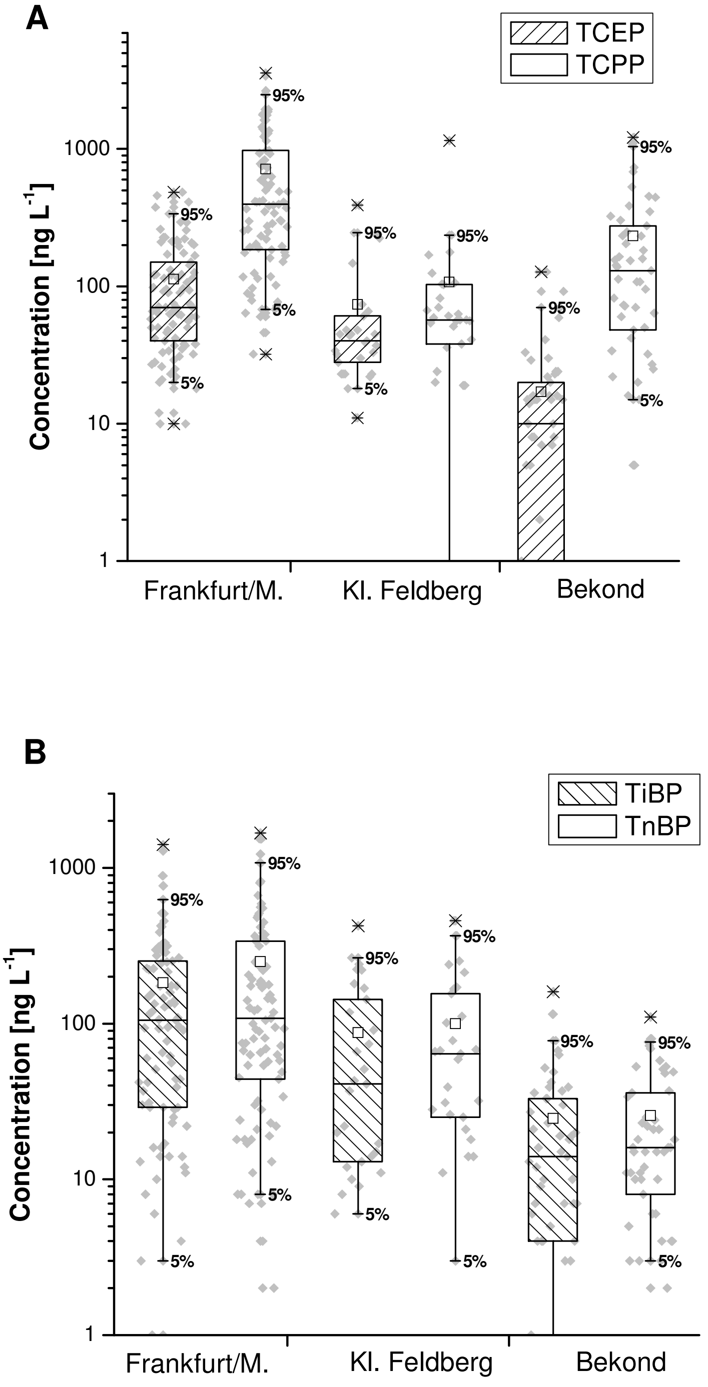


Fig. III-1. Box plots of TCEP, TCPP, TiBP, and TnBP concentrations in precipitation samples from sampling sites Frankfurt/Main (n = 90), Kleiner Feldberg (n = 29), and Bekond (n = 48) (all-season sampling).

The box plots of the concentrations of TiBP and TnBP measured in precipitation samples from Frankfurt/Main, Kleiner Feldberg, and Bekond are shown in Fig. III-1B. The concentration variation between both substances at each sampling site is lower than the variation observed for the chlorinated OPs TCEP and TCPP. This could either point to a similar use and disposal of TiBP and TnBP or to similarities in the atmospheric photodegradation half-life. The atmospheric photodegradation half-life of TnBP is reported to be less than 1 hour and therefore much shorter than the half-life ($t_{½}$ = 4.3 h) of TiBP (*58*). Therefore, higher amounts of TnBP compared to TiBP can be expected to be released into atmosphere. The supposed vapor pressures of TnBP (0.465 Pa) and TiBP (1.71 Pa) at 25 °C do not diverge considerably. Both compounds are used in the same product scale, mainly in aircraft hydraulic fluids or as antifoaming agents (*79*). In 2007, the total annual use of TnBP and TiBP in the Nordic countries Denmark, Finland, Norway, and Sweden were 117.8 t and 37.1 t, respectively (SPIN, database for substances in preparations in Nordic countries). However, TnBP concentrations in storm water runoff samples collected from both investigated SWHTs are significantly lower than TiBP concentrations (Table III-1). The median values for TnBP and TiBP were 57 ng L^{-1} and 117 ng L^{-1} at SWHT Kalbach and 138 ng L^{-1} and 359 ng L^{-1} respectively at SWHT Bekond. This can be explained by the faster biodegradation of TnBP compared to TiBP as discussed later.

The median TCPP and TBEP concentrations in the storm water runoff samples from SWHT Kalbach and SWHT Bekond are considerably higher than the median concentrations measured at the precipitation sampling sites placed close to both basins (Table III-1). That applies also to the median TCEP, TiBP, and TnBP concentrations at SWHT Bekond. The monthly averaged OP concentrations measured at SWHT Kalbach are displayed in Fig. III-2. Within the sampling period May 2008–April 2009, monthly averaged concentrations of the chlorinated flame retardants (Fig. III-2A) ranged between 199–2670 ng L^{-1} (TCPP), 38–230 ng L^{-1} (TCEP), and 1–36 ng L^{-1} (TDCP). TCEP showed lowest average values in August and November and highest average values in December and January whereas TDCP minima were detected in July, December, and April. The lowest and highest average values of TCPP were in August and March, respectively. Fig. III-2B displays the monthly averaged concentrations of the non-chlorinated OPs ranging between 1–807 ng L^{-1} (TBEP), 32–656 ng L^{-1} (TiBP), and 18–275 ng L^{-1} (TnBP). TiBP and TnBP showed lower average values from August to November, TBEP from May to November, too. Compared to the chlorinated compounds a seasonal trend with decreasing concentrations in summer/autumn is evident for the non-chlorinated OPs.

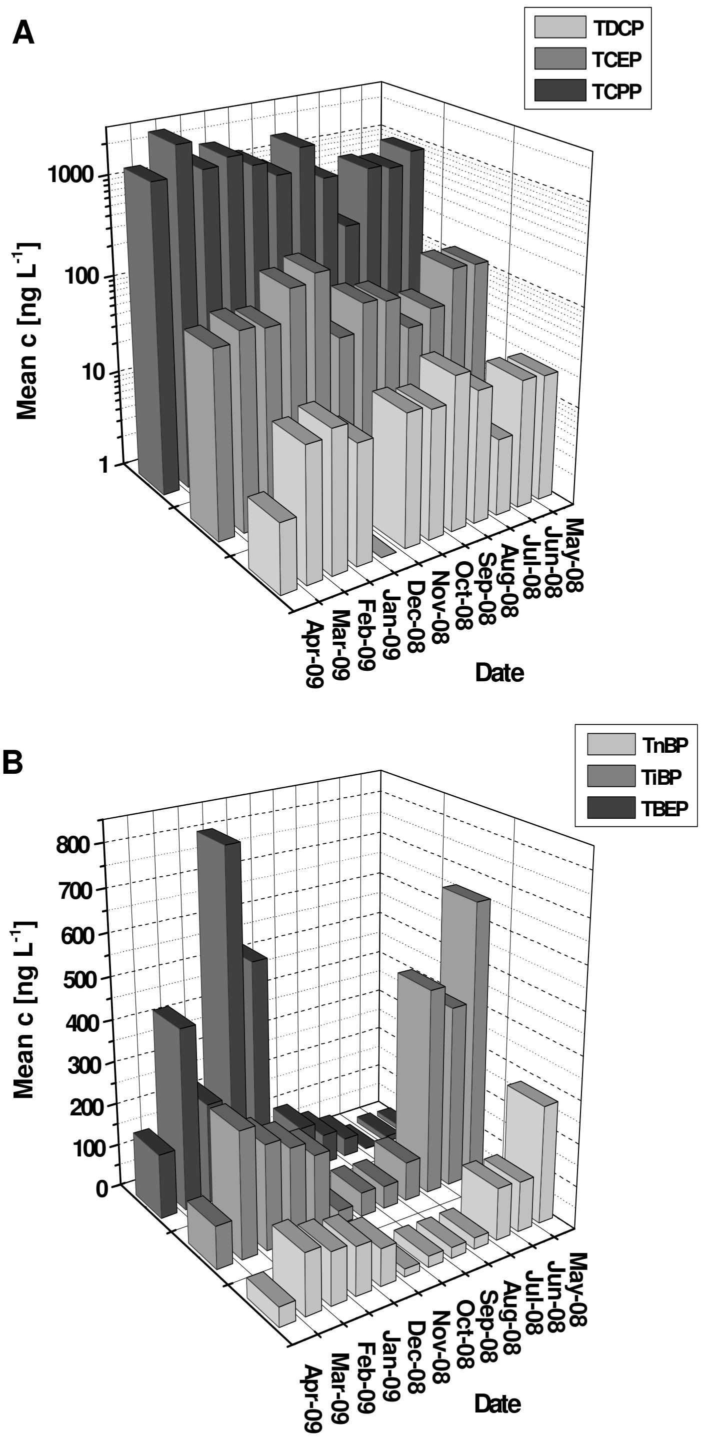


Fig. III-2. Monthly averaged OP concentrations at storm water holding tank (SWHT) Kalbach from May 2008 to April 2009.

Based on the observations described above, an accumulation of OPs in SWHTs, especially in rural areas, can be expected. TCPP is the substance with the highest concentrations. Maximum TCPP levels of 5791 ng L^{-1} and 4847 ng L^{-1} respectively have been detected at both SWHT Kalbach and Bekond. For instance, substances like copper and zinc are known to be mobilized from rooftops or buildings by rainwater runoff (*80*). Therefore, mobilization of OPs from buildings (e. g., insulation materials, concrete) and sealed urban areas by storm water can also be assumed (*81*). However, data of indoor measurements from wallpapers and a newly built house show high emissions of diverse OPs in indoor environments with TCPP being detected in wallpaper, TnBP in wall and ceiling coverings, and TBEP in wooden flooring cleaned with floor polish agent (*82,83*). Ni et al. (*82*) concluded for indoor environments that materials containing high amounts of organophosphorus flame retardants can result in high emission rates particularly at increasing ambient temperatures. From building and vehicle interiors the released flame retardants reach the outdoor environments via ventilation systems or cleaning procedures. In Tokyo outdoor air TBEP, TnBP, and TCPP were detected with maximum concentrations ranging between 1.1 ng m^{-3} and 3.1 ng m^{-3}. Maximum levels of TCPP, TCEP, and TBEP in indoor air were 1260 ng m^{-3}, 136 ng m^{-3}, and 118 ng m^{-3}, respectively (*83*). In Oslo (Norway) TiBP (0.32–4.4 ng m^{-3}), TnBP (0.3–3.7 ng m^{-3}), TCEP (0.51–6.2 ng m^{-3}), and TCPP (0.24–3.7 ng m^{-3}) were measured in outdoor air samples from an urban air quality measurement station with high traffic impact. TiBP (0.14 ng m^{-3}), TCEP (0.27 ng m^{-3}), TCPP (0.33 ng m^{-3}), and TDCP (0.25 ng m^{-3}) were also detected in outdoor air samples from a Norwegian observatory in an undisturbed Arctic environment, but their concentrations were in the range of the detection limits (*79*).

The discharge of the cumulated storm water runoff into creeks and rivers usually occurs without any treatment. Infiltration into the ground is also possible if the retention basins are not sufficiently sealed off. As bank filtration studies have shown (*21,45*), compounds with a high sorption tendency can be effectively retained in soils, while substances with lower soil sorption coefficients will reach the groundwater. For TCEP and TCPP breakthrough during bank filtration/underground passage has been reported (*81*). Furthermore, contamination of a karst spring from overflow of a nearby storm water tank for combined wastewater after heavy rainfall events has been reported (*5*). Against the background of recent climate change predictions with an increasing number of storm events, more investigations in view of contaminated urban storm water runoff will be necessary.

Variations of OPs in precipitation. Fig. III-3 gives an indication about monthly fluctuations of TCEP, TCPP, and TnBP in precipitation at Frankfurt/Main (November 2007 to April 2009). The average values of TCEP, TCPP, and TnBP were in the range of 42–182 ng L^{-1}, 249–1277 ng L^{-1}, and 26–634 ng L^{-1}, respectively. Highest TCPP levels (956–1277 ng L^{-1}) were detected in November/December 2007, May 2008, and February/March 2009 whereas lowest TCPP levels (249–326 ng L^{-1}) were detected in June/July/December 2008 and April 2009. The highest monthly averaged TnBP concentration has been measured in April 2008 (n = 4); the lowest in April 2009 (n = 3). The monthly averaged TCEP levels show neither seasonal nor other distinctive fluctuations. Nevertheless, no significant seasonal trend can be observed for TCPP and TnBP, too.

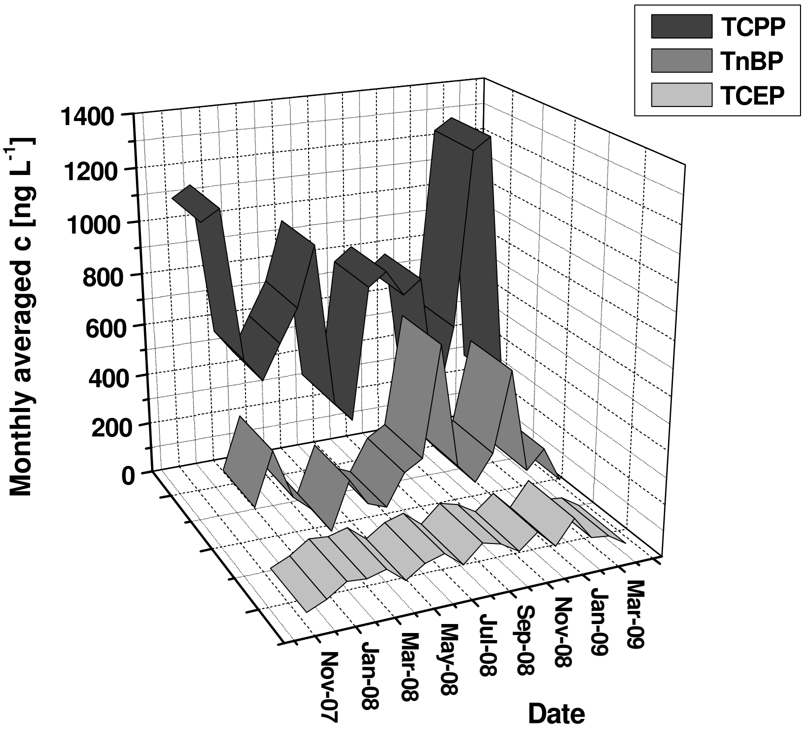


Fig. III-3. Fluctuations of monthly averaged TCPP, TCEP, and TnBP concentrations in precipitation from urban sampling site Frankfurt/Main (November 2007 to April 2009).

In contrast to the measured TnBP concentrations in storm water runoff with a lower level in summer/autumn months (Fig. III-2B), no obvious concentration decrease of TnBP in precipitation of Frankfurt/Main can be observed during that time. This observation is also valid for TiBP. The median (mean) concentrations of TiBP in urban precipitation from April–September and October–March were 134 ng L^{-1} (243 ng L^{-1}) and 96 ng L^{-1} (161 ng L^{-1}), respectively; those for TnBP 96 ng L^{-1} (256 ng L^{-1}) and 113 ng L^{-1} (235 ng L^{-1}). As reported previously (*77*), no correlation of OP concentrations in precipitation with ambient air temperature has been detected. Furthermore, no direct relationship between OP variations and rainfall amount or global irradiance has been observed. Higher releases of OPs in summer months caused by higher ambient temperatures might be counterbalanced by higher photochemical degradation rates in the atmosphere as global irradiance is increasing in summer and decreasing in winter.

To test for seasonal OP variation in precipitation at the rural sampling site Kleiner Feldberg, median values of summer (June–September, n = 13) and winter (November–March, n = 16) months were compared. The results are presented in Fig. III-4 and show considerably lower median TiBP (17 ng L^{-1}, 131 ng L^{-1}) and TnBP (25 ng L^{-1}, 133 ng L^{-1}) concentrations in summer than in winter. The summer/winter concentrations of TCEP (33 ng L^{-1}, 46 ng L^{-1}) and TCPP (54 ng L^{-1}, 65 ng L^{-1}) remain largely constant. These findings are consistent with the shorter atmospheric half-lives of TnBP and TiBP ($t_{½}$ = <1–4.3 h) compared to the chlorinated OPs ($t_{½}$ = 8.6–21.3 h) (*77*). During the atmospheric transportation of TiBP and TnBP from urban settlements to more remote areas the photodegradation rate is expected to be higher in months with higher global irradiance compared to the chlorinated OPs. There was no concentration decrease of TiBP and TnBP in summer at urban sampling site Frankfurt/Main. This can be explained by lower degree of photodegradation of OPs when precipitation is sampled close to the points of emission.

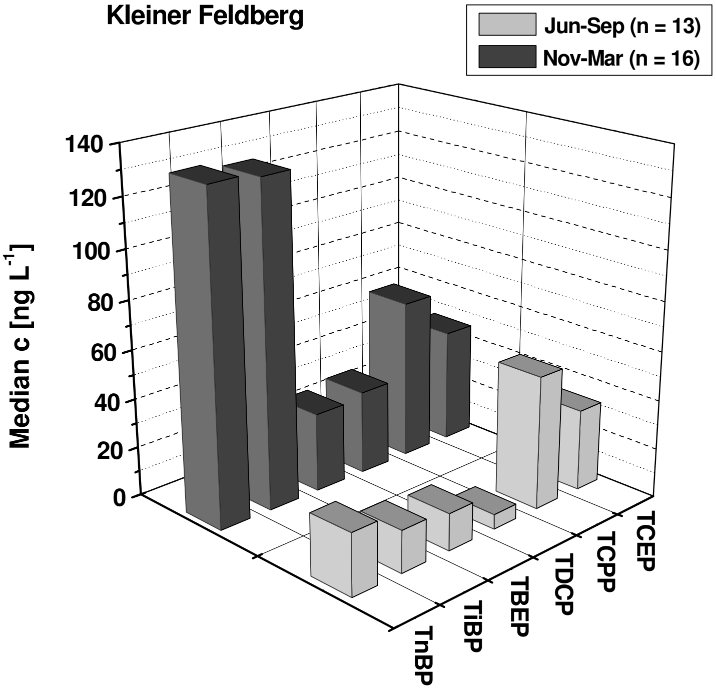


Fig. III-4. Seasonal variation of OPs in precipitation at sampling site Kleiner Feldberg.

Degradation of non-chlorinated OPs in SWHTs. As displayed in Fig. III-2B, the non-chlorinated OPs (TiBP and TnBP) show a significant concentration decrease in summer/autumn months at SWHT Kalbach compared to winter/spring months, while no concomitant decrease was seen in precipitation. The seasonal dependency of the concentration decrease of TBEP in summer/autumn months in surface water is visible but less pronounced than for TiBP and TnBP. In contrast, no significant concentration decrease of the chlorinated flame retardants is observed in the SWHTs during summer/autumn months (Fig. III-2A). For the non-chlorinated OPs two possible degradation pathways in water are expected: biodegradation and photochemical decomposition.

A study with river water demonstrated that some phosphate esters were subject of primary biodegradation when exposed to natural microbial river populations. In river water, TnBP was completely degraded in less than 7 days, while controls with sterile water showed no significant losses of TnBP. A stepwise enzymatic hydrolysis of the phosphate esters was supposed (*41*). In another study the degradation of TnBP by bacteria (Pseudomonas diminuta) isolated from river water occurred faster after adapting the bacteria to OPs for two months. More than 50% of TnBP (2 mg L^{-1}) were degraded after 2 hours and finally 100% after 43 hours at a temperature of 40 °C (*58*). Quintana et al. (*42*) measured the removal of TiBP and TBEP in an aerobic laboratory degradation test with activated sludge and an additional carbon source. For both substances, 16 days were required for complete microbial degradation. The results of an aerobic biodegradation test with domestic sewage for TiBP and TnBP have also shown that biodegradation of TnBP occurred faster than biodegradation of TiBP. Almost 89% of TnBP were decomposed after 28 days whereas only 63% of TiBP have been degraded within 27 days (*58*). These findings are consistent with results from previous studies indicating that chlorinated flame retardants are more stable in aquatic and atmospheric environments than non-chlorinated OPs (*1,24*). Laboratory experiments have shown that TCEP and TnBP are poor light-absorbers in the UV-C range and therefore no direct photolysis was observed in model surface water. A second order photodegradation reaction of TCEP and TnBP was observed in UV-irradiated solutions containing hydrogen peroxide (H_2O_2). However, to achieve for TCEP the same removal rates (90–100%) than for TnBP, a 10-fold higher UV fluency was needed in case of TCEP (*40*).

The decrease of the non-chlorinated phosphoric acid triesters TiBP, TnBP, and TBEP in lentic surface waters appears to consist of several degradation processes. In summer microbial and maybe photochemical decomposition of the non-chlorinated OPs TiBP, TnBP, and TBEP would be expected to proceed faster than in winter because of an increased water temperature and global irradiance, and higher amounts of organic material required for bacterial growth.

Conclusion

The results of the present study emphasize the importance of precipitation as an all-season entry-pathway for OPs in the aquatic environment, especially in densely populated urban environments with high traffic volume. Even if atmospheric photooxidation reduces transport of non-chlorinated OPs from urban to remote areas in months with higher global irradiance, no seasonal trend can be observed at the urban sampling site Frankfurt/Main. Higher photochemical degradation rates in the atmosphere are probably counterbalanced by higher releases of OPs in summer months. Furthermore, an accumulation of deposited OPs in SWHTs is expected. If their discharges into natural surface waters, e. g. creeks and rivers, are not sufficiently diluted, they are additional sources of OPs in the aquatic environment. Nevertheless, long-term monitoring studies for OPs in precipitation at various urban and remote areas are required for conducting a widespread environmental assessment. The increasing use of flame-protected products will raise the OP emissions into the atmosphere and finally into surface waters.

IV Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany

Abstract

Within this study, concentration levels and distribution of the organophosphates tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) were investigated at nine lentic surface waters under different anthropogenic impact between June 2007 and October 2009. Furthermore, the possibility of in-lake photochemical degradation of the analytes was studied in laboratory experiments using spiked ultrapure water and lake water samples incubated in Teflon bottles (which transmit sunlight). TBEP, TiBP, and TnBP were photochemically degraded in spiked lake water samples upon exposure to sunlight. Organophosphate concentrations in the more remote lakes were often below or close to the limits of quantitation (LOQ). TCPP was the substance with the highest median concentration in rural volcanic lakes (7–18 ng L^{-1}) indicating an atmospheric transport of the compound. At urban lakes their median concentrations were in the range of 23–61 ng L^{-1} (TCEP), 85–126 ng L^{-1} (TCPP), <LOQ–53 ng L^{-1} (TBEP), 8–10 ng L^{-1} (TiBP), and 17–32 ng L^{-1} (TnBP). High variability but no significant seasonal trends were observed for all five organophosphates in urban lake water samples.

Introduction

The environmental occurrence and fate of organophosphates (OPs) that are employed as flame retardants and plasticizers in a large variety of consumer products has increasingly been subject of research activities over the last decade. The chlorinated OPs tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloro-1-methylethyl) phosphate (TCPP) are predominantly used as flame retardants whereas the non-chlorinated esters tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) are mostly applied as plasticizers, antifoaming agents, and additives (*6*). These compounds are high production volume chemicals (HPV) with an estimated annual total consumption of altogether 91,000 t yr^{-1} in Western Europe in 2006 (http://www.cefic-efra.com). Several studies have shown the occurrence of the OPs in the aquatic, terrestrial, and atmospheric environment as a result of anthropogenic activities (*1*). The potential adverse effects of OPs to the ecosystem and human health have been discussed in several studies (*6,7*) and risk assessments (*32,33*). The chlorinated flame retardant TCEP was mainly substituted by TCPP in Europe since mid 1990s due to its toxic effects to aquatic organisms and its classification in the European Union (EU) as “potential human carcinogen” (Carcinogen Category 3). Nevertheless, TCEP is still present in the aquatic environment (*7,19,84*) with concentrations exceeding often 0.1 µg L^{-1}. According to a toxicological assessment, TCPP is expected to be non-toxic to aquatic organisms at concentrations less or equal than 1 mg L^{-1} (*33*), even though its data base is not as extensive as the data base available for TCEP. Data gaps for TCPP are still existing, e. g., referring to carcinogenicity (*2*). The non-chlorinated OPs TBEP and TiBP are not classified at EU level, whereas TnBP is labeled as a carcinogenic substance in the online European chemical substances information system (ESIS).

The contribution of treated and untreated wastewater discharges as a main source for OPs in surface waters has been extensively discussed in former studies (*6,20*). Furthermore, the resistance of the chlorinated flame retardants to biodegradation and to removal from potable water and wastewater by several treatment methods apart from activated carbon filtration is well documented (*50,65,76*). Infiltration experiments with waste water for groundwater recharge indicated little TCEP attenuation causing a high potential of the compound to reach groundwater (*21,45*). Therefore, groundwater contaminated with chlorinated OPs might cause problems for drinking water production (*1*). So far, only few studies focused on the occurrence and fate of OPs in lentic surface waters that are not affected by wastewater discharges or other industrial sources of contamination (*4,60*). Particularly in hydrographic closed systems like small lakes, the only possible sources of OPs are precipitation, runoff processes, and local anthropogenic activities. The impact of precipitation and storm water runoff as an entry-pathway for OPs in the aquatic environment has been discussed in recent studies (*77,84*). In the present study, concentration levels, distribution and degradation of the OPs TCEP, TCPP, TBEP, TnBP, and TiBP were determined from June 2007 till May 2009 at five lentic surface waters under different anthropogenic impacts. Additionally, three partly remote montane reservoirs and one lake were sampled once in October 2009 to investigate the atmospheric transport of OPs. Furthermore, in laboratory experiments ultrapure water and lake water samples were spiked with the five target compounds and incubated in Teflon bottles (which transmit sunlight) for about two weeks to simulate in-lake degradation of the analytes.

Material and methods

Chemicals. Individual and composite stock solutions (1 µg μL^{-1}) of the target compounds TCEP, TiBP, TnBP, TBEP (Sigma Aldrich, Steinheim, Germany), and TCPP (Akzo Nobel, Amersfoort, The Netherlands) were prepared in methanol/acetonitrile (1/1 v/v). The stock solution (1 µg μL^{-1}) of the internal standard squalane (Sigma Aldrich) was prepared in hexane. Working solutions were prepared by appropriate dilution of the stock solutions. Mercury dichloride was purchased from Merck (Darmstadt, Germany) and diluted in ultrapure water (2 µg μL^{-1}). Acetonitrile (J. T. Baker, Deventer, The Netherlands) was ultrapure HPLC grade and was used as received. All other solvents were of analytical grade (Merck) and were distilled before use. Ultrapure water was generated using an Astacus ultrapure water purification system (MembraPure, Bodenheim, Germany).

Study area and sampling. A schematic map showing all sampling sites in Germany is provided in Fig. IV-1. Grid values, altitudes and the surface areas of the lakes and reservoirs, the analyzed sample numbers and the sampling time spans are listed in Table IV-1. Lake water samples were collected in the Eifel region from June 2007 to March 2009 and at the urban area of Frankfurt am Main from June 2008 to May 2009. Sampling intervals of the volcanic lakes Holzmaar, Meerfelder Maar, and Lake Windsborn (Eifel) were randomly once a month whereas samplings of Pond Eastpark and the oxbow lake of river Nidda (both Frankfurt am Main) were carried out biweekly. The three montane reservoirs (Thuringian Forest) and the montane lake (Hessian Rhoen) were sampled once in October 2009. In general, the samplings were performed in duplicate. Twice a volume of 2 L surface water was collected from each lake or reservoir at a depth of 0.2 m.

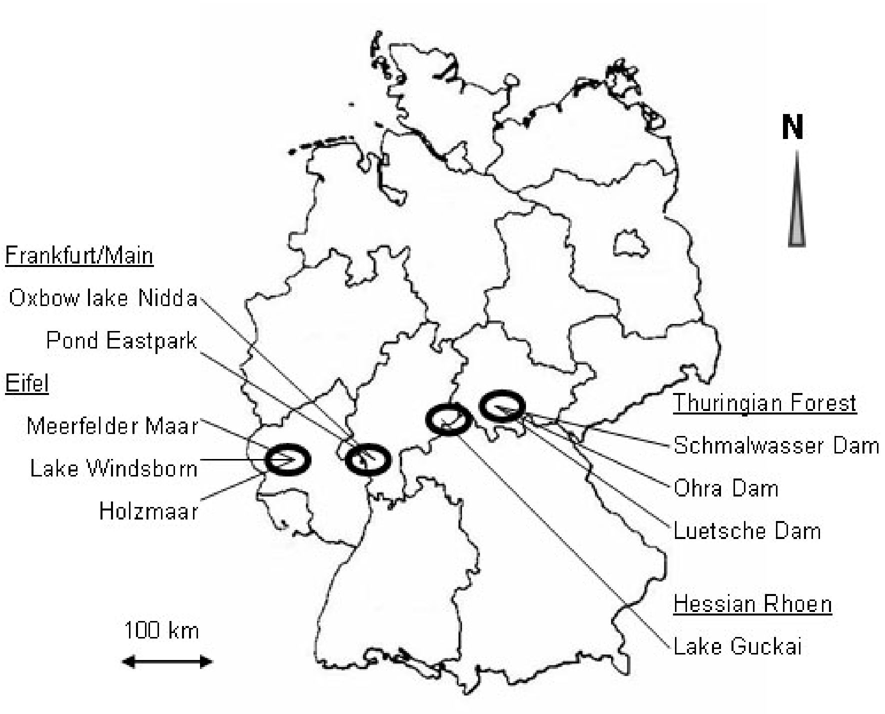


Fig. IV-1. Schematic map of the surface water sampling sites at Germany.

Table IV-1. Grid values of sampling sites.

Lake	N (°)	E (°)	Altitude (m)	Surface area (m²)	Samples (n)	Date
Eastpark pond	50 07161	8 43228	100	42,000	42	Jun 08–May 09
Oxbow lake Nidda	50 10473	8 39520	107	11,000	41	Jun 08–May 09
Lake Windsborn	50 05088	6 46306	474	13,000	20	Jun 07–Mar 09
Holzmaar	50 07110	6 52378	436	58,000	20	Jun 07–Mar 09
Meerfelder Maar	50 06026	6 45467	349	248,000	20	Jun 07–Mar 09
Schmalwasser Dam	59 46192	10 38455	575	800,000	2	Oct 09
Ohra Dam	50 45419	10 42519	534	820,000	2	Oct 09
Luetsche Dam	50 44045	10 45192	593	140,000	2	Oct 09
Lake Guckai	50 29048	9 55211	690	5,000	2	Oct 09

The Eifel region is a sparsely populated low mountain range area in western Germany with agriculture and tourism as dominating economic resources. The selected lakes Meerfelder Maar, Holzmaar, and Lake Windsborn are of volcanic origin and are protected by environmental legislation. Anthropogenic activities around these lakes are principally restricted to hiking. The montane reservoirs Schmalwasser Dam, Ohra Dam, and Luetsche Dam are located in the Thuringian Forest near Mount Schmuecke at a height of 500–600 m above sea level. Schmalwasser Dam and Ohra Dam are mainly used for drinking water supply while Luetsche Dam is used for recreation purposes. All three reservoirs are surrounded by forest. Lake Guckai is located southwest of these dam reservoirs in the Hessian Rhoen near to Mount Wasserkuppe at a height of 690 m above sea level. The drinking water reservoirs and the volcanic lakes are both only marginally affected by anthropogenic activities. Two different surface waters located in the greenbelt of the urban area Frankfurt am Main were investigated as contrasting localities influenced by severe anthropogenic activities. The oxbow lake of river Nidda is part of a local recreation area in the northern greenbelt of Frankfurt am Main. The lake resulted from the artificial straightening of river Nidda in 1962/63. The downstream side of the lake is still connected to river and therefore influenced by river water. Pond Eastpark is located at a park straight close to an autobahn in the eastern part of the Frankfurt urban area. The pond originates from an oxbow lake of river Main since the beginning of the 19th century.

Degradation experiment. To assess the effect of sunlight on OP behavior in water bodies, laboratory experiments were conducted on top of the Geosciences Center of Frankfurt University (Riedberg campus) in 2008 and 2009. 1 L-Teflon bottles were filled with ultrapure water and lake water, respectively and were spiked with 2 µg of each target compound. Lake water samples were collected at sampling site Holzmaar by filling 1 L-Teflon bottles with surface water. These samples were kept cool in the dark at 5 °C until they were spiked with OPs and placed on top of the Geosciences Center. Two sample sets were subjected to different treatments: (1) absence of light (black Teflon bottles); (2) presence of sunlight (transparent Teflon bottles). The transparent bottles have been shown to be permeable to visible and UV-light, whereas black bottles do not transmit sunlight (*85*). Controls of spiked lake water, poisoned with 1 mg L^{-1} of Hg(II) (*42*), were prepared in black and transparent Teflon bottles. All experiments were carried out in duplicate and were repeated twice at least. The bottles were exposed to natural sunlight for a time period of 15 days. Subsequently, the water samples were analyzed as described below, but without filtration. At the beginning of an experimental series, ultrapure water and lake water samples were analyzed as control. Global irradiance data were obtained from the automatic weather station of the Hessian Agency for the Environment and Geology on Mount Kleiner Feldberg (Taunus, Germany).

Analytical methods. The analytes were extracted and enriched from the water samples (1–2.5 L) by solid phase extraction (SPE) using styrene-divinylbenzene copolymer as adsorbing material in the cartridges (Bond Elut PPL, 1 mL; Varian, Darmstadt, Germany). To avoid cartridge plugging during SPE, water samples containing high amounts of insoluble organics were filtered by pressure filtration with a 142 mm diameter borosilicate glass fiber filter (filter pore size 1 µm; type A/E, Pall, Dreieich, Germany) prior to SPE. After elution of the cartridges with 1 mL methanol/acetonitrile (1/1 v/v) the extracts were analyzed by GC-MS in full scan mode (m/z 50 to 600). Analytes were quantified in selected ion monitoring mode by the internal standard method using squalane as internal standard. Quantitative GC-MS analyses (June 2007–July 2008) were performed on a Fisons GC 8000 coupled to a Fisons MD 800

(Thermo Fisher, Dreieich, Germany). Since August 2008 samples were analyzed by a Trace GC Ultra coupled to a DSQ II MS (Thermo Scientific, Dreieich, Germany) using the same type of column and the same oven temperature program as in the Fisons GC-MS system. Data processing was performed using Excalibur software (Thermo Fisher Scientific, version 2.0.7). See research paper I in chapter 2 and references (*77*) and (*84*) for a detailed description of the applied analytical method.

To avoid sample contamination, all laboratory equipment consisted of glass, stainless steel, or Teflon and was regularly controlled to be OP-free. Glass and Teflon bottles for sampling and degradation experiments were rinsed with ultrapure water and methanol, respectively, and were then heated to 110 °C for a minimum of 6 h. Prior to pressure filtration the glass fiber filters were heated in an oven for more than 2 h at 400 °C. Procedural blanks with ultrapure water treated in the same way as field samples were periodically performed to test for sample contamination during transportation and preparation. All samples were stored in brown glass bottles at 5 °C until they were extracted within 7 days.

In accordance with DIN 32645 (DINTest, University of Heidelberg, $\alpha = 1\%$) the limit of detection (LOD) of 1 ng L^{-1} for TCEP, TCPP, TBEP, TiBP, and TnBP was estimated on the basis of calibration curves using the Thermo Scientific GC-MS system. Ultrapure water samples (1 L) spiked with standard mixtures of target compounds at concentration levels of 1 ng L^{-1}, 2 ng L^{-1}, 5 ng L^{-1}, 20 ng L^{-1}, 50 ng L^{-1}, 200 ng L^{-1}, and 1000 ng L^{-1} were extracted by SPE. Seven-point calibration curves were generated using three replicates of each concentration. For TCEP, TCPP, and TnBP the limit of quantitation (LOQ) was estimated as three times the LOD and ranged between 3 ng L^{-1} (TCEP) and 4 ng L^{-1} (TCPP, TnBP). As TBEP (6 ng L^{-1}) and TiBP (1 ng L^{-1}) have been detected in the blanks (mean, n = 11), their LOQ was calculated adding six times the standard deviation (4 ng L^{-1} and 1 ng L^{-1}, respectively) to the mean blank value. LOQs of TBEP and TiBP were 30 ng L^{-1} and 7 ng L^{-1}. SPE recovery rates and relative standard deviations were 95±2.7% (TCEP), 91±5.5% (TCPP), 93±7.2% (TBEP), 89±4.6% (TnBP), and 85±6.2% (TiBP) in ultrapure water (n = 6) and 99±3.5% (TCEP), 81±8.0% (TCPP), 88±4.1% (TBEP), 82±9.2% (TnBP), and 72±9.9% (TiBP) in Holzmaar lake water (n = 3). Concerning natural water samples, no adjustments were made for differences in recoveries of individual OPs during SPE.

Results and discussion

OP concentrations in urban lentic surface waters. The median, 5 and 95 percentile concentration values of TCEP, TCPP, TBEP, TiBP, and TnBP in urban lentic surface waters are presented in Table IV-2. TCEP, TCPP, and TnBP were detected in almost all water samples from Pond Eastpark (n = 42) and oxbow lake Nidda (n = 41). TCPP was the most abundant chlorinated OP in urban lake water samples with median concentrations of 85 ng L^{-1} and 126 ng L^{-1}, respectively.

Table IV-2. Concentrations of OPs (ng L^{-1}) in urban and rural lentic surface waters of Germany [a].

	Pond Eastpark	**Oxbow lake Nidda**	**Meerfelder Maar**	**Holzmaar**	**Lake Windsborn**
[ng L^{-1}]	n = 42	n = 41	n = 20	n = 20	n = 20
TCEP	23 (9-66)	61 (14-184)	3 (<LOQ-15)	3 (<LOQ-9)	3 (<LOQ-27)
TCPP[b]	85 (27-175)	126 (52-379)	14 (<LOQ-46)	7 (<LOQ-32)	18 (<LOQ-115)
TBEP	<LOQ (<LOQ-30)	53 (<LOQ-652)	[c]	[c]	[c]
TiBP	10 (<LOQ-82)	8 (<LOQ-62)	<LOQ (<LOQ-56)	7 (<LOQ-101)	9 (<LOQ-77)
TnBP	32 (9-122)	17 (<LOQ-83)	4 (<LOQ-23)	<LOQ (<LOQ-33)	5 (<LOQ-29)

[a] Median (5 and 95 percentile).

[b] Sum of two isomers; tris(2-chloro-1-methylethyl) phosphate, CAS 13674-84-5; bis(1-chloro-2-propyl)-2-chloropropyl phosphate, CAS 76025-08-06.

[c] Not quantified.

The median TCPP level in oxbow lake Nidda exceeded the acceptable TCPP concentration of 0.1 µg L^{-1} as proposed by the Federal Environmental Agency of Germany (*31*). Except of TiBP and TnBP, the median concentrations of the OPs in oxbow lake Nidda were significantly higher than those in Pond Eastpark. TCEP was detected in these lakes with median concentrations of 23 ng L^{-1} and 61 ng L^{-1}. The monthly averaged TCEP, TCPP, TiBP, and TnBP concentrations found in Pond Eastpark and in oxbow lake Nidda are displayed in Fig. IV-2 and Fig. IV-3, respectively. Considering the OP distribution pattern of both lentic surface waters, monthly fluctuations regarding occurrence and concentration levels become apparent. Especially in November, increased TiBP concentrations were detected in Pond Eastpark (88 ng L^{-1}) and oxbow lake Nidda (88 ng L^{-1}). In general, TiBP concentrations in Pond Eastpark and oxbow lake Nidda were lower than TnBP levels.

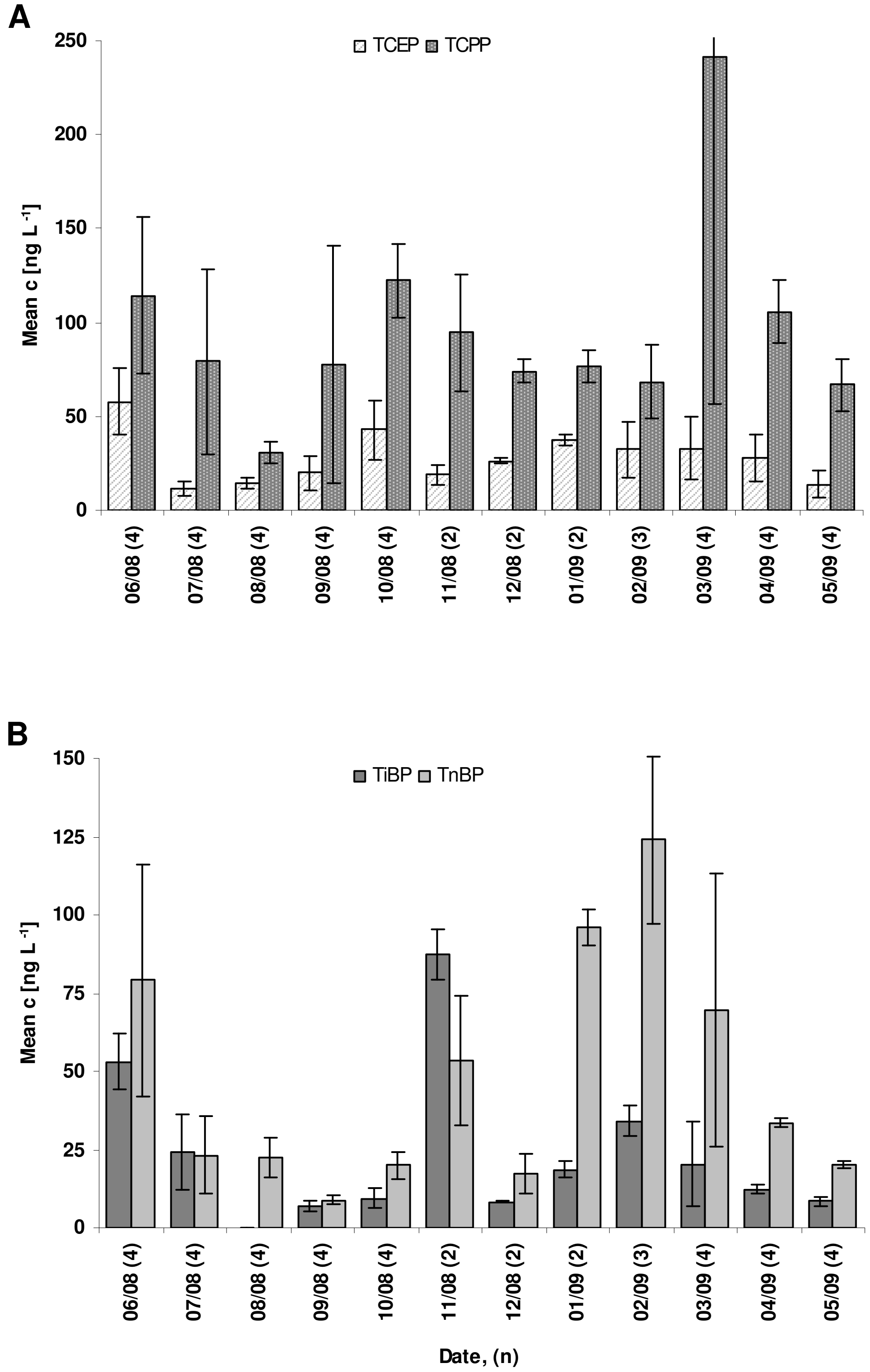


Fig. IV-2. Monthly averaged concentrations and standard deviations of chlorinated (A) and non-chlorinated (B) organophosphates in surface water samples of Pond Eastpark (Frankfurt am Main) from June 2008–May 2009. Sample amounts are given in parenthesis.

The data of TiBP and TnBP basically show a similar distribution in both lakes (Fig. IV-2B and IV-3B).

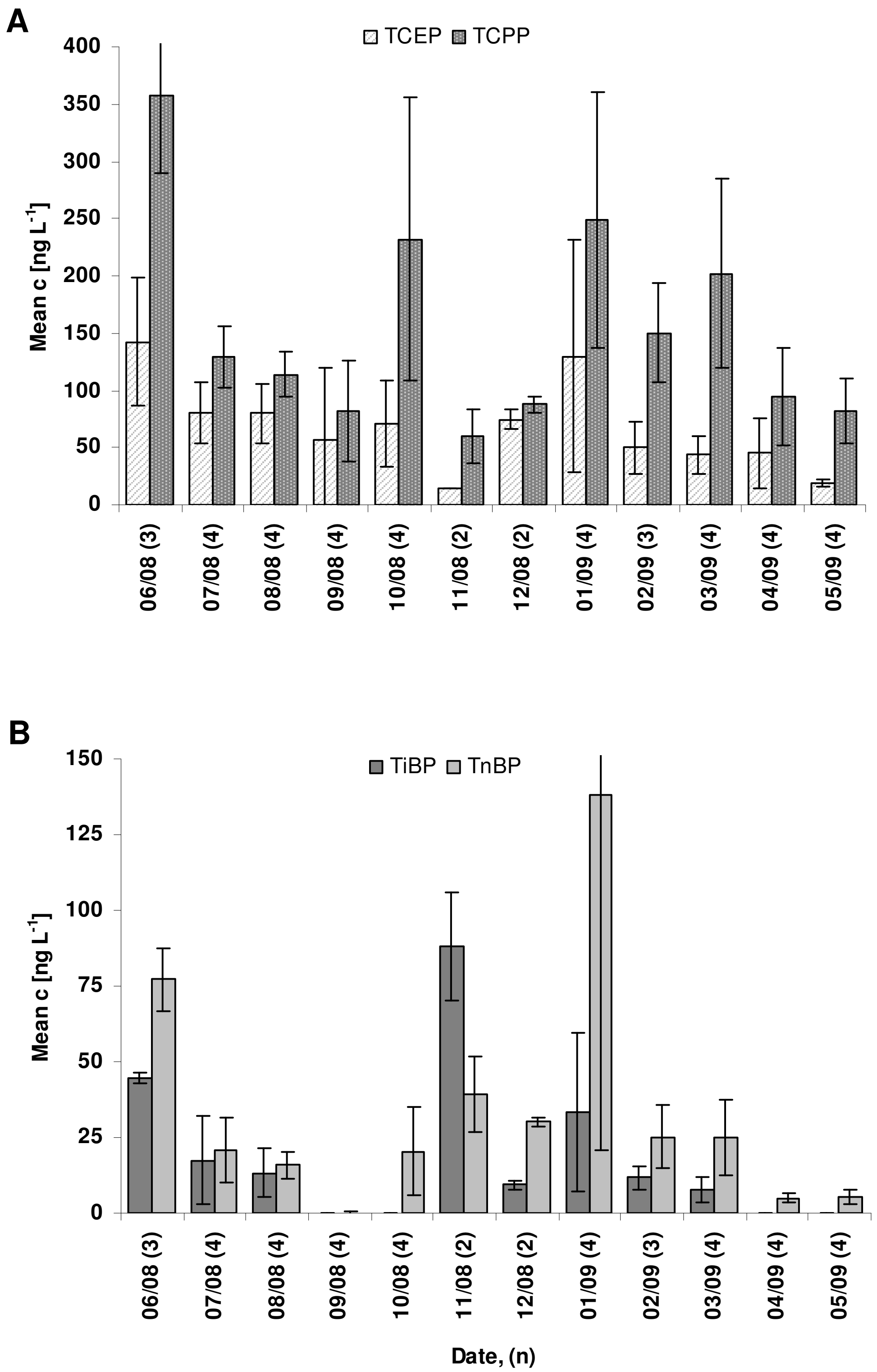


Fig. IV-3. Monthly averaged concentrations of chlorinated (A) and non-chlorinated (B) organophosphates in surface water samples of the oxbow lake of river Nidda (Frankfurt am Main) from June 2008–May 2009. Sample amounts are given in parenthesis.

Apart from TCPP in March 2009 (242 ng L^{-1}), the monthly averaged concentration values of TCEP and TCPP varied not significantly in Pond Eastpark throughout the year, but was more distinctive in oxbow lake Nidda (Fig. IV-2A and IV-3A). However, their concentrations varied almost in parallel with time. The highly fluctuating TBEP concentration in oxbow lake Nidda differed significantly from this variation. TBEP provided high monthly averaged values in January 2009 (688 ng L^{-1}) and August 2008 (433 ng L^{-1}), but concentrations below LOQ in September 2008 and April/May 2009. TBEP concentrations in water samples from Pond Eastpark were mostly below LOQ. Water supplies of Pond Eastpark are in general limited to wet and dry deposition, surface runoff, and groundwater, whereas water of oxbow lake Nidda is additionally influenced by water from the river Nidda containing treated wastewater discharges. The wastewater proportion of the river Nidda (river mouth) is in the range of 26% during mean annual discharge and up to 90% during mean low discharge (*86*). Additionally, the median TBEP concentration of oxbow lake Nidda (53 ng L^{-1}, Table IV-2) is more than twice as high as the median TBEP level measured in precipitation of urban area Frankfurt am Main (21 ng L^{-1}, n = 90) (*84*). This also confirms a major influence of sewage water on the water from oxbow lake Nidda. TBEP concentrations in the range of 663 ng L^{-1} and 543 ng L^{-1} were reported from two point measurements of Nidda river water in March and November 2000 (*54*).

In Italy, Bacaloni et al. (*4*) reported seasonal fluctuations of TiBP and TnBP concentrations in volcanic lake water with maximum levels of both compounds in October/November and minimum levels in March/April. These trends were also reported for the chlorinated OPs TCEP and TCPP. Only TBEP was detected in lake water at almost similar concentrations throughout the whole sampling period (*4*). Within the present study neither significant seasonal trends for the non-chlorinated OPs nor for the chlorinated OPs have been observed.

OP concentrations in rural lakes. Concentrations of TCEP, TCPP, TiBP, and TnBP in water samples collected from the three volcanic lakes are also listed in Table IV-2. TBEP was not detected above the LOQ in all of these samples. In general, the OP levels in these remote lakes were considerably lower than in urban lakes, but the target compounds were still detectable. TCPP was the substance with the highest median concentration in Meerfelder Maar (14 ng L^{-1}), Holzmaar (7 ng L^{-1}), and Lake Windsborn (18 ng L^{-1}). The concentration variation of TCPP between different samplings was low for each lake but the concentration levels differed between the three lakes. During most samplings, e. g. October 2008, TCPP concentrations of Lake Windsborn (40 ng L^{-1}, mean, n = 2) were higher than concentrations measured at lakes Meerfelder Maar (33 ng L^{-1}) and Holzmaar (27 ng L^{-1}). The higher TCPP levels at Lake Windsborn can only be explained by an exclusive origin from precipitation and surface runoff since the water of this lake is not influenced by groundwater due to the volcanic rock substratum of its drainage basin (*87*). At Lake Meerfelder Maar, highest mean values of TiBP (23 ng L^{-1}, 47 ng L^{-1}) and TnBP (26 ng L^{-1}, 14 ng L^{-1}) were observed in November 2007 and November 2008. This observation was also valid for Holzmaar and Lake Windsborn. The analyzed OPs may have the same diffuse origin (road traffic, urban settlements) and reached lake water via precipitation after atmospheric transport.

The target compounds were also detected in samples from Schmalwasser Dam, Ohra Dam, Luetsche Dam, and Lake Guckai. The mean OP concentrations (n = 2) of the four montane surface waters are summarized in Table IV-3. The occurrence of OPs in Schmalwasser Dam, Ohra Dam, and Lake Guckai can be attributed to atmospheric deposition, surface runoff, and the inflow of small mountain streams. Particularly, the reservoirs Schmalwasser Dam and Ohra Dam are only marginally affected by anthropogenic activities since the water is used for drinking water supply. Luetsche Dam is partly surrounded by a small road and a campground is situated at the waterside, which both might contribute as additional (local) OP sources for the reservoir water. This is reflected by a significantly higher mean TCPP concentration (312 ng L^{-1}) in samples from Luetsche Dam compared to the other dams. Although sampling took place only once in October 2009, the results indicate that the montane reservoirs as well as the montane lake were influenced by wet and dry deposition of airborne OPs. Two precipitation sampling campaigns were carried out in winter 2007/2008 (n = 43) and winter 2008/2009 (n = 45) to determine OP concentrations in rain and snow samples from the nearby mountains Mount Schmuecke (montane reservoirs) and Mount Wasserkuppe (montane lake). The median OP concentrations in precipitation ranged between 16–49 ng L^{-1} for TCEP, 52–120 ng L^{-1} for TCPP, 12–99 ng L^{-1} TiBP, and 24–63 ng L^{-1} for TnBP (*77*).

Table IV-3. Mean OP concentrations (ng L^{-1}) in three montane reservoirs and one montane lake of Germany in October 2009.

Compound	**Schmalwasser Dam**	**Ohra Dam**	**Luetsche Dam**	**Lake Guckai**
mean c [ng L^{-1}]	n = 2	n = 2	n = 2	n = 2
TCEP	15	22	33	6
TCPP	41	49	312	31
TBEP	<LOQ	<LOQ	31	<LOQ
TiBP	<LOQ	<LOQ	11	<LOQ
TnBP	4	5	7	<LOQ

The results show that predominantly the chlorinated OPs were detectable in lentic water bodies of altitudes up to 690 m above sea level without surrounding local anthropogenic pollution sources. In order to find out whether the OPs are also detectable in lakes of higher altitude, three subalpine lakes located at Berchtesgaden National Park in the southeast of Bavaria (Germany) were sampled in July 2009. The altitudes of these remote subalpine lakes (Gruensee, Schwarzensee, and Funtensee) range between 1,500 and 1,600 m above sea level. In all water samples collected from these lakes, the five OPs were below the detection limit. Unfortunately, only few data of OPs in remote aquatic environments exist so far. However, reported concentration levels (*4,18,60*) were in accordance to those obtained within this study.

Laboratory degradation experiments. The results of the laboratory degradation experiments are shown in Fig. IV-4. Concentration values in these experiments were normalized via OP recovery rates. The displayed relative standard deviations for TCEP (0.04), TCPP (0.08), TBEP (0.13), TiBP (0.05), and TnBP (0.1) were calculated from recovery tests (n = 4) with spiked ultrapure water samples in Teflon bottles. The averaged daily global irradiance during the 15-day experiment was about 251 W m^{-2}. Both, in samples of spiked ultrapure water (Fig. IV-4B) and spiked lake water (Fig. IV-4A) as well as in the poisoned controls (Fig. IV-4C), no concentration decreases were detectable in case of the chlorinated flame retardants TCEP and TCPP after sunlight exposure. Furthermore, no differences between transparent and black bottles were observed since concentrations varied within standard deviation. In contrast, the concentrations of the non-chlorinated OPs TBEP, TiBP, and TnBP disappeared after 15 days of sunlight exposure almost completely in transparent Teflon bottles filled with spiked lake water (Fig. IV-4A). The concentrations of the non-chlorinated OPs in black bottles as well as the concentrations of all OPs in transparent and black bottles filled with spiked ultrapure water (Fig. IV-4B) remained nearly constant. Concentrations of non-chlorinated OPs in the poisoned transparent Teflon bottles filled with spiked lake water (Fig. IV-4C) decreased too, whereas their concentrations in poisoned black bottles remained constant. Results of the experiments with poisoned controls implicate that degradation of the non-chlorinated OPs depends to a large extent on photochemical processes and not only on microbial processes.

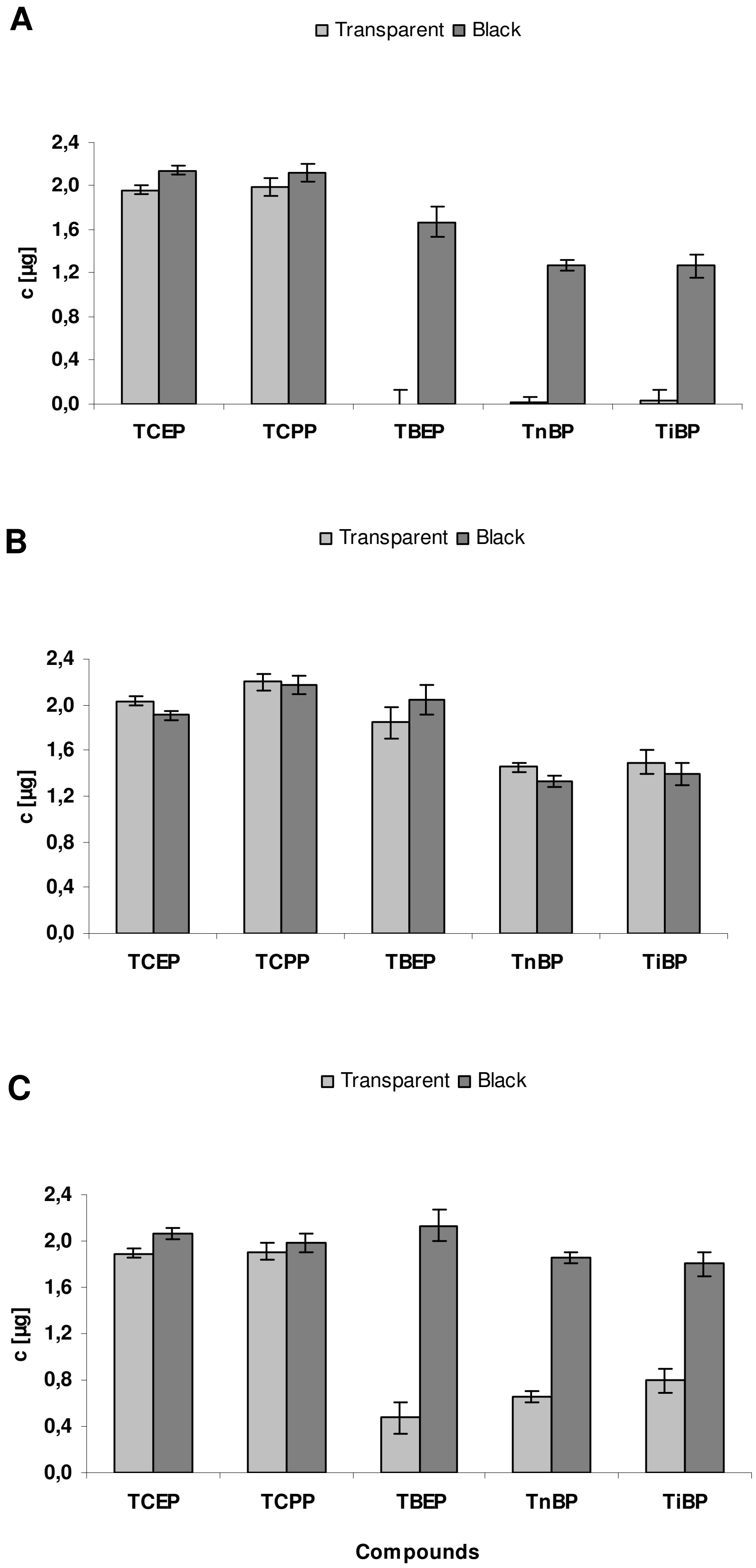


Fig. IV-4. Organophosphate degradation in spiked (2 µg L^{-1}) lake water samples (A), ultrapure water samples (B), and lake water samples poisoned with mercury dichloride (C) incubated for 15 days (23.06.-07.07.2008) in black and transparent Teflon bottles to natural sunlight.

Saeger et al. (*41*) demonstrated that some phosphate esters were subject of primary biodegradation when exposed to natural microbial river populations. For the observed biodegradation processes, a stepwise enzymatic hydrolysis of the phosphate esters was supposed (*41*). Phosphoric acid mono- and diesters were detected as microbially catalyzed hydrolysis products of phosphoric acid triesters (e. g., TnBP) by ion pair liquid chromatography (*42*). Due to the high polarity and acidity of the free phosphoric acid residues, detection by GC-MS can only be realized after derivatization (*88*).

Phosphoric acid triesters were previously assumed to be not subjected to direct photodegradation in surface waters since they are poor light-absorbers in the natural light range (>280 nm), but indirect photolysis via OH-radicals was observed for TnBP and TCEP in UV-irradiated model surface waters containing H_2O_2 (*40*). However, the degradation of non-chlorinated OPs in spiked lake water, observed in the present study, appears to be dependent on sunlight as the concentrations of TBEP, TiBP, and TnBP decreased significantly only in transparent Teflon bottles but not in black Teflon bottles (Fig. IV-4A). Further studies will be necessary to investigate the mechanism of the observed alkyl phosphate degradation in lake water. For instance, dissolved organic matter (DOM) is able to absorb solar irradiation and generate reactive oxygen species (e. g., OH-radicals, H_2O_2) in water (*89,90*). These reactive transients have previously been proposed to induce the indirect OP photolysis (*40*) and might therefore influence the photochemical fate and persistence of the OPs in natural water.

Conclusion

In the present study the occurrence of chlorinated and non-chlorinated OPs in urban and remote lentic surface waters of Germany has been shown. The OPs were detected in samples from two urban lakes (Frankfurt am Main) and three volcanic lakes located at the rural low mountain range area Eifel (altitude 349–474 m above sea level). One of the volcanic lakes is a small crater lake whose water supplies are limited to rainfalls and drainage from forested surrounding areas. Additionally, the OPs were detected in samples from four montane surface waters (altitude 534–690 m above sea level) during one sampling in October 2009. Concentrations of non-chlorinated OPs were often below LOQ in the remote lakes. According to these data atmospheric short- and medium-range transport of OPs after their release by volatilization from products and their atmospheric washout by precipitation represents an entry-pathway especially for chlorinated OPs into lentic surface waters located at elevation up to approximately 700 m. The OPs have so far not been detected in lakes located at altitudes above 1,000 m, but further studies have to verify this.

In general, the OP levels in the rural lakes were considerably lower than in lakes of the urban area Frankfurt am Main. High variability but no significant seasonal trends were observed for all five organophosphates in urban lake water samples. Results from laboratory experiments have shown the rapid degradation of non-chlorinated OPs and the resistance of chlorinated OPs in natural waters upon sunlight irradiation. However, further investigations will be necessary to prove that photodegradation also affects OP concentrations in lentic surface waters.

V Occurrence and distribution of organophosphorus flame retardants and plasticizers in anthropogenically-affected groundwater

Abstract

Occurrence and distribution of chlorinated and non-chlorinated organophosphates in 72 groundwater samples from Germany under different recharge/infiltration conditions were investigated. Tris(2-chloro-1-methylethyl) phosphate (TCPP) and tris(2-chloroethyl) phosphate (TCEP) were the most frequently detected organophosphates in groundwater samples. Highest organophosphate concentrations (>0.1 µg L^{-1}) were determined in groundwater polluted by infiltrating leachate or groundwater recharged via bank filtration of organophosphate-loaded recipients. In samples from springs and deep groundwater monitoring wells that are not affected by surface waters, organophosphate concentrations were mostly below the limit of detection. The occurrence (3–9 ng L^{-1}) of TCPP and TCEP in samples from aquifers with groundwater ages between 20–45 years indicates the persistence of both compounds within the aquifer. At urban sites organophosphate-loaded precipitation, surface runoff, and leakage of wastewater revealed to influence groundwater quality, but at rural sites with groundwater recharge only influenced by precipitation, organophosphates were only occasionally detectable in groundwater.

Introduction

In conjunction with safeguarding the local supply of clean drinking water, contamination of groundwater with trace organic pollutants has become of great interest during the last decade. Among pesticides, pharmaceuticals, steroid hormones, and personal care products, organophosphorus flame retardants and plasticizers such as tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) have been detected in groundwater (*4,20,21*) and drinking water (*46,91*). These organophosphates (OPs) are widely used industrial chemicals with an estimated total consumption of 91,000 t yr^{-1} in the European Union in 2006 (http://www.cefic-efra.com). The chlorinated OPs TCEP, TCPP, and TDCP are preferentially applied as flame retarding additives in polyurethane foam in domestic, public, and automotive applications while the non-chlorinated OPs TBEP, TiBP, and TnBP are mainly added as plasticizing, antifoaming or flame retarding agents to plastic materials and hydraulic fluids (*1*). TiBP is also applied as a common antifoaming agent in pharmaceutical production (*92*). According to an increasing global demand of fire protected materials and products, the production volume of chlorinated and non-chlorinated OPs is expected to further increase worldwide (*29*).

Due to their physicochemical properties (Fig. 1-1, chapter 1.2), the chlorinated flame retardants TCEP, TCPP, and TDCP can be classified as persistent organic compounds in the aquatic environment (*38*). Several studies (*6,7*) and risk assessments (*32-34*) debated on their potential adverse effects to the ecosystem and human health. TnBP, TCEP, and TDCP are known, or in case of TCPP, are suspected to be carcinogenic for animals (*14,29*). Although TCEP was largely substituted by TCPP in Europe around 1995 based on a voluntary agreement of industry, it is still frequently detected in the environment (*19,84*). Bis(2-chloroethyl) phosphate, a metabolite of TCEP, was recently found in 15 of 30 native urine samples of the German general population during a biomonitoring study (*13*). The metabolite of TCPP, the dialkyl phosphate bis(2-chloro-1-methylethyl) phosphate was detected in three urinary samples of 25 tested persons (*14*). This indicates a significant uptake of both compounds by humans. Recent studies have shown that OPs are transported via the atmosphere after their emission from urban agglomerations and road traffic. They reach soil surfaces and surface waters through atmospheric washout by precipitation and dry deposition (*4,77*). Particularly in urban areas, OP-loaded precipitation and surface runoff are presumed to be important sources of OP pollution in surface waters adjacent to treated wastewater discharges (*81,84*). The obvious question arising from these results can be posed whether and to which extent groundwater is influenced by precipitation and surface water contaminated with OPs during groundwater recharge.

To investigate the occurrence and distribution of chlorinated and non-chlorinated OPs in natural aquifers under different recharge/infiltration conditions, a total of 72 groundwater samples from Germany were analyzed within this study by use of gas chromatography-mass spectrometry (GC-MS) after solid phase extraction (SPE).

Material and methods

Sampling and field sites. Groundwater of the Hessian Ried (12 monitoring sites) and the Oderbruch polder (13 monitoring wells) was sampled to investigate the migration of OPs into the aquifer during bank filtration. Ten further groundwater monitoring wells located at the Hessian Ried were sampled to analyze the impact of seepage water. At these shallow monitoring wells groundwater is exclusively recharged by infiltration of precipitation. Additionally, groundwater samples from four leachate-affected wells next to the closed landfill site Monte Scherbelino (Frankfurt am Main) and six monitoring sites distributed across middle and north Hesse were collected. Sampling took place in 2009. Measurements of the pH-value, temperature, conductivity, dissolved oxygen, and redox potential were carried out in the field using a flow cell. Pre-cleaned brown glass bottles (1 L) were filled with groundwater at each monitoring well after the field parameters were on a constant level. Raw water of two springs (Trier-Biewer, Bekond) used for domestic and agricultural purposes respectively was analyzed once in September 2009. These samples were directly taken from the tap. The ID codes as well as grid values, sampling depths, sampling dates, and sample amounts of all investigated groundwater wells are listed in Table V-1.

1. Hessian Ried

The Hessian Ried represents a densely populated area of approximately 1,200 km^2 in the south of Frankfurt am Main and is crossed by an extended net of rivers and creeks. The four river systems Schwarzbach (with Landgraben), Modau, Winkelbach, and Weschnitz are tributaries to the Rhine River and drain the region from east to west. Their annual mean discharge volumes are in the range of approximately 0.3–3.2 m^3 s^{-1}. At regular flow conditions the estimated wastewater proportion of the river water ranges between 15% in Weschnitz River and 50% in Schwarzbach River (*19*). As a part of the Upper Rhine Valley, the Hessian Ried has a predominantly flat landscape composed of tertiary and quaternary fluvial and aeolic sediments. These sediments enable the storage of groundwater. Therefore, today the region is an important resource and supplier of drinking water.

Table V-1. ID codes, grid values, sampling depths, sampling dates, and sample amounts (n) of all monitoring wells.

ID	Region	Name	N°	E°	Depth (m)	Sampling	n
5171	Reinhardswald	Hombressen	51°29,8620'	9°30,2817'	16.5	May 09	1
7673	Westerwald	Elz	50°25,3587'	8°02,5604'	54.0	May 09	1
8617	Hessian Rhoen	Gersfeld (spring)	50°29,5193'	9°57,2072'	-	Apr 09	1
14749	Hessian Rhoen	Ulster (spring)	50°27,9137'	9°59,8919'	-	Apr 09	1
14751	Spessart	Rohrbach (spring)	50°16,5130'	9°30,3494'	-	Apr 09	1
10335	Spessart	Orb (spring)	50°11,5178'	9°24,0378'	-	Apr 09	1
TrQ	Mosel River	Trier-Biewer (spring)	49°47,0028'	6°39,2595'	-	Aug 09	2
BeQ	Mosel River	Bekond (spring)	49°51,0968'	6°48,7840'	-	Sep 09	2
15846	Hessian Ried	WRRL 1	49°51,3550'	8°27,4366'	< 14.0	Jun 09	1
15847	Hessian Ried	WRRL 2	49°41,4733'	8°26,8765'	< 14.0	Jun 09	1
15848	Hessian Ried	WRRL 3	49°41,8657'	8°26,6808'	< 14.0	Jun 09	1
15850	Hessian Ried	WRRL 5	49°42,8896'	8°27,1450'	< 14.0	Jun 09	1
15823	Hessian Ried	WRRL 55	49°56,3419'	8°22,3732'	< 14.0	Jun 09	1
15824	Hessian Ried	WRRL 56	49°53,9503'	8°22,3315'	< 14.0	Jun 09	1
15825	Hessian Ried	WRRL 57	49°52,0611'	8°22,4111'	< 14.0	Jun 09	1
15826	Hessian Ried	WRRL 58	49°54,8582'	8°25,7824'	< 14.0	Jun 09	1
15827	Hessian Ried	WRRL 59	49°51,1001'	8°31,9539'	< 14.0	Jun 09	1
15828	Hessian Ried	WRRL 60	49°52,2579'	8°32,5445'	< 14.0	Jun 09	1
11268	Hessian Ried	Heusenstamm	50°02,9899'	8°48,5715'	8.7	Apr 09	1
11735	Hessian Ried	Berkach	49°54,1186'	8°28,3785'	15.3	Apr, Jul 09	2
11746	Hessian Ried	Groß-Gerau	49°55,2529'	8°27,6477'	9.0	Aug 09	1
11758	Hessian Ried	Astheim	49°56,3669'	8°22,7122'	7.5	Aug 09	1
11761	Hessian Ried	Nauheim	49°56,6814'	8°27,3224'	15.0	Aug 09	1
12573	Hessian Ried	Darmstadt	49°48,8249'	8°37,6813'	25.5	Apr 09	1
12894	Hessian Ried	Nordheim	49°42,2578'	8°24,2816'	5.2	Apr 09	1
13489	Hessian Ried	Hofheim	49°39,1722'	8°23,2806'	5.2	Apr 09	1
13498	Hessian Ried	Biblis	49°40,6198'	8°26,8620'	9.0	May 09	1
13635	Hessian Ried	Heppenheim	49°37,8089'	8°35,9465'	9.4	Apr, Jul 09	2
15150	Hessian Ried	Dornheim	49°52,5133'	8°28,8952'	8.1	Apr, Jul 09	2
15154	Hessian Ried	Biblis	49°41,2095'	8°27,5521'	8.2	May 09	1
6/99T	Oderbruch	Bahnbruecke	52°48,7980'	14°13,0820'	19.6	Oct 09	2
9536F	Oderbruch	Bahnbruecke	52°48,7810'	14°13,0580'	7.0	Oct 09	2
9/99F	Oderbruch	Bahnbruecke	52°48,7020'	14°13,0890'	8.0	Oct 09	2
9560T	Oderbruch	Bahnbruecke	52°48,5420'	14°12,9370'	20.0	Oct 09	2
9561F	Oderbruch	Bahnbruecke	52°48,5400'	14°12,9380'	7.0	Oct 09	2
6/05F	Oderbruch	Bahnbruecke	52°48,2320'	14°12,8030'	9.0	Oct 09	2
6/05T	Oderbruch	Bahnbruecke	52°48,2320'	14°12,8030'	22.0	Oct 09	2
4/05T	Oderbruch	Bahnbruecke	52°47,7820'	14°11,7720'	22.0	Oct 09	2
3/05T	Oderbruch	Bahnbruecke	52°47,6960'	14°11,5390'	22.0	Oct 09	2
2144T	Oderbruch	Bahnbruecke	52°47,4440'	14°11,0890'	23.0	Oct 09	2
4/05F	Oderbruch	Bahnbruecke	52°47,7820'	14°11,7700'	9.6	Oct 09	2
3/05F	Oderbruch	Bahnbruecke	52°47,6960'	14°11,5390'	9.0	Oct 09	2
2144F	Oderbruch	Bahnbruecke	52°47,4390'	14°11,0930'	9.0	Oct 09	2
GWM 1.1	Frankfurt a. M.	Monte Scherbelino	50°04,1596'	8°43,1127'	5.0	Feb, Apr 09	2
GWM 1.2	Frankfurt a. M.	Monte Scherbelino	50°04,1585'	8°43,1144'	9.0	Feb, Apr 09	2
GWM 2.1	Frankfurt a. M.	Monte Scherbelino	50°04,1527'	8°43,1488'	5.0	Feb, Apr 09	2
GWM 2.2	Frankfurt a. M.	Monte Scherbelino	50°04,1527'	8°43,1488'	7.6	Feb, Apr 09	2
GWM S1	Frankfurt a. M.	Monte Scherbelino	50°04,1873'	8°43,1677'	< 1.0	Feb, Apr 09	2
GWM S2	Frankfurt a. M.	Monte Scherbelino	50°04,2130'	8°43,1893'	< 3.0	Apr 09	1

2. Oderbruch polder

The agricultural intensely used Oderbruch polder is situated about 60 km east of Berlin and covers an area of more than 800 km². The eastern boundary of the German part of the Oderbruch polder is the Oder River, and the western boundary is the till plateau of Barnim/Lebus. Due to extensive draining activities and the building of a levee along river during the past 250 years, major parts of the polder surface are now below river water level. The hydrological situation is characterized by permanent bank filtration of Oder water into the aquifer and groundwater movement towards the slightly inclined polder area. The aquifer consists of fine to medium sized sands of Pleistocene glaciofluvial origin with an average thickness of about 25 m. It is covered by a 0.2 to 4.0 m thick impermeable layer of Holocene alluvial loam. The base of the aquifer is attached to Saalian till. A main drainage ditch is running parallel to the river levee at 100–200 m distance. More than 80% of the infiltrating Oder water discharges into this main ditch. The bank-filtrate travel time from the river to the main ditch is in the order of months (flow velocity between 0.5–1.5 m d^{-1}) while the travel time to the central polder is in the order of decades up to 100 years. In general, geochemical conditions in the aquifer across the whole polder area are anoxic. The investigated transect of monitoring wells called 'Bahnbruecke' comprises a dense network of piezometers. The screens of the sampled shallow wells were installed between 7 m and 9 m and the screens of the deeper wells between 19 m and 23 m below surface (Table V-1). Hydraulic and hydrochemical processes of this field site were intensively determined in previous studies (*93-95*).

3. Monte Scherbelino

Between 1925 and 1968 about 20 million m³ industrial and domestic wastes were deposited at the landfill site Monte Scherbelino in the south-east of urban area Frankfurt am Main. Restoration began in 1972 when the landfill site was covered, but separation of landfill body and adjacent aquifer by a surrounding cut off wall was accomplished not until 1995. The aquifer consists of quaternary heterogeneous sandy layers with silt and gravel and has a thickness of approximately 12 m. The base of the aquifer is composed of Oligocene marl. Two ditches drain the aquifer in downstream direction of the landfill. Groundwater flow velocities range between 1 m d^{-1} in the north-western area and 0.01 m d^{-1} in the eastern area of the landfill site. After passing the separated landfill body, emergent groundwater discharges immediately downstream into a former fire water pond with a surface area of 15,000 m² close to the western edge of the landfill body. The pond is now aerated with ambient air as an enhanced natural attenuation process to improve its decomposition capacity for groundwater pollutants (*96*). The investigated four monitoring wells are located nearby the groundwater pond in the downstream area of the landfill.

Analytical methods. The analytical method for quantitation of OPs in aqueous samples has previously been described in detail (*77,84*). Filtration of the groundwater samples (1 L) prior to SPE was not required. The samples were extracted by Bond Elut PPL cartridges (1 mL; Varian, Darmstadt, Germany), Elutd with 1 mL methanol/acetonitrile (1/1 v/v), and analyzed by GC-MS. Quantitation of the analytes in the sample extracts was carried out using a Trace GC Ultra gas chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich, Germany). GC separation was performed using a TR-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 µm film thickness; Thermo Scientific). The following temperature program was used: 80 °C (1 min) → 4 °C min^{-1} → 300 °C (25 min). Helium (5.0) was applied as carrier gas at a constant flow of 1.1 mL min^{-1}. Sample injection (1 µL) was accomplished in splitless mode at an injector temperature of 240 °C. The mass spectrometer was operated in full scan mode (m/z 50–600) with electron impact ionization (70 eV).

Quantitation of the analytes was performed using squalane (Sigma Aldrich, Steinheim, Germany) as internal calibration standard (*77*). The squalane stock solution (1 µg µL^{-1}) was prepared in hexane while the individual stock solutions of TCEP, TiBP, TnBP, TBEP (Sigma Aldrich), TCPP, and TDCP (Akzo Nobel, Amersfoort, The Netherlands) were prepared in methanol/acetonitrile (1/1 v/v) at 1 µg µL^{-1} concentration. The stock solutions were diluted to obtain appropriate working standard solutions and were regularly renewed.

Hydrochemical data (nitrate) of Hessian groundwater samples were provided from the Hessian Agency for the Environment and Geology (HLUG).

Quality assurance. All glass bottles used in this study were thoroughly pre-cleaned and were immediately closed after complete filling to avoid sample contact with ambient air. Samples were stored in the dark at 5 °C and were generally extracted within 72 h after sampling. Ultrapure water samples (Astacus Analytical, MembraPure, Bodenheim, Germany) treated in the same way as groundwater samples were used as blanks to identify possibly contamination during transport and laboratory treatment. A limit of detection (LOD) of 1 ng L^{-1} for each of the analytes TCEP, TCPP, TDCP, TBEP, TnBP, and TiBP was calculated from measured calibration curves in accordance with DIN 32645 (DINTest, University of Heidelberg, α = 1%). Except for TDCP and TBEP, the limit of quantitation (LOQ) was estimated as three times the LOD and ranged between 3 ng L^{-1} (TCEP) and 4 ng L^{-1} (TCPP, TiBP, TnBP). LOQs of TDCP (40 ng L^{-1}) and TBEP (33 ng L^{-1}) were calculated as mean of blank value plus six times the standard deviation of the mean as both compounds (TDCP: 4±6 ng L^{-1}, TBEP: 3±5 ng L^{-1}) were detected in the blanks (n = 8). SPE recovery rates (n = 6) were in the range of 85–99% for all analyzed OPs.

Results and discussion

OP infiltration via precipitation. During spot sampling in June 2009, TDCP and TnBP were not detected in groundwater samples from agriculturally used areas at the Hessian Ried (ID 15823–15850) reflecting the missing impact of infiltrating precipitation on groundwater quality for both compounds. However, TBEP and TiBP were detected in 20%, TCPP in 30%, and TCEP in 40% of these groundwater samples (n = 10) from shallow aquifer depths (8–14 m, Table V-1). Groundwater of monitoring wells 15823, 15825, and 15828 contained more than one OP though all measured TBEP concentrations ranged between LOQ and LOD. All other OP values were above or equal to LOQ. The median and maximum concentrations for TCEP, TCPP, TBEP, and TiBP are displayed in Table V-2. Nitrate concentrations of three monitoring wells were increased (13–68 mg L^{-1}), indicating that groundwater is superimposed by anthropogenic influences, e. g. agriculture. However, OPs were not detected in groundwater of these monitoring wells.

Table V-2. OP concentrations (ng L^{-1}) of groundwater monitoring wells (Hessian Ried, n = 10) influenced by infiltrating precipitation.

Compound	Frequency of detection [%]	Median c [ng L^{-1}]	Max. c [ng L^{-1}]
TCEP	40	< LOQ	24
TCPP	30	< LOQ	6
TBEP	20	< LOQ	< LOQ
TiBP	20	< LOQ	7

So far, data related to OP behavior during soil infiltration under natural rainfall conditions are missing. Prösch et al. (*60*) analyzed groundwater of 573 house wells at rural areas of Mecklenburg-Vorpommern, Germany. TCEP (LOQ = 10 ng L^{-1}) and TCPP (LOQ = 20 ng L^{-1}) were only found in 0.3% and 2.3% of the anthropogenic widely unaffected house wells. A soil infiltration experiment with treated effluent passing a soil filled column at an average rate of 5.3 cm per day over a time span of 23-days indicated the potential of TCEP, TDCP, and TnBP to reach groundwater under recharge conditions (*45*). Nevertheless, infiltration of urban roof and surface runoff from seepage reservoirs into soils with high permeability represents a high pollution potential endangering groundwater quality and drinking water resources (*97*). Analysis of an urban storm water holding tank already pointed to an accumulation of several OPs in urban storm water runoff (*84*).

OP infiltration via bank filtration. Concentration levels of the six OPs detected in groundwater samples nearby groundwater infiltrating recipients (n = 15) from the Hessian Ried are summarized in Table V-3.

Table V-3. OP concentrations (ng L^{-1}) of groundwater samples (Hessian Ried, n = 15) influenced by bank filtration.

Compound	Frequency of detection [%]	Median c [ng L^{-1}]	Max. c [ng L^{-1}]
TCEP	67	7	148
TCPP	74	38	1795
TDCP	20	< LOQ	< LOQ
TBEP	40	< LOQ	1813
TiBP	67	5	105
TnBP	67	5	51

Except for samples from monitoring wells 11268 and 12573, OPs were detected in all other groundwater samples with maximum concentrations exceeding 0.1 µg L^{-1} for TCEP, TCPP, TBEP, and TiBP. Concentrations of TDCP ranged between LOD and LOQ, whereas TCEP, TCPP, and TBEP levels were above LOQ when detected. TCPP was the most frequently detected OP (74%) in groundwater influenced by bank filtration which is in accordance with the well known presence of chlorinated OPs in wastewater-impacted surface waters. Furthermore, TCPP concentrations (38 ng L^{-1}, median) were in general higher than those of TCEP (7 ng L^{-1}, median). At monitoring wells 11735, 13635, and 15150 samplings were carried out twice in April and July 2009. In July the OP concentrations were in general more than twice as high (except for TCEP) than in April. This can be explained by a broad decline of the groundwater level and therefore higher infiltration rates of surface water from the surrounding recipients to the groundwater aquifer (*98*). In addition, the proportions of treated wastewater in surface water will increase during low-flow conditions primarily in summer (*21*). Nevertheless, it is unclear why TCEP values at monitoring wells 11735 and 13635 remained in the same concentration range of 12–13 ng L^{-1} and 146–148 ng L^{-1}, respectively during both samplings. At monitoring well 15150 concentrations of TCEP (7 ng L^{-1}), TCPP (840 ng L^{-1}), TBEP (65 ng L^{-1}), TiBP (12 ng L^{-1}), and TnBP (7 ng L^{-1}) measured in April raised up to 12 ng L^{-1}, 1795 ng L^{-1}, 180 ng L^{-1}, 19 ng L^{-1}, and 20 ng L^{-1} during sampling in July. In general, high OP concentrations were only obtained in groundwater samples of the Hessian Ried taken from monitoring wells located at settlements or directly adjacent to burdened recipients (distance <100 m).

The characteristics of TCEP concentrations (mean, n = 2) during bank filtration at Oderbruch polder are displayed in Fig. V-1. The concentrations of TCEP within the groundwater aquifer, both at shallow (A) and deep (B) monitoring wells, decreased with increasing distance to Oder River (Fig. V-1, I) and increasing groundwater ages (Fig. V-1, II). The higher concentrations of well 9/99F can be explained by the local groundwater flow field. Due to the discharge effect of the main ditch, flow paths in the aquifer show upward gradients towards the ditch floor in this region. The ascending groundwater is directly influenced by the percolating bank filtrate and therefore contains higher proportions of Oder River water. 9536F is less affected by this flow field. Groundwater ages at Oderbruch polder have been determined in previous studies (*99-101*). Correlation of TCEP and TCPP concentrations in groundwater of bank filtration was very high (R = 0.9943). TCPP concentrations (mean, n = 2) in Oder (2353 ng L^{-1}) and main ditch (958 ng L^{-1}) as well as in monitoring wells 6/99T (291 ng L^{-1}), 9536F (261 ng L^{-1}), 9/99F (447 ng L^{-1}), 9560T (66 ng L^{-1}), and 6/05T (31 ng L^{-1}) were significantly higher than those of TCEP: 540 ng L^{-1} (Oder), 171 ng L^{-1} (main ditch), 51 ng L^{-1} (6/99T), 30 ng L^{-1} (9536F), 96 ng L^{-1} (9/99F), 20 ng L^{-1} (9560T), and 9 ng L^{-1} (6/05T). The groundwater ages of these monitoring wells are younger than ten years (*100*). Concentration levels of TCEP and TCPP were in a similar range (4–9 ng L^{-1}) in samples of groundwater ages older than 20 years (Fig. V-1, II). TiBP and TnBP have also been detected in Oder River (54–99 ng L^{-1}) and main ditch (14–19 ng L^{-1}) samples as well as groundwater samples from monitoring wells 6/99T, 9536F, and 9/99F (4–12 ng L^{-1}). Concentrations of the non-chlorinated OPs TiBP and TnBP correlate with each other (R = 0.9594). However, their concentration levels decreased rapidly in the groundwater during infiltration with increasing distance from river. Their concentrations were in the range of LOQ in groundwater sampled close to the Oder River but below LOD in more distant samples. Details of OP infiltration into groundwater aquifer at Oderbruch polder will be discussed in a further publication (see research paper VI in chapter 2).

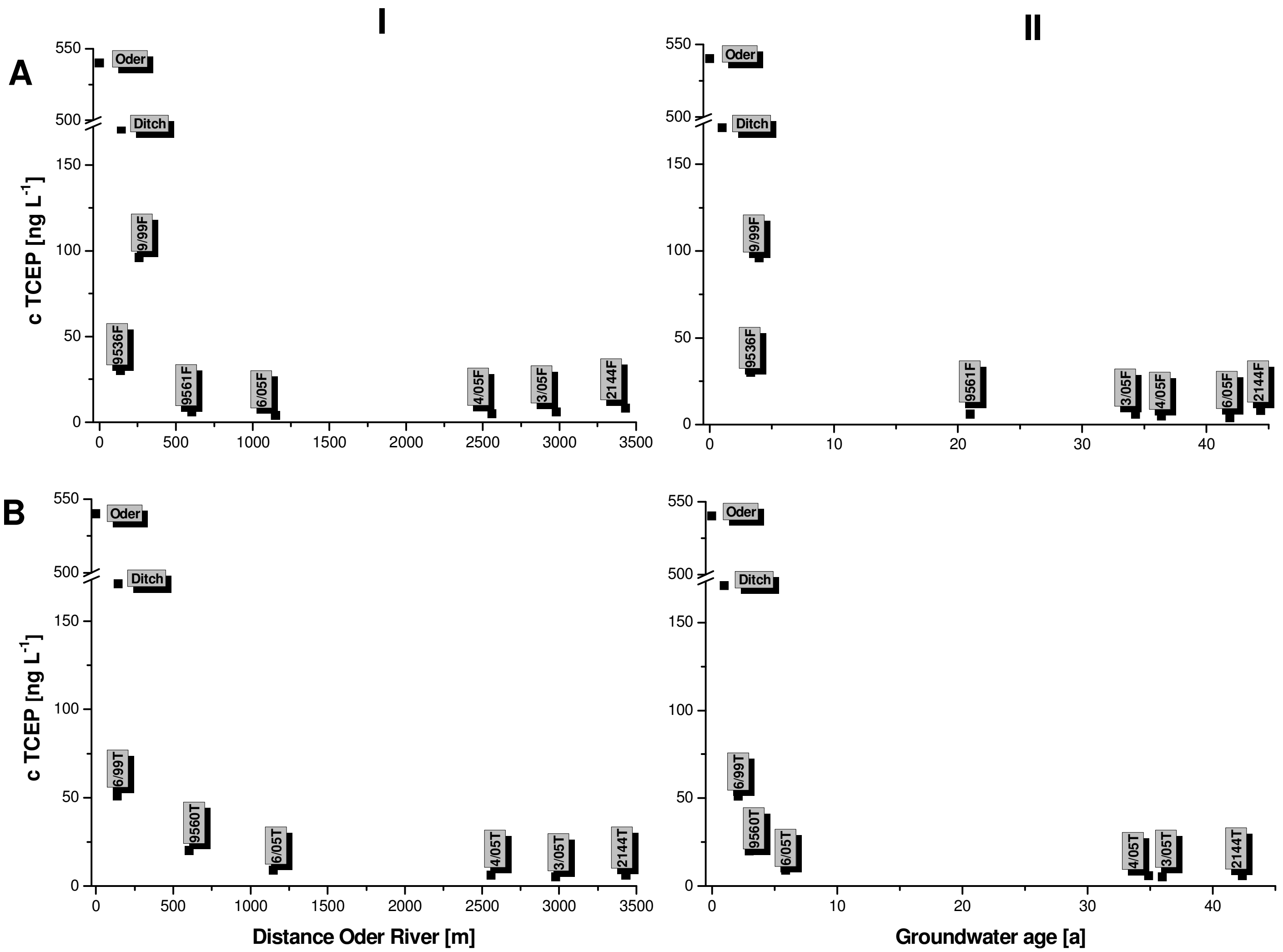


Fig. V-1. Mean (n = 2) TCEP concentrations (ng L^{-1}) in groundwater of shallow (A) and deep (B) monitoring wells at Oderbruch polder in dependency on distance from river (I) and groundwater age (II).

OP infiltration via landfill leachate. The landfill body Monte Scherbelino is separated from the adjacent aquifer by a cut-off wall since approximately 15 years. However, the shallow groundwater aquifer is still polluted with considerable amounts of TCEP, TCPP, TiBP, and TnBP. Detection frequencies, median and maximum concentrations of the analyzed OPs are presented in Table V-4. TBEP was found only in one sample.

Table V-4. Groundwater samples (n = 11) from a polluted landfill site.

Compound	Frequency of detection [%]	Median c [ng L^{-1}]	Max. c [ng L^{-1}]
TCEP	91	141	318
TCPP	91	191	343
TDCP	55	< LOQ	45
TBEP	9	< LOQ	199
TiBP	100	92	697
TnBP	100	90	213

Median concentrations (n = 11) of the four OPs TCEP, TCPP, TiBP, and TnBP were in the range of 90–191 ng L^{-1}. Their concentration values were slightly higher during groundwater sampling in February compared to sampling in April. Nevertheless, the mean TiBP concentration during both sampling campaigns (n = 2) was significantly higher in samples from the deeper monitoring wells GWM 1.2 (544 ng L^{-1}) and GWM 2.2 (407 ng L^{-1}) than concentrations found in the shallow monitoring wells GWM 1.1 (49 ng L^{-1}), GWM 2.1 (82 ng L^{-1}), and the groundwater pond (64 ng L^{-1}). For TnBP the concentration differences between the deeper monitoring wells GWM 1.2 (181 ng L^{-1}) and GWM 2.2 (119 ng L^{-1}) and the more shallow wells GWM 1.1 (62 ng L^{-1}) and GWM 2.1 (71 ng L^{-1}) were less distinctive. However, the chlorinated OPs TCEP and TCPP showed an opposing behavior with decreased concentrations (mean, n = 2) at monitoring wells GWM 1.2 (12 ng L^{-1}, 50 ng L^{-1}) and GWM 2.2 (114 ng L^{-1}, 142 ng L^{-1}) according to monitoring wells GWM 1.1 (161 ng L^{-1}, 256 ng L^{-1}) and GWM 2.1 (167 ng L^{-1}, 267 ng L^{-1}). Highest TCEP concentrations were determined in samples of the groundwater pond (318 ng L^{-1} and 301 ng L^{-1}), while highest TCPP concentrations (343 ng L^{-1}, 335 ng L^{-1}) were found in groundwater of the shallow monitoring wells. Multilevel groundwater samples analyzed by Fach (*96*) indicated a strong vertical concentration gradient for organic contaminants at Monte Scherbelino site with main fluxes of contaminated groundwater in the lowest part of the aquifer. Within that study it was concluded that degradation and sorption processes of leaching contaminants were restricted to the lower third of the aquifer due to measured hydrochemical parameters, e. g. redox conditions. Photochemical as well as microbiological degradation of non-chlorinated OPs in surface waters has been proven in several studies (*24,41*) while aeration of the groundwater pond is not supposed to enhance the degradation of the chlorinated OPs TCEP and TCPP (*24*).

TDCP was detected in groundwater samples taken from the monitoring wells only in April and in samples from the groundwater pond during both samplings. However, it was not detected in samples from the monitoring wells during February sampling. The median TDCP concentration at the landfill site is clearly below LOQ. Therefore, TDCP can be assumed as having been of minor importance as flame retardant in deposited consumer products between 1925 and 1968, the closing year of the landfill site. Since the 1940s trialkyl and chlorinated trialkyl phosphates were widely used as flame retarding plasticizers in industrial and consumer products but their consumption increased greatly between 1960 and 1980 (*37*). In Germany, approximately 80% of TCEP and TCPP were used as a mixture at a ratio of 1:1 (w/w) in polyurethane foams until mid 1990s, when TCEP was reportedly phased out due to toxicity issues and consumption of TCPP increased (*31*). According to this fact, groundwater concentration levels of TCEP and TCPP at sampling site Monte Scherbelino were supposed to be in the same range at that time, while concentration levels of TCPP reported from recent surface water and precipitation samples (*84*) are manifold higher. Nevertheless, TCEP concentrations in groundwater from landfill Monte Scherbelino were in general lower than those of TCPP. This observation points to the assumption that either TCEP is stronger retained and possibly degraded within the aquifer than TCPP, or the groundwater aquifer is additionally influenced by percolating urban precipitation and surface runoff from the surrounding highways. High OP concentrations in precipitation of urban agglomeration Frankfurt am Main with maximum TCPP concentrations exceeding 1 µg L^{-1} have already been reported in previous studies (*77,84*). Depending on the excellent soil permeability and low groundwater depth in this area, influences of deicing salts from percolating street runoff on the groundwater composition in winter have already been observed at Monte Scherbelino site (*102*).

Distribution and behavior of OPs in groundwater. In general, OP concentrations were below LOD in samples from springs (monitoring sites 8617, 14749, TrQ, BeQ) and deep groundwater monitoring wells (7673, 12573) that are not affected by surface waters. OP levels (8–41 ng L^{-1}) found at spring 14751 indicated the influence of two infiltrating recipients (creek, pond) next to the monitoring site. Highest OP concentrations were determined in groundwater affected by seepage water from a polluted landfill site and groundwater recharged via bank filtration of OP-loaded recipients. Infiltration of precipitation at rural sites was found to be no prominent entry-pathway for OPs into groundwater. One reason are lower OP concentrations in the rainfall in comparison to urban areas. Concentrations of OPs in urban rainwater were significantly higher than those from background monitoring stations in rural areas (*77*). Furthermore, retardation of OPs in soils and in the unsaturated zone can be suggested. Retention of OPs by means of activated charcoal filtration is well known (*64,65*). The adsorption behavior of the chlorinated OPs TCEP, TCPP, and TDCP in soils was described as being proportional to its organic carbon content. Adsorption to soil components other than organic carbon was not found to be significant (*33*). Although the regional concentrations of OPs in the groundwater of rural landscapes were low, point source contamination must be considered. Heinz et al. (*5*) ascertained contamination of a karst spring from overflow of a nearby storm water tank for combined wastewater after heavy rainfall events. High OP concentrations in the urban aquifers can be explained by high concentrations of OPs in urban rain water and the direct influence of surface water contaminated by surface runoff. Little or no additional data are available regarding the infiltration of OPs into groundwater via precipitation or surface runoff in cities.

Apart from its relatively high LOQ, TDCP was the compound with lowest appearance in groundwater of the chlorinated OPs in all analyzed groundwater samples with respect to the detection frequency. Compared to TCEP and TCPP, TDCP has the highest log K_{oc} value (Fig. 1-1, chapter 1.2). Based on their solids-water partition coefficients for soils, both, TCEP (2.2 L kg^{-1}) and TCPP (3.48 L kg^{-1}) possess a high to intermediate and TDCP (35.6 L kg^{-1}) a low mobility (*32-34,103*) within the aquifer. Hence, for TCEP and TCPP breakthrough during bank filtration/underground passage has been referred (*81*). Nevertheless, several studies reported a significant degradation of TCEP and TCPP attributed to biotransformation in the aquifer during managed aquifer recharge processes, e.g., bank filtration and artificial groundwater recharge (*21,104*). The results of Amy and Drewes (*104*) indicated that anoxic conditions enhance the attenuation of TCEP and TCPP in soils while inconsistent results were reported by Rauch-Williams et al. (*43*) conducting column experiments under aerobic and anoxic recharge conditions.

While natural attenuation of the chlorinated OPs during bank filtration is still controversial (*105*), non-chlorinated OPs are supposed to be less stable within the aquifer due to biotransformation processes. According to its relatively high log K_{oc} value (5.67), TBEP is furthermore predicted to adsorb to soils (*35*). Besides TDCP, TBEP was the compound with lowest appearance in all analyzed groundwater samples. However, TnBP and TBEP were used as hydrophilic marker substances for biotransformation by several authors (*5,44*). Elimination rates up to approximately 89% were reported for TnBP and TBEP during bank filtration as well as soil filtration experiments (*44,105*). Decreasing TnBP values in seepage-affected groundwater with increasing distance from a landfill by implication of attenuation processes were also observed (*106*). A significant concentration decrease of TiBP within the leachate plume of a Danish landfill site was explained by attenuation under strongly anaerobic conditions and not only dilution processes compared to the conservative tracer chloride (*92*).

However, the attenuation efficiency during natural recharge processes seems to depend on parameters like soil characteristics, residence times, and hydrochemical conditions within the aquifer. So far, no qualified data are available concerning the degradation of chlorinated and non-chlorinated OPs in soils or groundwater.

Conclusion

The occurrence of chlorinated and non-chlorinated OPs in groundwater was dependent on the anthropogenic impact during groundwater recharge/natural replenishment. Infiltration of precipitation at rural sites was found to be no prominent entry-pathway for OPs into groundwater, but OP-loaded precipitation and surface runoff is supposed to influence groundwater quality at urban sites. Highest OP concentrations were determined in groundwater polluted by percolating leachate from contaminated sites or groundwater recharged via bank filtration of OP-loaded recipients. Nevertheless, concentrations of non-chlorinated OPs in groundwater decreased immediately with increasing distance from the recipient during bank filtration due to biotransformation and adsorption processes. TCEP and TCPP were the most frequent OPs detected in groundwater samples in the present study. Both compounds are known to be problematical regarding drinking water purposes and should be analyzed when drinking water is supplied from bank filtration or from urban groundwater. Further research is necessary to understand the fate of chlorinated OPs TCEP, TCPP, and TDCP during soil infiltration into groundwater with respect to their persistence, biotransformation, and adsorption on soil organic matter.

VI Are organophosphorus flame retardants and plasticizers suitable as conservative organic tracers in groundwater?

Abstract

Concentrations of the organic trace pollutants tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCP), tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) in groundwater of Oderbruch polder (Brandenburg, Germany) were compared with defined groundwater ages. The aim of this study was to evaluate the potential of the chlorinated organophosphates TCEP and TCPP as conservative organic tracers. Initial river water levels of TCEP (540 ng L^{-1}), TCPP (2353 ng L^{-1}), TiBP (54 ng L^{-1}), and TnBP (99 ng L^{-1}) decreased immediately between 89–97% during 3 years of residence in the aquifer. TCPP and TCEP concentrations of 4–9 ng L^{-1} in samples from monitoring wells with groundwater ages between 20–45 years indicate their stability within the aquifer. However, both compounds are not suitable as conservative organic tracers in groundwater, due to their strong concentration decline in the beginning of bank filtration. In contrast, concentration levels of the polyethers triglyme ($R^2 = 0.8976$) and tetraglyme ($R^2 = 0.9942$) decreased approximately linear in groundwater with increasing distance from Oder River. These compounds were detected in river water and Oder-near groundwater in the range of 6–245 ng L^{-1} and 150–1849 ng L^{-1}, respectively.

Introduction

Contamination of groundwater with trace organic pollutants such as organophosphates (OPs) via bank filtration of surface waters or artificial recharge of treated wastewaters has been proven in several studies (*20,21,107*). The chlorinated flame retardants tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCP) as well as the non-chlorinated plasticizers tris(2-butoxyethyl) phosphate (TBEP), tri-iso-butyl phosphate (TiBP), and tri-n-butyl phosphate (TnBP) are widely used industrial chemicals (91,000 t yr^{-1} in the European Union in 2006) according to the European Flame Retardant Association (EFRA). OPs are added as flame retarding and plasticizing agents to industrial and consumer products since 1940 but their usage rose significantly between 1960 and 1980 (*37*). Since TCEP, TDCP, and TnBP are classified as human carcinogen category 3 (European chemical substances information system, ESIS) and TCPP was considered as a possible human carcinogen (*6*), concerns about the potential environmental risks of OPs in groundwater aquifer systems have arisen. Differences in the physicochemical properties of these OPs are due to the specific moieties of organic ester functional groups. Their water solubility is relative high and ranges between 18.1 mg L^{-1} for TDCP and 7820 mg L^{-1} for TCEP. The n-octanol/water partition coefficient (log K_{ow}) and the solid-water partition coefficient for soils (log K_{oc}) values are in the range of 1.7 (TCEP) to 4.0 (TnBP) and 2.48 (TCEP) to 5.67 (TBEP), respectively (*38*). The mobility of TCEP and TCPP in groundwater was indicated to be intermediate to high whereas the mobility of TDCP and TBEP was rather low (*32-35,103*).

The non-chlorinated OPs, opposing to chlorinated OPs, are expected to be degradable in the aquatic environment to some extent (*24,41*) (research paper IV in chapter 2). However, the behavior of the compounds in groundwater aquifer systems varies considerably from other aqueous compartments due to differences in the redox conditions (*104*). Long residence times, lower temperatures, marginal dilution effects and low microbial activity often increase the persistence of organic trace pollutants in groundwater (*108*), whereas some biogeochemical redox processes are known to enhance transformation processes of organic contaminants in groundwater (*109*). Adsorption, dilution, and biological or chemical transformations are the most important processes causing the attenuation of OPs in groundwater during bank filtration. These processes have so far only been studied with respect to the attenuation of OPs in sewage treatment plants (*43,44*) but are not yet sufficiently understood for groundwater, surface water and in systems with interaction of groundwater and surface water (bank filtration). Results of previous studies concerning their persistence, biotransformation or adsorption in soils and groundwater are inconsistent (*21,43,44,104*).

Polyethers such as diethylene glycol dimethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme), and tetraethylene glycol dimethyl ether (tetraglyme) are widely used as solvents in the chemical industry and have already been detected as common groundwater contaminants in the United States (*110*). They are expected to be highly mobile in groundwater due to their infinite miscibility in water. The log K_{ow} values of triglyme and tetraglyme are in the range of -0.8 and -1.0, respectively (*111*). Furthermore, the ether bonds of these compounds show only low biodegradability in water under aerobic as well as anoxic conditions (*112,113*).

In the present study groundwater samples of thirteen monitoring wells at Oderbruch polder (Brandenburg, Germany) were analyzed to investigate the behavior of the six OPs TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP within groundwater aquifer during permanent natural river water infiltration. The main objectives were (1) to determine the transport behavior of OPs in groundwater in comparison to the polyethers triglyme and tetraglyme, (2) to identify possible attenuation processes of the chlorinated and non-chlorinated OPs and the polyethers during bank filtration, and (3) to compare environmental concentration levels of OPs and polyethers in groundwater with defined groundwater ages.

Materials and methods

Groundwater samples. The Oderbruch polder is located about 60 km east of Berlin and covers an area of more than 800 km². The eastern boundary of the German part of the Oderbruch polder is the Oder River, whereas the western boundary is the till plateau of Barnim/Lebus (Fig. VI-1). Major parts of the region are intensively used for agriculture and are therefore influenced by massive hydraulic and water management measures. Levee construction, damming measures, and drainage with ditches and pumping stations had enabled intensive land use in the last centuries. The hydrological situation is characterized by permanent bank filtration of Oder water into the aquifer. The unrestrained hydraulic contact between river and groundwater and the highly permeable river base lead to permanent groundwater movement towards the slightly inclined polder area river. The mostly confined groundwater drains out into a wide drainage network stretching over the entire region. Infiltration of river water is supposed to be consistent within the last 250 years. Approximately 80% of the infiltrating Oder water (flow velocity between 0.5–1.5 m d^{-1}) discharges after a few months into a main ditch running parallel to the river levee at 100–200 m distance (*94*). Bank-filtrate travel times from the river to the central polder are in the order of decades up to 100 years (*99*). The aquifer at Oderbruch polder (on average 25 m thick) is composed of fine to medium sized sands of Pleistocene glaciofluvial origin covered by a 0.2 to 4.0 m thick and widely impermeable layer of Holocene alluvial loam. The aquifer base is attached to Saalian till.

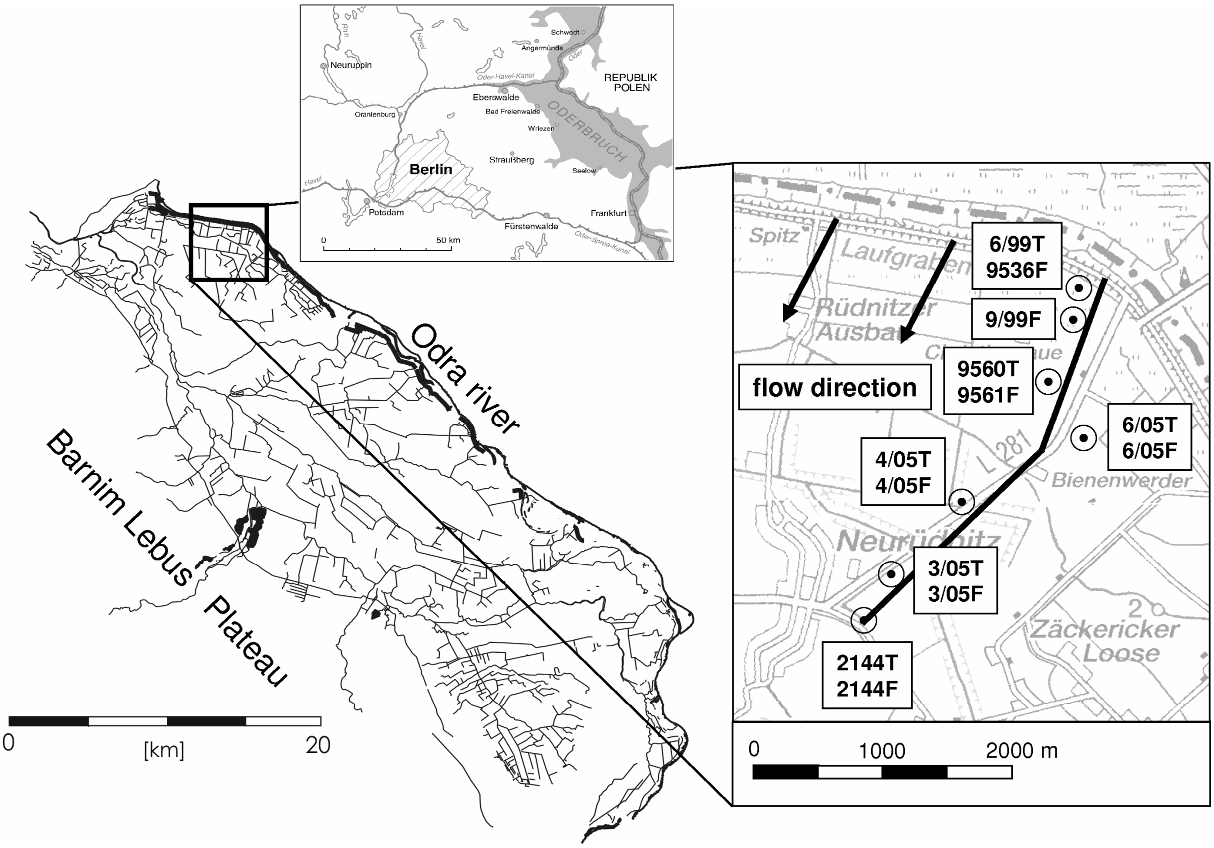


Fig. VI-1: Sampling site transect Bahnbruecke at Oderbruch polder, Germany.

The hydrochemical situation in the groundwater of the Oderbruch is characterized by anaerobic redox conditions with redox values of <100 mV, the absence of free oxygen, and relatively high concentrations of redox-sensitive trace metals like iron and manganese. The transition of oxic river water to anaerobic groundwater proceeds quickly during the bank filtration process. After a short travel and reaction time, O_2 and NO_3 are consumed within the first few meters of the infiltration path. Hydraulic and hydrochemical processes of this field site were intensively studied by several authors (*93,94,100*). A transect comprising seven shallow (7–10 m) and six deep (19–23 m) groundwater monitoring wells was investigated at the Oderbruch polder (Bahnbruecke site) on 27/10/2009 (Fig. VI-1). ID codes, grid values, and sampling depths in the monitoring wells as well as their distance to Oder River are displayed in Table VI-1. At each monitoring well, the field parameters pH-value, temperature, conductivity, dissolved oxygen, and redox potential were measured using a flow cell. Sampling of groundwater (1 L) was performed in duplicate after all field parameters were on a constant level.

Table VI-1. ID codes, grid values, sampling depths, distances to Oder River, and groundwater ages of the monitoring wells at Oderbruch polder, Germany.

ID	N°	E°	Depth [m]	Distance to river [m]	Groundwater age [a] [a]
6/99T	52°48,7980'	14°13,0820'	19.6	138	2.1
9536F	52°48,7810'	14°13,0580'	7.0	138	3.3
9/99F	52°48,7020'	14°13,0890'	8.0	260	-
9560T	52°48,5420'	14°12,9370'	20.0	604	3.0
9561F	52°48,5400'	14°12,9380'	7.0	604	21.0
6/05F	52°48,2320'	14°12,8030'	9.0	1,150	41.9
6/05T	52°48,2320'	14°12,8030'	22.0	1,150	5.9
4/05T	52°47,7820'	14°11,7720'	22.0	2,560	34.9
4/05F	52°47,7820'	14°11,7700'	9.6	2,560	36.4
3/05T	52°47,6960'	14°11,5390'	22.0	2,980	36.0
3/05F	52°47,6960'	14°11,5390'	9.0	2,980	34.3
2144T	52°47,4440'	14°11,0890'	23.0	3,434	42.4
2144F	52°47,4390'	14°11,0930'	9.0	3,434	44.4

[a] (*99-101*)

Analytical methods. A detailed description of the analytical method can be found in references (*77*) and (*84*). Hence, only a brief description is given. Groundwater samples (1 L) were not filtered prior to solid phase extraction (SPE). The samples were extracted by a styrene-divinylbenzene polymeric SPE cartridge (Bond Elut PPL, 1 mL; Varian, Darmstadt, Germany), Elutd with 1 mL methanol/acetonitrile (1/1 v/v), and analyzed by gas chromatography-mass spectrometry in full scan mode (m/z 50–600). Quantitative analyses of the target compounds in the sample extracts were performed using a Trace GC Ultra gas chromatograph coupled to a DSQ II mass spectrometer (Thermo Scientific, Dreieich, Germany). A TR-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 µm film thickness; Thermo Scientific) was used for GC separation among the following temperature program: 80 °C (1 min) → 4 °C min^{-1} → 300 °C (25 min). Target analytes were quantified using squalane (Sigma Aldrich, Steinheim, Germany) as internal calibration standard (*77*). Individual stock solutions (1 µg µL^{-1}) of TCEP, TiBP, TnBP, TBEP, tetraglyme (Sigma Aldrich), TCPP, TDCP (Akzo Nobel, Amersfoort, The Netherlands), and triglyme (Alfa Aeser, Karlsruhe, Germany) were prepared in methanol/acetonitrile (1/1 v/v), whereas squalane stock solution (1 µg µL^{-1}) was prepared in hexane. Acetonitrile (J. T. Baker, Deventer, The Netherlands) was ultrapure HPLC grade and was used as received. All other solvents (Merck, Darmstadt, Germany) were of analytical grade and were distilled before use. Working standard solutions were obtained by appropriate dilution. All stock and working standard solutions were regularly renewed.

Analyses of groundwater hydrochemistry were performed at the Institute of Landscape Hydrology at Leibniz-Centre for Agricultural Landscape Research (ZALF e.V.). Water samples were analyzed for Ca, Mg, K, Na, Cl, NO_3, NO_2 and SO_4 by ion chromatography (DX500, Dionex, Idstein, Germany) using IonPac column CS12A for the cations and AS9-HC4 for the anions. Iron and Manganese were determined by ICP-AES (Jobin Yvon, Unterhaching, Germany). Alkalinity was determined by titration and NH_4 and PO_4 were measured by photometry (SPECORD 200, Analytik Jena, Jena, Germany).

Quality assurance. To avoid sample contamination, all brown glass bottles used in this study were thoroughly pre-cleaned before sampling. Samples were extracted within 72 h after sampling. Blanks of ultrapure water (Astacus Analytical, MembraPure, Bodenheim, Germany) were handled identical to groundwater samples as control for possible contamination during transport and laboratory treatment. Sample data were not corrected in terms of SPE recovery rates. Recoveries were in the range of 85–99% with relative standard deviations below 10%. A limit of detection (LOD) of 1 ng L^{-1} for each of the analytes TCEP, TCPP, TDCP, TBEP, TnBP, TiBP, and tetraglyme as well as 2 ng L^{-1} for triglyme was calculated from seven-point calibration curves of standard mixtures in accordance with DIN 32645 (DINTest, University of Heidelberg, α = 1%). For TCEP, TCPP, TiBP, TnBP, triglyme, and tetraglyme the limit of quantitation (LOQ) was estimated as three times the LOD and ranged between 3 ng L^{-1} (TCEP) and 5 ng L^{-1} (triglyme). As TDCP (4±6 ng L^{-1}) and TBEP (3±5 ng L^{-1}) were detected in the blanks (n = 8), LOQs of both compounds were calculated as mean of blank value plus six times the standard deviation of the mean resulting in LOQs of 40 ng L^{-1} (TDCP) and 33 ng L^{-1} (TBEP).

Results and discussion

OP concentration levels at Oderbruch polder. TCEP, TCPP, TiBP, and TnBP concentration levels (mean, n = 2) at transect Bahnbruecke are summarized in Table VI-2. TCEP and TCPP concentrations within the aquifer, both at shallow and deep monitoring wells decreased with increasing distance from Oder River as well as increasing groundwater ages. Concentrations of the chlorinated flame retardants TCPP and TCEP correlated highly (correlation coefficient, R = 0.9943) with each other while TDCP levels (44 ng L^{-1}, Oder River) were below LOQ in samples from main ditch and groundwater wells. However, mean TCPP concentrations in samples from Oder River, main ditch, and monitoring wells 6/99T, 9536F, 9/99F, 9560T, and 6/05T were significantly higher than those of TCEP (Table VI-2). Groundwater ages of these monitoring wells are younger than ten years (*100*). In samples from wells with groundwater ages between 20 and 45 years, TCEP and TCPP concentrations were rather similar in a range of 4–9 ng L^{-1}. The higher TCPP (also TCEP) concentrations of well 9/99F compared to well 9536F (Table VI-2) were caused by the local groundwater flow field. At well 9/99F aquifer flow paths show upward gradients towards the ditch floor due to discharge effects of the main ditch. The ascending groundwater is directly influenced by the percolating bank filtrate and contains higher proportions of Oder River water. Ages of groundwater at Oderbruch polder were defined in previous studies (*99-101*) by ^{3}H/He and ^{36}Cl/Cl methods.

The non-chlorinated OPs TiBP and TnBP were detected in Oder River (54 ng L^{-1}, 99 ng L^{-1}) and in main ditch samples (14 ng L^{-1}, 19 ng L^{-1}) as well as in groundwater samples from monitoring wells 6/99T, 9536F, and 9/99F (4–12 ng L^{-1}). Concentrations of both compounds correlate with each other (R = 0.9594). However, their concentration levels decreased rapidly in the groundwater during infiltration with increasing distance from river (Table VI-2). Their concentrations were in the range of LOQ in groundwater sampled close to the Oder River (<600 m distance) but below LOD in more distant samples with groundwater ages >5 years. TBEP (104 ng L^{-1}) was analyzed in Oder water but its concentrations were also below LOQ in samples from main ditch and groundwater wells.

Table VI-2. Mean (n = 2) concentrations of OPs, polyethers (ng L^{-1}), Cl^{-}, and Na^{+} (mg L^{-1}) in river water and groundwater samples.

Monitoring site	Compound [ng L^{-1}]						[mg L^{-1}]	
	TCEP	**TCPP [a]**	**TiBP**	**TnBP**	**Tri-glyme**	**Tetra-glyme**	**Cl^{-}**	**Na^{+}**
Oder River	540	2353	54	99	151	1260	131.9 [b]	77.1 [b]
Main ditch	171	958	19	14	106	967	-	-
6/99T	51	291	4	4	98	1230	128.9	78.8
9536F	30	261	12	4	245	1849	119.1	76.8
9/99F	96	447	8	7	81	1426	102.3	67.3
9560T	20	66	6	4	74	849	115.2	69.4
9561F	6	9	<LOQ	<LOQ	6	150	129.6	63.3
6/05F	4	5	<LOQ	<LOQ	<LOQ	<LOQ	64.8	26.9
6/05T	9	31	5	<LOQ	19	442	109.8	64.0
4/05T	6	8	<LOQ	<LOQ	<LOQ	<LOQ	49.0	27.1
4/05F	5	9	<LOQ	5	<LOQ	<LOQ	-	-
3/05T	5	4	<LOQ	<LOQ	<LOQ	<LOQ	48.1	19.0
3/05F	6	4	<LOQ	<LOQ	<LOQ	<LOQ	-	-
2144T	6	7	<LOQ	<LOQ	<LOQ	<LOQ	33.0	18.9
2144F	8	7	<LOQ	<LOQ	<LOQ	<LOQ	-	-

[a] Sum of two isomers; tris(2-chloro-1-methylethyl) phosphate, CAS 13674-84-5; bis(1-chloro-2-propyl)-2-chloropropyl phosphate, CAS 76025-08-05.

[b] Averaged concentration (n = 9) (*93*).

Hydrochemistry. Groundwater of transect Bahnbruecke is generally not influenced by percolation of precipitation due to an impermeable layer of alluvial loam on top of the aquifer. Nevertheless, the ascending groundwater of the Oder-near shallow wells (9/99F, 9536F) is influenced by discharge effects of the main ditch. Therefore, only groundwater samples of the six deep monitoring wells (19–23 m, Table VI-1) were considered regarding the transport processes during bank filtration.

Redox conditions were anoxic throughout the whole transect with redox potential E_h ranging between +40 and +92. Dissolved O_2 was consumed within the first meters of river water infiltration and was mostly 0.1 mg L^{-1} in the aquifer. Groundwater temperature was in the range of 10.0–11.1 °C. The pH-value of groundwater varied only slightly and decreased from 7.03 (6/99T) to 6.25 (2144F) with increasing distance from Oder River. Electrical conductivity in groundwater samples also decreased with growing groundwater ages (842–531 µS). However, electrical conductivity and Cl^- concentration were slightly increased at the shallow well 9561F. The DOC level rose linear (coefficient of determination, $R^2 = 0.9464$) with growing distance to Oder River and higher groundwater ages in samples from the deep wells. Fe^{2+} concentrations in the range of 3.39–6.88 mg L^{-1} were determined in groundwater older than 20 years. Mn^{2+} concentrations decreased to 1 mg L^{-1} at a distance of 600–700 m from the Oder. The Mn^{2+} -sink could be the precipitation of rhodochrosite as described by Massmann et al. (*93*). In the groundwater older than 20 years, Mn^{2+} increased up to 5.7 mg L^{-1} (2244T) parallel to the concentration of Fe^{2+}.

Transport of OPs in groundwater. The inorganic species chloride (Cl^-) and sodium (Na^+) were used as conservative tracers to determine the dilution process of infiltrating river water in the aquifer during bank filtration. Both ions have a high mobility in groundwater due to negligible sorption and low chemical interaction (*114*). Concentrations of the conservative tracers Cl^- and Na^+ (Table VI-2) in river water and groundwater of the six deep monitoring wells are plotted against the distance to Oder River in Fig. VI-1. The decrease of Cl^- ($R^2 = 0.9824$) and Na^+ ($R^2 = 0.9783$) indicated a linear dilution of infiltrating river water in the aquifer during bank filtration. Average concentrations (n = 9) of Cl^- (131.9±22.7 mg L^{-1}) and Na^+ (77.0±13.1 mg L^{-1}) in Oder water were previously published by Massmann et al. (*93*). Both values are in line with the linear fit of the groundwater data obtained in the present study.

Concentration levels of TCEP and TCPP in river water and groundwater of the deep wells are also displayed in Fig. VI-1. In contrast to these inorganic species, TCEP and TCPP showed no conservative transport within the aquifer. Concentrations of both compounds showed a strong decline in the beginning of bank filtration and provided almost constant values in more distant groundwater older than 20 years. This distribution pattern can not be exclusively explained by dilution processes in groundwater. Hence, adsorption as well as possibly degradation processes (second-order kinetic) seem to occur in the aquifer during transport. Heberer et al. (*21*) reported also removal for TCEP and TCPP during groundwater recharge at Lakes Tegel and Wannsee (Berlin, Germany). However, it has to be considered that usage of chlorinated flame retardants such as TCEP and TCPP increased greatly not until 1970's (*37*). Furthermore, both compounds were previously used in equal proportions in polyurethane foams in Germany, until TCEP was phased out in Europe based on a voluntary agreement of industry around 1995 (*31*). The discharging amounts of OPs from Oder water to groundwater were expected to be much lower in previous years (>20 years ago). This may also have led to the observation that concentration levels of TCEP and TCPP were in the same range in these groundwater samples, other than samples of younger groundwater and present surface water with significant higher TCPP values.

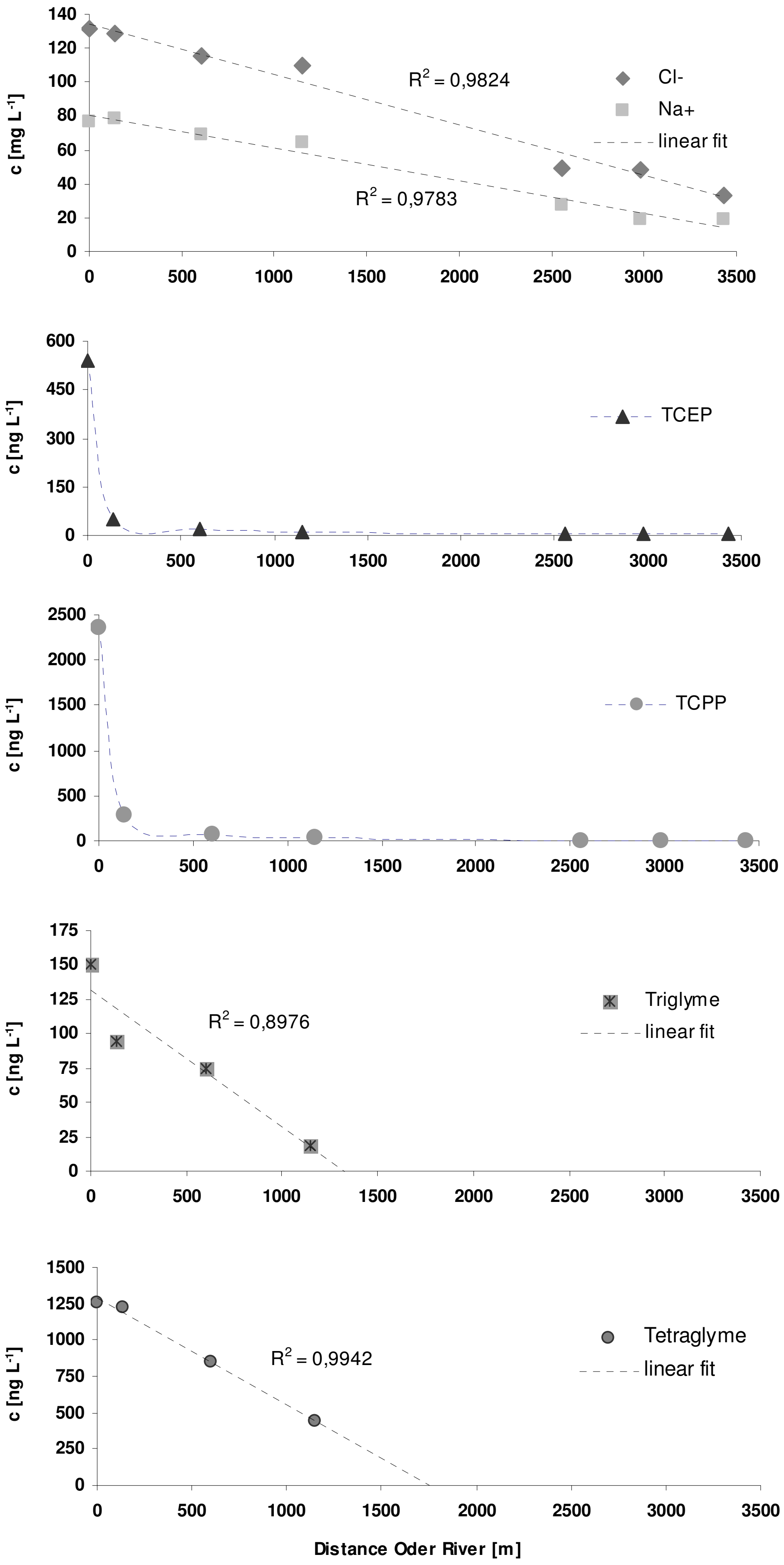


Fig. VI-1. Concentrations of TCEP, TCPP, triglyme, tetraglyme, and the inorganic conservative tracers

Cl^- and Na^+ in Oder River water (0 m distance) and groundwater of the six deep monitoring wells (6/99T, 9560T, 6/05T, 4/05T, 3/05T, 2144T). Triglyme and tetraglyme are not detectable in groundwater samples of the more distant monitoring wells with higher groundwater ages.

The polyethers triglyme and tetraglyme were detected in river water and Oder-near groundwater in the range of 6–245 ng L^{-1} and 150–1849 ng L^{-1}, respectively (Table VI-2). As displayed in Fig. VI-1, concentration levels of triglyme ($R^2 = 0.8976$) and tetraglyme ($R^2 = 0.9942$) in groundwater decreased almost linear with increasing distance from Oder River. The linear concentration decrease indicates a conservative transport behavior of both polyethers in the aquifer caused rather by dilution than adsorption processes similar to Cl^- and Na^+. Due to the polar characteristics of such ethers, these compounds (e. g., methyl *tert*-butyl ether, MTBE) migrate through the aquifer only with marginal retardation (*115*). However, both compounds were not detected in samples of groundwater older than 21 years (Table VI-1) which might be explained by the absence of these polyethers in Oder River at that time.

The chlorinated flame retardants have previously been proposed as hydrophilic marker substances for conservative transport of trace organic pollutants by Heinz et al. (*5*). Present results have shown that TCEP and TCPP are not suitable as conservative organic tracers in groundwater under the present aquifer conditions, though they are excellent indicators for contamination of groundwater with OP-loaded surface waters. TDCP and also TBEP are assumed to possess only low mobility in the aquifer due to their relatively high log K_{ow} and log K_{oc} values. They were, as well as TiBP and TnBP, not quantifiable in groundwater older than a few years. Instead, polyethers such as triglyme and tetraglyme revealed an excellent potential to be used as conservative organic tracers.

Attenuation of OPs during bank filtration. The concentrations of all OPs decreased immediately within the first few hundred meters of river water percolation into the aquifer. Based on the concentrations measured in Oder water and groundwater of the deep well 9560T in about 600 m distance to river, levels of TCEP, TCPP, TiBP, and TnBP decreased between 89–97% during 3 years of residence. This rapid decline of OPs in groundwater can be explained by both, adsorption and degradation processes during bank filtration and not by dilution effects. This is documented by the linear decline of other trace organic compounds (triglyme and tetraglyme) which are not affected by retardation and degradation. The mixing zone of surface water and subsurface water (hyporheic zone) in the upper few centimeters of sediments beneath the surface water body of river Oder is characterized by intensified biogeochemical activity (*116*). Adsorption and degradation processes of organic contaminants during bank filtration are significantly affected by the conditions in the hyporheic zone. These conditions can not be equated with those in aquifers or soils (*98*). So far, detailed experimental data on the OP behavior in hyporheic zones are not available. The data clearly indicate that triglyme and tetraglyme are not affected in the same way as OPs by the hyporheic zone since a rapid concentration decrease is not observed from the Oder River to the first groundwater sampling point in the aquifer.

As TCEP and TCPP, other than TiBP and TnBP, were detectable in groundwater with ages up to 45 years, stability in the anoxic groundwater can certainly be attributed for both chlorinated compounds. Nevertheless, removal of the chlorinated OPs during bank filtration is still controversial (*105*). Non-chlorinated OPs are expected to be less stable within the aquifer due to biotransformation processes. Elimination rates up to 89% were reported for TnBP and TBEP during bank filtration and soil filtration experiments (*44,105*).

The adsorption behavior of the chlorinated OPs in soils has been described to be a function of the soil organic carbon content and adsorption to soil components other than organic carbon was suggested to be not significant (*33*). This behavior can also be assumed for the non-chlorinated OPs TBEP, TiBP, and TnBP. According to modeled Freundlich parameters, TDCP is considerably better adsorbed to organic carbon surfaces than TCPP or TCEP (*117*). The organic carbon composition of the river bottom and the hyporheic zone is of high importance for the removal of OPs during river-aquifer interaction. Depending on sedimentation conditions, concentrations of total organic carbon (TOC) in Oder River sediments varied between 0.2–11.0% (*118*). The aquifer at Oderbruch polder consists of fine to medium sized sands and sediments and contains less than 0.1% TOC (*93*). However, high concentrations of organic matter in river sediments and river-near soils will enhance the sorption of OPs during subsurface transport of percolating river water within the first few centimeters to meters. Sorption of trace organic pollutants such as OPs can additionally be influenced by interactions with other compounds present in river water (*119*). Nevertheless, adsorbability of trace organic pollutants is significantly reduced when competing against background organic matter, e. g. dissolved organic carbon (DOC) (*117*). At Oderbruch polder the DOC value increased from 4.9 mg L^{-1} (6/99T) in Oder-near to 11.2 mg L^{-1} (2144T) in Oder-far groundwater samples. Together with the fact that lower initial trace organic pollutant concentrations cause a significant reduction of their adsorption capacity, nearly constant TCEP and TCPP levels in the range of 4–9 ng L^{-1} in samples with groundwater ages >20 years become feasible.

An additional sampling of groundwater at the same sampling site on 21/11/2009 confirmed the results of the present study (data not shown). Only OP concentrations in river and ditch water varied according to different discharge flows of Oder River and main ditch during both sampling campaigns. However, OP concentrations in groundwater were in the same range and revealed no short-time variations comparing the results from both sampling campaigns. At both sampling times, OP concentrations in the Oder-near groundwater decreased dramatically during the first few meters whereas a linear decrease was observed for polyether concentrations. Further investigations will be necessary to verify if groundwater contains degradation products of chlorinated and non-chlorinated OPs (e.g., bi- and mono-alkyl phosphates). Knowledge of possible transformation or degradation processes of OPs within groundwater or soil is fairly scarce. Dilution effects within the aquifer are easily accessible based on the conservative tracers Cl^- and Na^+ (inorganic) as well as triglyme and tetraglyme (organic). Additional attenuation factors such as microbial or chemical degradation and adsorption effects decreasing the OP concentrations during bank filtration, e. g. in the hyporheic zone, can not be differentiated at the moment. It is planned to study this issue by further investigations.

3 Summary, conclusions, and outlook

3.1 Summary

Within this doctoral thesis the occurrence and fate of the six OPs TCEP, TCPP, TDCP, TBEP, TiBP, and TnBP in precipitation (rainwater and snow), lake water, surface runoff, and groundwater from urban and remote areas in Germany were investigated. As listed in chapter 1.3, the research focused on the three main topics (1) atmospheric washout of OPs by precipitation, (2) temporal variation of OP concentrations in precipitation and lentic surface waters, and (3) pollution of groundwater by OPs via bank filtration or leachate of precipitation.

1) **Atmospheric washout of OPs by precipitation:** The data in papers II, III, and IV show that precipitation (rain and snow), especially in densely populated areas with high traffic volumes, is important as an all-season diffuse source of OPs in surface waters, although direct sources such as treated and untreated wastewaters are still the main entry-pathways for OPs. TCPP dominated in all precipitation samples with maximum concentrations exceeding 1 µg L^{-1}. In SWHTs an accumulation of deposited OPs was observed. Related to photooxidation, chlorinated OPs are sufficiently stable for short- and medium-range atmospheric transportation. The occurrence of OPs in only marginal anthropogenically-affected reservoirs and lakes reveals that these surface waters are influenced by wet and dry deposition of airborne OPs.

2) **Temporal variation of OP concentrations:** As presented in papers II and III, no seasonal trends were observed for all analytes in precipitation at the urban sampling site. However, atmospheric photooxidation is expected to reduce particularly concentrations of non-chlorinated OPs during transport from urban to remote areas in summer months with higher global irradiation. In the SWHT (paper III) a seasonal trend with decreasing concentrations in summer/autumn was evident for the non-chlorinated OPs TiBP and TnBP due to in-lake degradation but not for the chlorinated OPs. Laboratory experiments (paper IV) showed the rapid photochemical degradation of non-chlorinated OPs and the resistance of chlorinated OPs in natural water upon sunlight irradiation in summer. In urban lake water samples (paper IV) high variability but no significant seasonal trends were observed for all analyzed OPs.

3) **Groundwater polluted by OPs:** Paper V indicates that the occurrence of chlorinated and non-chlorinated OPs in groundwater is dependent on the individual processes

causing groundwater recharge/natural replenishment. Infiltration of precipitation at rural sites was found to be no important entry-pathway for OPs into groundwater. Highest OP concentrations were determined in groundwater polluted by percolating leachate from contaminated sites or in groundwater recharged via bank filtration of OP-loaded recipients. As shown in paper VI, concentrations of non-chlorinated OPs in groundwater decreased immediately with increasing distance from the recipient during bank filtration due to biotransformation and/or adsorption processes. Although TCEP and TCPP are stable within the aquifer, they are not suitable as conservative organic tracers in groundwater.

3.2 Conclusions

As mentioned before, significant knowledge gaps still are existing concerning the distribution and behavior of chlorinated and non-chlorinated OPs in the aquatic environment. The present investigation of 255 precipitation samples, 210 lentic surface water samples and 72 groundwater samples from urban and remote areas in Germany between June 2007 and October 2009 provided results which helped to close these knowledge gaps. The research results are discussed in the following.

Precipitation

In papers II and III, the role of precipitation as an important source of, and entry-pathway for, OPs into the aquatic environment was shown. TCEP, TCPP, TiBP, and TnBP were detected in almost all rain and snow samples from urban and remote areas, whereas TDCP and TBEP concentrations were often below LOD in samples from the rural sampling sites. Among the six analyzed OPs, TCPP dominated in all precipitation samples with maximum concentrations exceeding 1 µg L^{-1}. Highest TCPP values (3562 ng L^{-1}) were found in samples from the urban sampling site Frankfurt am Main. In general, concentrations of OPs in urban rainwater were three to four times higher than those at background monitoring stations, e. g. Schmuecke (Thuringian Forest). Variable concentrations of chlorinated flame retardants were found in precipitation, but their occurrence was not correlated with air temperature or rainfall amount. For all analytes, no seasonal trends were observed at the urban precipitation sampling site, although atmospheric photooxidation was expected to reduce particularly concentrations of non-chlorinated OPs during transport from urban to remote areas in summer months with higher global irradiation. Higher photochemical degradation rates in the atmosphere are probably counterbalanced by higher releases of OPs in summer months. However, the results indicate that volatilization of OPs from objects protected by flame retardants, including vehicles and buildings, causes these compounds to reach the aquatic environment via washout from the atmosphere, despite their reported short atmospheric half-lives (<24 h). Photooxidation is regarded as a degradation pathway for both, non-chlorinated and chlorinated OPs in the atmospheric environment, but the chlorinated substances ($t_{½}$ = 8.6–21.3 h) are more stable during short- and medium-range atmospheric transportation compared to non-chlorinated OPs ($t_{½}$ = <1–4 h). Unfortunately, neither predicted degradation data for particle-adsorbed OPs in the atmosphere nor experimental photodegradation studies are available. Nevertheless, a significant contribution of precipitation as an entry-pathway for chlorinated OPs into surface waters has been documented in the present study.

OP-loaded precipitation might influence water protection areas, groundwater, or drinking water wells that are not affected by wastewater discharges. The results of the model scenarios in the European Union risk assessment of TCPP (*33*) indicate that most TCPP in air will be precipitated to soil and water. However, the conclusion of the TCPP risk assessment study concerning atmospheric distribution is inconsistent with the data obtained in this doctoral thesis. The risk assessment concluded that: “Given the low levels of releases, the relatively low volatility and moderate solubility and adsorption coefficient of TCPP, together with its short predicted atmospheric half-life for degradation by hydroxyl radicals, it is not expected that exposure via the atmosphere will be significant”. Data from the present doctoral thesis indicate a significant transfer of TCPP through the atmosphere into the aquatic environment. This finding is also valid for other OPs, particularly TCEP. The diffuse sources wet and dry atmospheric deposition and surface runoff might have a percentage in the range of 70–90% on the observed OP concentrations in lentic surface waters if direct sources such as treated wastewater, leakage etc. can be excluded.

The increasing use of flame-protected products based on polyurethane, e. g., thermal insulation materials in external walls of buildings, will lead to increasing emissions of OPs into the atmosphere and finally into surface waters, particularly in densely populated areas.

Lentic surface waters

After clarifying the role of precipitation as an important source of OPs in the environment, the occurrence and fate of OPs in urban and remote lentic surface waters that are not affected by wastewater discharges or other industrial sources of contamination was investigated in paper IV. Only few studies focused on this issue so far (*4,60*). Totally nine lentic surface waters such as volcanic lakes, oxbow lakes, and reservoirs under different anthropogenic impact (paper IV) as well as two storm water holding tanks (SWHTs, paper III) were regularly sampled within this doctoral thesis. Furthermore, in-lake destruction of the OPs in spiked ultrapure water and lake water samples incubated in Teflon bottles (which transmit sunlight) was simulated in laboratory experiments.

As expected, OP concentrations of the urban lakes were in general higher than concentrations of the more remote lakes. The median TCPP level in the urban oxbow lake exceeded for instance the acceptable TCPP concentration of 0.1 µg L^{-1} as proposed by the Federal Environmental Agency of Germany (*31*). OP concentrations in the more remote lakes were often below or close to the limits of quantitation (LOQ). Nevertheless, TCPP was the substance with the highest median concentration in rural volcanic lakes (7–18 ng L^{-1}) indicating the expected atmospheric transport of the compound. However, the occurrence of OPs in only marginal anthropogenically-affected reservoirs and lakes reveals that these montane water bodies are influenced by wet and dry deposition of airborne OPs. The results have shown that predominantly the chlorinated OPs are detectable in lentic surface waters of altitudes up to 690 m above sea level without surrounding local anthropogenic pollution sources.

In the urban SWHT a seasonal trend with decreasing concentrations in summer/autumn was evident for the non-chlorinated OPs due to in-lake degradation. At both urban lakes a high variability but no significant seasonal trend of TiBP and TnBP concentrations was observed. The chlorinated OPs showed no seasonal trend at all. For the non-chlorinated OPs two possible degradation pathways in water are expected: biodegradation and photochemical decomposition. In literature, phosphoric acid triesters were previously assumed to be no subject of direct photodegradation in surface waters since they are poor light-absorbers in the natural light range (*40*). However, reactive transients (e. g., OH-radicals, H_2O_2) can induce the indirect photolysis of OPs and therefore influence their photochemical fate and persistence in natural water. Based on the results from the photochemical degradation experiments (paper IV), concentration decreases of non-chlorinated OPs in lentic surface waters can be explained by photochemical degradation due to reactive oxygen species formed from DOM, although microbial degradation will also take place. In summer, an increased water temperature and global irradiance as well as higher amounts of organic material enhance the degradation processes of non-chlorinated OPs in lentic surface waters. Even though the non-chlorinated OPs are photochemically and microbially degradable in natural lake water, they are (as well as the chlorinated OPs) frequently detected in surface waters due to their continuous release into the environment.

Furthermore, an accumulation of OPs deposited in SWHTs was observed with concentrations often exceeding those determined in wet precipitation. Median concentrations of some OPs at the SWHT were more than twice as high as median concentrations measured at the urban precipitation sampling site. Mobilization of OPs from buildings (e. g., insulation materials, concrete) and sealed urban areas by rainwater runoff similar to that of copper and zinc from rooftops or buildings is assumed. Further problems might arise as the discharge of the cumulated storm water runoff into creeks and rivers usually occurs without any treatment. So if the discharges into natural surface waters are not sufficiently diluted or if the retention basins are not sufficiently sealed off, SWHTs are additional sources of OPs in the aquatic environment. Under consideration of recent climate change predictions with an increasing number of storm events, more investigations in view of contaminated urban storm water runoff will be necessary.

Groundwater

The potential danger of groundwater contamination with organophosphorus flame retardants and plasticizers via OP-loaded surface water and storm water runoff has previously been discussed in several publications (*81,108*). According to the results obtained in papers II–IV, the obvious question had to be posed whether and to which extent groundwater is influenced by precipitation and surface water contaminated with OPs during groundwater recharge. As reported in papers V and VI, the occurrence of chlorinated and non-chlorinated OPs in groundwater is largely dependent on the anthropogenic impact during groundwater recharge/natural replenishment. In general, OP concentrations were below LOD in samples from springs and deep groundwater monitoring wells that are not affected by surface waters. Infiltration of precipitation at rural sites was shown to be no prominent entry-pathway for OPs into groundwater, but OP-loaded precipitation and surface runoff is supposed to influence groundwater quality at urban sites. So far, data related to OP behavior during soil infiltration under natural rainfall conditions are missing. Highest OP concentrations (>0.1 µg L^{-1}) were determined in groundwater polluted by percolating leachate from contaminated sites or groundwater recharged via bank filtration of OP-loaded recipients.

At Oderbruch polder, initial river water levels of TCEP (540 ng L^{-1}), TCPP (2353 ng L^{-1}), TiBP (54 ng L^{-1}), and TnBP (99 ng L^{-1}) decreased between 89% and 97% in the aquifer during a bank-filtrate travel time of 3 years. TDCP and also TBEP are assumed to possess only low mobility in the aquifer due to their relatively high log K_{ow} and log K_{oc} values. They were as well as TiBP and TnBP, not quantifiable in groundwater older than a few years, while TCPP and TCEP concentrations of 4–9 ng L^{-1} in samples from monitoring wells with groundwater ages between 20–45 years indicate their persistence within the aquifer under anoxic conditions. Furthermore, it has to be considered in which amounts these compounds were released into the environment in the past. Usage of TDCP is assumed to be of minor importance as a flame retardant in consumer products compared to TCEP and TCPP at that time. TCEP and TCPP were previously used in equal proportions in polyurethane foams in Germany, until TCEP was phased out in Europe based on a voluntary agreement of industry around 1995 (*31*).Therefore concentration levels of both compounds were in the same range in groundwater samples older than 20 years other than samples of younger groundwater and present surface water with significant higher TCPP proportions.

However, the chlorinated flame retardants TCEP and TCPP were the most frequent OPs detected in groundwater samples in this doctoral thesis. They were proposed as hydrophilic marker substances for conservative transport of trace organic pollutants by Heinz et al. (*5*). Results from the present study have shown that TCEP and TCPP are not suitable as conservative organic tracers in groundwater, though they are excellent indicators for contamination of groundwater with OP-loaded surface waters. Their strong decline in the beginning of bank filtration is possibly caused by adsorption/degradation processes in the hyporheic zone. In contrast, concentration levels of the highly water soluble polyethers triglyme and tetraglyme decreased almost linear in groundwater with increasing distance to Oder River.

The attenuation efficiency of organic tracers during natural recharge processes seems to depend on parameters like soil characteristics, residence times, and hydrochemical conditions within the aquifer. Anyhow, these processes are not yet sufficiently understood depending on the complex interactions between groundwater and surface water. Additionally, long residence times, lower water temperatures, marginal dilution effects and low microbial activity often increase the persistence of organic trace pollutants in groundwater whereas biogeochemical redox processes are known to enhance transformation processes of organic contaminants in groundwater.

3.3 Outlook

The results of this doctoral thesis provide comprehensive responses to important research questions concerning the occurrence and fate of OPs in the aquatic environment. Nevertheless, further investigations are required to close all significant knowledge gaps concerning the occurrence and fate of OPs in the environment.

So far, the available amount of data is to low for an estimation of the proportion by which the atmospheric washout of OPs by precipitation or dry deposition contributes to the currently observed surface water pollution. The proportion is presumeably higher in densely populated areas compared to rural areas. Additional data on inputs, flows, or bulk parameters etc. are necessary to quantify the atmospheric entry of OPs into the aquatic environment. The chlorinated OPs TCEP, TCPP, and TDCP do not fulfill the POP criteria as they are not sufficiently persistent enough in atmosphere (*74*). However, their inclusion in monitoring studies modeling the atmospheric transport and deposition of POPs might be an auxiliary approach to gain more information about atmospheric OP loads. It has been shown that their calculated photooxidation half-lives in air are nevertheless sufficient for short-range or medium-range atmospheric transportation. Moreover, further data on the seasonal fluctuations and trends of OP concentrations in precipitation are required for the assessment of the influence of photodegradation on the OP concentrations in precipitation. No experimental studies on photodegradation of OPs adsorbed to atmospheric particles have been undertaken so far (*32-34*).

Furthermore, additional research is necessary to understand the fate of chlorinated OPs TCEP, TCPP, and TDCP during soil infiltration into groundwater with respect to their persistence, biotransformation, and adsorption on soil organic matter. Amongst others, it has to be verified whether groundwater contains degradation products of chlorinated and non-chlorinated OPs (e.g., bi- and monoalkyl phosphates). Knowledge of possible transformation or degradation processes of OPs within groundwater or soil is fairly scarce. As TCEP and TCPP are known to be problematical regarding drinking water purposes, they should be routinely analyzed when drinking water is supplied from bank filtration or from urban groundwater.

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References

(1) Bester, K. *Personal Care Compounds in the Environment: Pathways, Fate and Methods for Determination*; WILEY-VCH: Weinheim, **2006**.

(2) Föllmann, W.; Wober, J. Investigation of cytotoxic, genotoxic, mutagenic, and estrogenic effects of the flame retardants tris-(2-chloroethyl)-phosphate (TCEP) and tris-(2-chloropropyl)-phosphate (TCPP) in vitro. *Toxicol. Lett.* **2006**, *161*, 124-134.

(3) Marklund, A.; Andersson, B.; Haglund, P. Traffic as a source of organophosphorus flame retardants and plasticizers in snow. *Environ. Sci. Technol.* **2005**, *39*, 3555-3562.

(4) Bacaloni, A.; Cucci, F.; Guarino, C.; Nazzari, M.; Samperi, R.; Lagana, A. Occurrence of organophosphorus flame retardant and plasticizers in three volcanic lakes of Central Italy. *Environ. Sci. Technol.* **2008**, *42*, 1898-1903.

(5) Heinz, B.; Birk, S.; Liedl, R.; Geyer, T.; Straub, K.; Andresen, J.; Bester, K.; Kappler, A. Water quality deterioration at a karst spring (Gallusquelle, Germany) due to combined sewer overflow: evidence of bacterial and micro-pollutant contamination. *Environ. Geol.* **2009**, *57*, 797-808.

(6) Reemtsma, T.; Quintana, J. B.; Rodil, R.; García-López, M.; Rodriguez, I. Organophosphorus flame retardants and plasticizers in water and air - I. Occurence and fate. *TrAC-Trend. Anal. Chem.* **2008**, *27*, 727-737.

(7) Ren, X.; Lee, Y. J.; Han, H. J.; Kim, I. S. Effect of tris-(2-chloroethyl)-phosphate (TCEP) at environmental concentration on the levels of cell cycle regulatory protein expression in primary cultured rabbit renal proximal tubule cells. *Chemosphere* **2008**, *74*, 84-88.

(8) Marklund, A.; Andersson, B.; Haglund, P. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere* **2003**, *53*, 1137-1146.

(9) Staaf, T.; Östman, C. Organophosphate triesters in indoor environments. *J. Environ. Monit.* **2005**, *7*, 883-887.

(10) Wensing, M.; Uhde, E.; Salthammer, T. Plastics additives in the indoor environment - flame retardants and plasticizers. *Sci. Total Environ.* **2005**, *339*, 19-40.

(11) Stapleton, H. M.; Klosterhaus, S.; Eagle, S.; Fuh, J.; Meeker, J. D.; Blum, A.; Webster, T. F. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environ. Sci. Technol.* **2009**, *43*, 7490-7495.

(12) Carlsson, H.; Nilsson, U.; Becker, G.; Ostman, C. Organophosphate ester flame retardants and plasticizers in the indoor environment: Analytical methodology and occurrence. *Environ. Sci. Technol.* **1997**, *31*, 2931-2936.

(13) Schindler, B.; Förster, K.; Angerer, J. Determination of human urinary organophosphate flame retardant metabolites by solid-phase extraction and gas chromatography-tandem mass spectrometry. *J. Chromatogr. B* **2009**, *877*, 375-381.

(14) Schindler, B.; Förster, K.; Angerer, J. Quantification of two urinary metabolites of organophosphorus flame retardants by solid-phase extraction and gas chromatography-tandem mass spectrometry. *Anal. Bioanal.Chem.* **2009**, *395*, 1167-1171.

(15) Sjodin, A.; Carlsson, H.; Thuresson, K.; Sjolin, S.; Bergman, A.; Ostman, C. Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environ. Sci. Technol.* **2001**, *35*, 448-454.

(16) Salthammer, T.; Fuhrmann, F.; Uhde, E. Flame retardants in the indoor environment - Part II: release of VOCs (triethylphosphate and halogenated degradation products) from polyurethane. *Indoor Air* **2003**, *13*, 49-52.

(17) Uhde, E.; Salthammer, T. Impact of reaction products from building materials and furnishings on indoor air quality -A review of recent advances in indoor chemistry. *Atmos. Environ. Indoor 2005* **2007**, *41*, 3111-3128.

(18) Weigel, S.; Bester, K.; Huhnerfuss, H. Identification and quantification of pesticides, industrial chemicals, and organobromine compounds of medium to high polarity in the North Sea. *Mar. Pollut. Bull.* **2005**, *50*, 252-263.

(19) Quednow, K.; Püttmann, W. Organophosphates and synthetic musk fragrances in freshwater streams in Hesse/Germany. *Clean-Soil Air Water* **2008**, *36*, 70-77.

(20) Fries, E.; Püttmann, W. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water (Oder, Germany). *J. Environ. Monit.* **2003**, *5*, 346 - 352.

(21) Heberer, T.; Mechlinski, A.; Fanck, B.; Knappe, A.; Massmann, G.; Pekdeger, A.; Fritz, B. Field studies on the fate and transport of pharmaceutical residues in bank filtration. *Ground Water Monitoring & Remediation* **2004**, *24*, 70-77.

(22) Marklund, A.; Andersson, B.; Haglund, P. Organophosphorus flame retardants and plasticizers in Swedish sewage treatment plants. *Environ. Sci. Technol.* **2005**, *39*, 7423-7429.

(23) Höhne, C.; Püttmann, W. Behaviour of selected organophosphates (flame retardants) and alkylphenols (antioxidants) in wastewater treatment plants. *GWF-Wasser/Abwasser* **2006**, *147*, 235-241.

(24) Kawagoshi, Y.; Nakamura, S.; Fukunaga, I. Degradation of organophosphoric esters in leachate from a sea-based solid waste disposal site. *Chemosphere* **2002**, *48*, 219-225.

(25) Scott, B.; Sverko, E.; Maguire, R. J. Determination of benzothiazole and alkylphosphates in water samples from the Great Lakes drainage basin by gas chromatography/atomic emission detection. *Water Qual. Res. J. Canada* **1996**, *31*, 341-360.

(26) Laniewski, K.; Boren, H.; Grimvall, A. Identification of volatile and extractable chloroorganics in rain and snow. *Environ. Sci. Technol.* **1998**, *32*, 3935-3940.

(27) Ciccioli, P.; Cecinato, A.; Brancaleoni, E.; Montagnoli, M.; Allegrini, I. Chemical composition of particulate organic matter (POM) collected at Terra Nova Bay in Antarctica. *Int. J. Environ. Anal. Chem.* **1994**, *55*, 47-59.

(28) Aston, L. S.; Noda, J.; Seiber, J. N.; Reece, C. A. Organophosphate flame retardants in needles of Pinus ponderosa in the Sierra Nevada Foothills. *Bull. Environ. Contam. Toxicol.* **1996**, *57*, 859-866.

(29) Martínez-Carballo, E.; González-Barreiro, C.; Sitka, A.; Scharf, S.; Gans, O. Determination of selected organophosphate esters in the aquatic environment of Austria. *Science of The Total Environment* **2007**, *388*, 290-299.

(30) García-López, M.; Rodríguez, I.; Cela, R. Pressurized liquid extraction of organophosphate triesters from sediment samples using aqueous solutions. *J. Chromatogr. A* **2009**, *1216*, 6986-6993.

(31) Leisewitz, A.; Kruse, H.; Schramm, E.; Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals - Vol. 1. Umweltbundesamt, Berlin, Germany, **2001**.

(32) European Commission; EU Risk Assessment Report, Tris(2-chloroethyl) phosphate, TCEP (Draft). Available through ORATS (Online EUropean Risk Assessment Tracking System), **2006**.

(33) European Commission; EU Risk Assessment Report, Tris(2-chloro-1-methylethyl) phosphate, TCPP (Draft). Available through ORATS (Online EUropean Risk Assessment Tracking System), **2007**.

(34) European Commission; EU Risk Assessment Report, Tris(2-chloro-1-(chloromethyl)ethyl) phosphate, TDCP (Draft). Available through ORATS (Online EUropean Risk Assessment Tracking System), **2007**.

(35) World Health Organization; Flame Retardants: Tris(2-butoxyethyl) phosphate, Tris(2-ethylhexyl) phosphate and Tetrakis(hydroxymethyl) phosphonium salts. Environmental Health Criteria 218, Geneva, Switzerland, **2000**.

(36) World Health Organization; Tributyl Phosphate. Environmental Health Criteria 112, Geneva, Switzerland, **1991**.

(37) Muir, D. C. G. In *The Handbook of Environmental Chemistry - Volume 3 Part C*; Hutzinger, O., Ed.; Springer: Berlin, **1984**; Vol. 3 - Part C.

(38) Verbruggen, E. M. J.; Rila, J. P.; Traas, T. P.; Posthuma-Doodeman, C. J. A. M.; Posthumus, R.; Environmental Risk Limits for Several Phosphate Esters, with Possible Application as Flame Retardant. National Institute for Public Health and the Environment, Bilthoven, Netherlands, **2005**.

(39) Kawagoshi, Y.; Fukunaga, I.; Itoh, H. Distribution of organophosphoric acid triesters between water and sediment at a sea-based solid waste disposal site. *J Mater Cycles Waste Manag* **1999**, *1*, 53-61.

(40) Watts, M. J.; Linden, K. G. Photooxidation and subsequent biodegradability of recalcitrant tri-alkyl phosphates TCEP and TBP in water. *Water Res.* **2008**, *42*, 4949-4954.

(41) Saeger, V. W.; Hicks, O.; Kaley, R. G.; Michael, P. R.; Mieure, J. P.; Tucker, E. S. Environmental fate of selected phosphate esters. *Environ. Sci. Technol.* **1979**, *13*, 840-844.

(42) Quintana, J. B.; Rodil, R.; Reemtsma, T. Determination of phosphoric acid mono- and diesters in municipal wastewater by solid-phase extraction and ion-pair liquid chromatography-tandem mass spectrometry. *Anal. Chem.* **2006**, *78*, 1644-1650.

(43) Rauch-Williams, T.; Hoppe-Jones, C.; Drewes, J. E. The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. *Water Research* **2010**, *44*, 449-460.

(44) Bester, K.; Schäfer, D. Activated soil filters (bio filters) for the elimination of xenobiotics (micro-pollutants) from storm- and waste waters. *Water Res.* **2009**, *43*, 2639-2646.

(45) Cordy, G. E.; Duran, N. L.; Bouwer, H.; Rice, R. C.; Furlong, E. T.; Zaugg, S. D.; Meyer, M. T.; Barber, L. B.; Kolpin, D. W. Do pharmaceuticals, pathogens, and other organic waste water compounds persist when waste water is used for recharge? *Ground Water Monit. Rem.* **2004**, *24*, 58-69.

(46) Williams, D. T.; LeBel, G. L. A national survey of tri(haloalkyl)-, trialkyl-, and triarylphosphates in canadian drinking water. *Bull. Environ. Contam. Toxicol.* **1981**, *27*, 450-457.

(47) Muir, D. C. G.; Yarechewski, A. L.; Grift, N. P. Environmental dynamics of phosphate esters. III. Comparison of the bioconcentration of four triaryl phosphates by fish. *Chemosphere* **1983**, *12*, 155-166.

(48) Kawai, S.; Fukushima, M.; Kitano, M.; Nishio, T.; Morishita, H. Degradation of organophosphoric acid triesters by the bacteria in the river water. (II) Properties of TBP degrading bacteria and their enzymes. *Annu. Rep. Osaka C. Inst. Pub. Health Environ. Sci.* **1987**, *49*, 160-166.

(49) Rozen, A. M.; Nikiforov, A. S.; Shmidt, V. S.; Nikolotova, Z. I.; Kartasheva, N. A.; Zakharkin, B. S. Optimizing extractant molecular structure for reprocessing spent nuclear power station fuel. *At. Energ.* **1985**, *58*, 45-51.

(50) Meyer, J.; Bester, K. Organophosphate flame retardants and plasticisers in wastewater treatment plants. *J. Environ. Monit.* **2004**, *6*, 599 - 605.

(51) Reemtsma, T.; Weiss, S.; Mueller, J.; Petrovic, M.; Gonzalez, S.; Barcelo, D.; Ventura, F.; Knepper, T. P. Polar pollutants entry into the water cycle by municipal wastewater: A European perspective. *Environ. Sci. Technol.* **2006**, *40*, 5451-5458.

(52) Andresen, J. A.; Grundmann, A.; Bester, K. Organophosphorus flame retardants and plasticisers in surface waters. *Sci. Total Environ.* **2004**, *332*, 155-166.

(53) Loock, F.; Lampe, T.; Bahadir, M. Examination of the emission of (semi-)volatile organic compounds from polymer materials used as interior trim materials in automobiles. *Fresenius J. Anal. Chem.* **1993**, *347*, 280-285.

(54) Fries, E.; Püttmann, W. Occurrence of organophosphate esters in surface water and ground water in Germany. *J. Environ. Monit.* **2001**, *3*, 621 - 626.

(55) Rodil, R.; Quintana, J. B.; Reemtsma, T. Liquid chromatography-tandem mass spectrometry determination of nonionic organophosphorus flame retardants and plasticizers in wastewater samples. *Anal. Chem.* **2005**, *77*, 3083-3089.

(56) Quintana, J. B.; Rodil, R.; Lopez-Mahia, P.; Muniategui-Lorenzo, S.; Prada-Rodriguez, D. Optimisation of a selective method for the determination of organophosphorous triesters in outdoor particulate samples by pressurised liquid extraction and large-volume injection gas chromatography-positive chemical ionisation-tandem mass spectrometry. *Anal. Bioanal.Chem.* **2007**, *388*, 1283-1293.

(57) Chung, H.-W.; Ding, W.-H. Determination of organophosphate flame retardants in sediments by microwave-assisted extraction and gas chromatography-mass spectrometry with electron impact and chemical ionization. *Anal. Bioanal.Chem.* **2009**, *395*, 2325-2334.

(58) IUCLID; International Uniform Chemical Information Database, CD-ROM edition. European Chemicals Bureau, Ispra, Italy, **2000**.

(59) Reemtsma, T.; Quintana, J. B. In *Organic Pollutants in the Water Cycle.*; Reemtsma, T., M. Jekel, Ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, **2006**; pp 1-40.

(60) Prösch, J.; Pansch, G.; Puchert, W. Occurence of TCEP and TCPP in bath lakes as well as house wells of rural areas Mecklenburg-Vorpommern, Germany. *Vom Wasser* **2002**, *98*, 159-164.

(61) World Health Organization; Flame retardants: A general introduction. Environmental Health Criteria 192, Geneva, Switzerland, **1997**.

(62) NICNAS; Triphosphates; Priority Existing Chemical Assessment Report No. 17. National Industrial Chemicals Notification and Assessment Scheme, Sydney, Australia, **2001**.

(63) Kemmlein, S.; Hahn, O.; Jann, O. Emissions of organophosphate and brominated flame retardants from selected consumer products and building materials. *Atmos. Environ.* **2003**, *37*, 5485-5493.

(64) Westerhoff, P.; Yoon, Y.; Snyder, S.; Wert, E. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.* **2005**, *39*, 6649-6663.

(65) Andresen, J. A.; Bester, K. Elimination of organophosphate ester flame retardants and plasticizers in drinking water purification. *Water Res.* **2006**, *40*, 621-629.

(66) World Health Organization; Flame Retardants: Tris(chloropropyl) phosphate and Tris(2-chloroethyl) phosphate. Environmental Health Criteria 209, Geneva, Switzerland, **1998**.

(67) Kemmlein, S.; Hahn, O.; Jann, O.; Emission of Flame Retardants from Consumer Products and Building Materials. Federal Institute for Materials Research and Testing (BAM), Berlin, **2003**.

(68) Marklund, A.; Levels and sources of organophosphorus flame retardants and plasticizers in indoor and outdoor environments. Ph.D. Thesis. Umeå University, Umeå, Sweden, **2005**.

(69) Sagunski, H.; Roßkamp, E. Richtwerte für die Innenraumluft: Tris(2-chlorethyl)phosphat. *Bundesgesundheitsbl - Gesundheitsforsch - Gesundheitsschutz* **2002**, *45*, 300-306.

(70) Schmidt, H. J.; Lüßmann-Geiger, H. Verunreinigung der Fahrzeuginnenraumluft - Quellen und Gegenmaßnahmen. *Gefahrst. Reinhalt. Luft* **1996**, *56*, 43-60.

(71) Fernández, P.; Grimalt, J. O. On the global distribution of persistent organic pollutants. *Chimia* **2003**, *57*, 514-521.

(72) UNEP Publication; Tributyl Phosphate - SIDS Initial Assessment Report for 12th SIAM. Organisation for Economic Co-Operation and Development **2001**.

(73) Van Jaarsveld, J. A.; Van Pul, W. A. J.; De Leeuw, F. A. A. M. Modelling transport and deposition of persistent organic pollutants in the European region. *Atmos. Environ.* **1997**, *31*, 1011-1024.

(74) Brown, T. N.; Wania, F. Screening chemicals for the potential to be persistent organic pollutants: A case study of Arctic contaminants. *Environ. Sci. Technol.* **2008**, *42*, 5202-5209.

(75) European Chemicals Bureau; European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). National Institute of Public Health and the Environment (RIVM Report no. 601900005), Bilthoven, The Netherlands, **2004**.

(76) Stackelberg, P. E.; Gibs, J.; Furlong, E. T.; Meyer, M. T.; Zaugg, S. D.; Lippincott, R. L. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. *Sci. Total Environ.* **2007**, *377*, 255-272.

(77) Regnery, J.; Püttmann, W. Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. *Clean-Soil Air Water* **2009**, *37*, 334-342.

(78) Hartmann, P. C.; Bürgi, D.; Giger, W. Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere* **2004**, *57*, 781-787.

(79) Green, N.; Schlabach, M.; Bakke, T.; Brevik, E. M.; Dye, C.; Herzke, D.; Huber, S.; Plosz, B.; Remberger, M.; Schøyen, M.; Uggerud, H. T.; Vogelsang, C.; Screening of selected metals and new organic contaminants 2007. Norwegian Pollution Control Authority, Oslo, **2008**.

(80) Göbel, P.; Dierkes, C.; Coldewey, W. G. Storm water runoff concentration matrix for urban areas. *J. Contam. Hydrol.* **2007**, *91*, 26-42.

(81) Bester, K.; Scholes, L.; Wahlberg, C.; McArdell, C. Sources and mass flows of xenobiotics in urban water cycles - an overview on current knowledge and data gaps. *Water Air Soil Poll. Focus* **2008**, *8*, 407-423.

(82) Ni, Y.; Kumagai, K.; Yanagisawa, Y. Measuring emissions of organophosphate flame retardants using a passive flux sampler. *Atmos. Environ.* **2007**, *41*, 3235-3240.

(83) Saito, I.; Onuki, A.; Seto, H. Indoor organophosphate and polybrominated flame retardants in Tokyo. *Indoor Air* **2007**, *17*, 28-36.

(84) Regnery, J.; Püttmann, W. Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff. *Chemosphere* **2010**, *78*, 958-964.

(85) Amyot, M.; McQueen, D. J.; Mierle, G.; Lean, D. R. S. Sunlight-induced formation of dissolved gaseous mercury in lake waters. *Environ. Sci. Technol.* **1994**, *28*, 2366-2371.

(86) Leisewitz, A.; Fengler, S.; Seel, P.; Exploratory analysis of hazardous substances. Hessian Agency for the Environment and Geology, Wiesbaden, **2003**.

(87) Brück, H. New physiographic data of maars in the Eifel. *Decheniana* **1985**, *138*, 193-220.

(88) Mong, G.; Campbell, J. Analysis of phosphate-related components in Hanford tank wastes. *J. Radioanal. Nucl. Chem.* **1999**, *241*, 297-306.

(89) Moran, M. A.; Zepp, R. G. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* **1997**, *42*, 1307-1316.

(90) Scully, N. M.; McQueen, D. J.; Lean, D. R. S.; Cooper, W. J. Hydrogen peroxide formation: The interaction of ultraviolet radiation and dissolved organic carbon in lake waters along a 43-75°N Gradient. *Limnol. Oceanogr.* **1996**, *41*, 540-548.

(91) Snyder, S. A. Occurrence, treatment, and toxicological relevance of EDCs and pharmaceuticals in water. *Ozone Sci. Eng.* **2008**, *30*, 65 - 69.

(92) Holm, J. V.; Ruegge, K.; Bjerg, P. L.; Christensen, T. H. Occurrence and distribution of pharmaceutical organic compounds in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environ. Sci. Technol.* **1995**, *29*, 1415-1420.

(93) Massmann, G.; Pekdeger, A.; Merz, C. Redox processes in the Oderbruch polder groundwater flow system in Germany. *Appl. Geochem.* **2004**, *19*, 863-886.

(94) Merz, C.; Schuhmacher, P.; Winkler, A.; Pekdeger, A. Identification and regional quantification of hydrochemical processes at the contact zone between anoxic groundwater and surface water in poldered floodplains (Oderbruch polder, Germany). *Appl. Geochem.* **2005**, *20*, 241-254.

(95) Merz, C.; Winkler, A.; Pekdeger, A. Trace elements in streambed sediments of floodplains: consequences for water management measures. *Environ. Earth Sci.* **2009**, *59*, 25-38.

(96) Fach, A.; On the effective contribution of discrete transport factors to the propagation of landfill leachate components in groundwater. Ph.D. Thesis. University of Berlin, Germany, **2006**.

(97) Ammann, A. A.; Hoehn, E.; Koch, S. Ground water pollution by roof runoff infiltration evidenced with multi-tracer experiments. *Water Res.* **2003**, *37*, 1143-1153.

(98) Sophocleous, M. Interactions between groundwater and surface water: the state of the science. *Hydrogeol. J.* **2002**, *10*, 52-67.

(99) Sültenfuß, J.; Massmann, G. Dating with the 3He-tritium-method: An example of bank filtration in the Oderbruch region. *Grundwasser* **2004**, *9*, 221-234.

(100) Massmann, G.; Sültenfuß, J.; Pekdeger, A. Analysis of long-term dispersion in a river-charged aquifer using tritium/helium date. *Water Resour. Res.* **2009**, *45*, doi: 10.1029/2007WR006746.

(101) Tosaki, Y.; Tase, N.; Massmann, G.; Nagashima, Y.; Seki, R.; Takahashi, T.; Sasa, K.; Sueki, K.; Matsuhiro, T.; Miura, T.; Bessho, K.; Matsumura, H.; He, M. Application of 36Cl as a dating tool for modern groundwater. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *259*, 479-485.

(102) Luckner, T.; Helling, C.; Raimann, S.; Umgang mit abfallablagerungsverursachten Gewässerschäden und Gefahrensituationen unter Berücksichtigung der Wirkungen natürlicher Rückhalte- und Abbau-Prozesse. Leitfaden - KORA Themenverbund 4. Dresdener Grundwasserforschungszentrum e.V. (DGFZ), Dresden, **2008**.

(103) Pitt, R.; Clark, S.; Field, R. Groundwater contamination potential from stormwater infiltration practices. *Urban Water* **1999**, *1*, 217-236.

(104) Amy, G.; Drewes, J. Soil aquifer treatment (SAT) as a natural and sustainable wastewater reclamation/reuse technology: fate of wastewater effluent organic matter (EfOM) and trace organic compounds. *Environ. Monit. Assess.* **2007**, *129*, 19-26.

(105) Schmidt, C. K.; Datenbank zum Verhalten organischer Spurenstoffe bei der Uferfiltration. DVGW-Technologiezentrum Wasser, Karlsruhe, Germany, **2005**.

(106) Reinhard, M.; Barker, J. F.; Goodman, N. L. Occurrence and distribution of organic chemicals in two landfill leachate plumes. *Environ. Sci. Technol.* **1984**, *18*, 953-961.

(107) Knepper, T. P.; Sacher, F.; Lange, F. T.; Brauch, H. J.; Karrenbrock, F.; Roerden, O.; Lindner, K. Detection of polar organic substances relevant for drinking water. *Waste Manage. (Oxford)* **1999**, *19*, 77-99.

(108) Díaz-Cruz, M. S.; Barceló, D. Trace organic chemicals contamination in ground water recharge. *Chemosphere* **2008**, *72*, 333-342.

(109) Borch, T.; Kretzschmar, R.; Kappler, A.; Cappellen, P. V.; Ginder-Vogel, M.; Voegelin, A.; Campbell, K. Biogeochemical redox processes and their impact on contaminant dynamics. *Environ. Sci. Technol.* **2009**, *44*, 15-23.

(110) Eckel, W.; Foster, G.; Ross, B. Glycol ethers as ground water contaminants. *Occup. Hyg.* **1996**, *2*, 97-104.

(111) Collombon, M. T.; Concentration of ‘Forgotten’ Substances Using the XAD Concentration Method. National Institute for Public Health and the Environment (RIVM), Bilthoven, The Netherlands, **2007**.

(112) Kameya, T.; Murayama, T.; Urano, K.; Kitano, M. Biodegradation ranks of priority organic compounds under anaerobic conditions. *Sci. Total Environ.* **1995**, *170*, 43-51.

(113) Grossmann, D.; Köser, H.; Kretschmer, R.; Porobin, M. Treatment of diglyme containing wastewater by advanced oxidation – process design and optimisation. *Water Sci. Technol.* **2001**, *44*, 287-293.

(114) Cox, M. H.; Su, G. W.; Constantz, J. Heat, chloride, and specific conductance as ground water tracers near streams. *Ground Water* **2007**, *45*, 187-195.

(115) Deeb, R. A.; Chu, K.-H.; Shih, T.; Linder, S.; Suffet, I.; Kavanaugh, M. C.; Alvarez-Cohen, L. MTBE and other oxygenates: environmental sources, analysis, occurrence, and treatment. *Environ. Eng. Sci.* **2003**, *20*, 433-447.

(116) Massmann, G.; Pekdeger, A.; Dünnbier, U.; Heberer, T.; Richter, D.; Sültenfuß, J.; Tosaki, Y. Hydrodynamic or hydrochemical aspects of anthropogenic and naturally induced bank filtration - examples from Berlin/Brandenburg. *Grundwasser* **2009**, *14*, 163-177.

(117) Nowotny, N.; Epp, B.; von Sonntag, C.; Fahlenkamp, H. Quantification and modeling of the elimination behavior of ecologically problematic wastewater micropollutants by adsorption on powdered and granulated activated carbon. *Environ. Sci. Technol.* **2007**, *41*, 2050-2055.

(118) Duft, M.; Tillmann, M.; Oehlmann, J.; Ökotoxikologische Sedimentkartierung der großen Flüsse Deutschlands. Umweltbundesamt, Berlin, Germany, **2002**.

(119) Li, J.; Zhou, B.; Shao, J.; Yang, Q.; Liu, Y.; Cai, W. Influence of the presence of heavy metals and surface-active compounds on the sorption of bisphenol A to sediment. *Chemosphere* **2007**, *68*, 1298-1303.

Publications

Peer-reviewed

Regnery, J. and Püttmann, W. (2010): Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. Water Research 44, 4097-4104.

Regnery, J. and Püttmann, W. (2010): Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff. Chemosphere 78, 958-964.

Regnery, J. and Püttmann, W. (2009): Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. Clean-Soil Air Water 37, 334-342.

Abstracts

Regnery, J. and Püttmann, W.: Organophosphorus flame retardants and plasticizers: Emerging pollutants in the aquatic environment; EuCheMS, Nuremberg, Germany, September 2010 (oral presentation).

Regnery, J. and Püttmann, W.: Temporal variation of organophosphate concentrations (flame retardants, plasticizers) in precipitation and storm water runoff; UEP, Boston, USA, June 2010 (poster presentation).

Regnery, J. and Püttmann, W.: Organophosphorus flame retardants and plasticizers: Emerging pollutants in the aquatic environment; UEP, Boston, USA, June 2010 (poster presentation).

Regnery, J. and Püttmann, W.: Zeitliche Variation von Organophosphat-Konzentrationen (Flammschutzmittel, Weichmacher) in Niederschlägen; GDCh, Trier, Germany, September 2009 (oral presentation).

Regnery, J. and Püttmann, W.: Chlorinated flame retardants: Emerging pollutants in the aquatic environment; Fourth environmental symposium of German-Arab scientific forum for environmental studies, Fez, Morocco, October 2008 (oral presentation).

Regnery, J. and Püttmann, W.: Chlorierte und unchlorierte Organophosphate (Flammschutzmittel, Weichmacher) in Niederschlägen and Oberflächengewässern; SETAC/GDCh, Frankfurt am Main, Germany, September 2008 (oral presentation).

Regnery, J. and Fischer, K.: Untersuchungen zum Metabolismus von p-Phenylendiamin (PPD); GDCh, Osnabrück, Germany, September 2007 (poster presentation).

Others

Regnery, J. and Korte, E. (2009): Determination of organophosphates in lake water. Varian, application note SI-02094.

Oetken, M., Püttmann, W., Kaiser, D., Regnery, J., Oehlmann, J. (2009): Erfolgreiche Dritte Gemeinsame Jahrestagung von SETAC-GLB und GDCh-Fachgruppe „Umweltchemie und Ökotoxikologie“. Umweltwiss Schadst Forsch 21, 110-112.

Regnery, J. and Püttmann, W. (2008): Nachweis von Organophosphaten in Stillgewässern. Laborpraxis 9, 30-32.

Regnery, J. (2007): Untersuchungen zum Metabolismus von p-Phenylendiamin (PPD) in der Haut zur Bewertung seines Gefährdungspotenzials; University of Trier, Germany, diploma thesis.

Curriculum Vitae

Personal Information

Name	Julia Regnery
Date of Birth	27.05.1982
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Experience

May 2007 – present	Research assistant and doctoral candidate at the Institute of Atmospheric and Environmental Sciences, Department of Environmental Analytical Chemistry, Goethe-University Frankfurt am Main, Germany Doctoral thesis: Organophosphates in precipitation, lake water, and groundwater from urban and remote areas (supervising tutor: Prof. Dr. W. Püttmann)
January 2007 – April 2007	Student research assistant at the Department of Analytical and Ecological Chemistry, University of Trier
July 2005 – April 2007	Student research assistant at engineering company FOA Landscaping, Trier
March 2005 – June 2005	Internship at the Federation of German Waste Management Industry (BDE) in Brussels, Belgium
May 2004 – February 2005	Student research assistant at university library, University of Trier

Education

October 2001 – April 2007	Diploma in Applied Environmental Sciences, University of Trier Courses: Chemistry, biogeography, soil sciences, climatology, environmental law Diploma thesis: Investigations to the metabolism of p-phenylene diamine (PPD) in skin for risk exposure estimation (supervising tutor: Prof. Dr. K. Fischer)
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