Emission, fate and behaviour of phosphororganic flame retardants and plasticisers in the aquatic environment

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Summary

Phosphororganic flame retardants and plasticisers are important contaminants in the aquatic environment. Whereas the non-chlorinated alkylphosphates were partly eliminated in wastewater treatment plants the amounts of the chlorinated flame retardants were hardly reduced. Thus these compounds are discharged into the aquatic environment by STP-effluents. The elimination efficiency of wastewater treatment depends on the one hand on the dimension of the respective STP and on the other hand on the treatment technique that is applied. The elimination was higher in larger STP (inhabitant equivalent values (IEV) 300,000-1,000,000) than in smaller ones (IEV below 100,000). Lower elimination rates were observed for the trickling filter plant that was sampled in comparison to the activated sludge plants. In degradation experiments of the selected organophosphates with activated sludge in batch reactors, bis-(2-chlorethyl) phosphate was identified as metabolite of tris-(2-chloroethyl) phosphate under aerobic conditions.

The selected organophosphate esters were detected in surface water that is used for drinking water purification. Thus it was studied if the drinking water quality is affected by these compounds. For this purpose samples from different waterworks in the Ruhr catchment area were analysed. Moreover the elimination efficiency of diverse treatment processes such as slow sand filtration, ozonisation and activated carbon filtration was studied. In the finished water the concentrations of the organophosphates were below the respective limit of quantification (LOQ).

The chlorinated alkylphosphates are very persistent in the aquatic environment as they have been detected and quantified in pristine waterbodies such as the German Bight and Lake Ontario. A reduction of these compounds in the German Bight was traced back to dilution effects only. The concentrations of the phosphororganic flame retardants in marine samples were one order of magnitude higher than for other contaminants such as herbicides and by-products of pesticide production. The non-chlorinated alkylphosphates have only been detected in the river Elbe plume. Similar results were obtained for samples of Lake Ontario.

As expected from the respective log K_{OW} values of the selected organophosphate esters the bioaccumulation of these substances in fish is low. The concentrations of tri-*n*-butylphosphate (T*n*BP), tri-*iso*-butylphosphate (T*i*BP), triphenylphosphate (TPP) and tris-(chloro*iso*propyl) phosphate TCPP in bream muscle from different sampling

locations in Germany were in the lower ng/g range (dry weight). Tris-(chloroethyl) phosphate (TCEP), tris-(dichloro*iso*propyl) phosphate (TDCP), tris-(butoxyethyl) phosphate (TBEP) and ethylhexyldiphenylphosphate (EHDPP) were not detected in any fish sample. Moreover a temporal trend in the concentrations was observed. The sampling location seems to be an important factor that influences the detected levels of these substances in fish muscle as in the conurbation area higher amounts were detected than in riverine ecosystems.

For the extraction of the selected organophosphate esters from water samples liquid-liquid extraction (LLE) and solid phase extraction (SPE) has been applied. Fish samples were extracted by accelerated solvent extraction (ASE) in combination with different clean up steps (SPE on silica gel and size exclusion chromatography (SEC)). The different compounds were detected by gas chromatography mass spectrometry with electron impact ionization (GC-EI-MS). For quantification purposes the isotopic labelled internal standards tri-*n*-butylphosphate d_{27} (T*n*BP d_{27}) and triphenylphosphate d_{15} (TPP d_{15}) were used. TPP d_{15} was synthesized from phenol d_6 and phosphorus oxytrichloride. The empiric formula of the product was confirmed by electrospray high resolution time of flight mass spectrometry (ESI-HR-TOF-MS).

The metabolites bis-(2-chloroethyl) phosphate (BCEP), bis-(methyl, 2-chloroethyl) phosphate (BCPP) and bis-(butoxyethyl) phosphate (BBEP) were synthesized from phosphorus oxytrichloride and the respective alcohols chloroethanol, 1-chloro-2-propanol and butoxyethanol. For the control of the reaction the respective products were measured after derivatisation with trimethylsulphoniumhydroxide (TMSH) by GC-EI-MS and gas chromatography positive chemical ionisation mass spectrometry (GC-PCI-MS).

Abbreviations and acronyms

AB	aeration basin
ACF	activated carbon filtration
ADI	acceptable daily intake
amu	atomic mass unit
ASE	accelerated solvent extraction
BBEP	bis-(butoxyethyl)phosphate
BCEP	bis-(2-chloroethyl)phosphate
BCPP	bis-(methyl, 2-chloroethyl)phosphate, bis-(2-chloro*iso*propyl)phosphate
BCR	bioconcentration ratio
BF	bank filtration
BOD	biological oxygen demand
BPA	bisphenol-A
c	concentration
c_0	start concentration
DBP	dibutylphosphate
d_n	n-fold deuterated
DOC	dissolved organic carbon
DPP	diphenylphosphate
effluent Cen	effluent centrifuge
effluent ST	effluent settling tank
EHDPP	ethylhexyldiphenylphosphate
EI	electron impact ionisation

ESI	electrospray ionisation
FST	final sedimentation tank
FW	finished water
GAC	granular activated carbon
GC	gas chromatography
HPLC	high performance liquid chromatography
IEV	inhabitant equivalent value
IST	intermediate settling tank
k	kinetic factor
LC	lethal concentration
LLE	liquid-liquid extraction
LOD	limit of detection
LOQ	limit of quantification
LVI	large volume injection
m/z	mass to charge ratio
MF	main filter
MLF	multi layer filtration
MPP	monophenylphosphate
MS	mass spectrometry
MTB	methylthiobenzothiazole
MTBE	methyl *tert.* butylether
MW	mixed water
n.d.	not detected

NBR	nitrile butadiene copolymere
NOEC	no observed effect concentration
NRW	North Rhine-Westphalia
PBDE	polybrominated diphenyl ether
PCI	positive chemical ionisation
PF	prefilter
log KOW	log octanol/water partition coefficient
Pre/Floc	precipitation/flocculation
PST	primary settling tank
PTFE	polytetrafluoroethylene
PTV	programmable temperature vaporizer
PUR	polyurethane
PVC	poly vinyl chloride
R	Ruhr
R^2	regression coefficient
RSD	relative standard deviation
S	sewage treatment plant discharge
SEC	size exclusion chromatography
SF	slow sand filtration
SIM	selected ion monitoring
SPo	sludge pond
SPE	solid phase extraction
STP	sewage treatment plant

SVOC	semi volatile organic compounds
T	tributary
$t_{1/2}$	half-life
t	time
TBEP	tris-(butoxyethyl) phosphate
TCEP	tris-(2-chloroethyl) phosphate
TCPP	tris-(methyl, 2-chloroethyl) phosphate, tris-(2-chloro*iso*propyl) phosphate
TDCP	tris-(chloromethyl, 2-chloroethyl) phosphate, tris-(dichloro*iso*propyl) phosphate
T*i*BP	tri-*iso*-butylphosphate
TMSH	trimethylsulphoniumhydroxide
T*n*BP	tri-*n*-butylphosphate
TOC	total organic carbon
TPP	triphenylphosphate
UP	underground passage
UV	ultraviolet irradiation
v	volume
v/v	volume by volume
w/w	weight by weight

List of publications

Publications in peer reviewed journals

J.A. Andresen, K. Bester: Elimination of organophosphate ester flame retardants and plasticisers in drinking water purification, Water Research (2006), in press

J. A. Andresen, I. Becker, K. Bester, M. Schöpel, N. Zullei-Seibert: Verhalten von Organophosphaten bei der Trinkwasseraufbereitung – Ergebnisse orientierender Untersuchungen, Ruhrgütebericht, Ruhrverband, Essen, 2005

J. Meyer, K. Bester: Organophosphate flame retardants and plasticisers in wastewater treatment plants. Journal of Environmental Monitoring, 6 (2004), pp. 599-605

J.A. Andresen, A. Grundmann, K. Bester: Organophosphorus flame retardants and plasticisers in surface waters. Science of the total Environment, 332 (2004), pp. 155-166

Poster presentation

J. Andresen, K. Bester: Eliminierung chlorierter phosphororganischer Flammschutzmitteln in der Trinkwasseraufbereitung, Jahreshauptversammlung der Gesellschaft deutscher Chemiker (GDCh), 11.09.-14.09.2005, Düsseldorf, Germany

J. Andresen, K. Bester: Eliminierung von phosphororganischen Flammschutzmitteln und Weichmachern in der Trinkwasseraufbereitung, Tagung der wasserchemischen Gesellschaft, 02.05.-04.05.2005, Bad Mergentheim, Germany

J. Andresen, K. Bester: Sources and elimination of phosphororganic plasticisers in the aquatic environment, SETAC-Europe, 22.5.-26.05.2005, Lille, France

J. Andresen, M. Norden, K. Bester: Comparison of degradation rate constants of diverse emerging pollutants in batch experiments with activated sludge, SETAC-Europe, 22.5.-26.05.2005, Lille, France

J. Meyer, K. Bester: Organophosphate flame retardants and plasticisers in wastewater treatment plants, SETAC-Europe, 18.04.-22.4.2004, Prague, Czech Republic

K. Bester, A. Grundmann, J. Meyer, M. Spiteller: Organophosphate flame retardants in surface waters, SETAC-Europe, 27.04-01.05.2003, Hamburg, Germany

K. Bester, A. Grundmann, J. Meyer, M. Spiteller: Organophosphate plasticisers in surface waters, Jahrestagung der Wasserchemischen Gesellschaft, May 2003, Stade, Germany

Platform presentations

J. A. Andresen: Phosphororganische Flammschutzmittel- Eintrag in Kläranlagen und Oberflächengewässer, Fachseminar, Bestimmung von Abbaubilanzen von Personal Care Produkten und Hormonen in Kläranlagen, 18.10.2005, Universität Duisburg-Essen, Essen, Germany

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Introduction

Application and consumption of phosphororganic flame retardants and plasticisers

Chlorinated and non-chlorinated alkylphosphates are used as additives for a large variety of products. Main applications are the use as flame retardants as well as plasticisers in diverse plastics. The total consumption of flame retardants was 1,200,000 t worldwide in 2001. Approximately 186,000 t of these were organophosphorus compounds. About 23 % of consumed flame retardants were chlorinated organophosphate esters. The market is expected to grow 3.0-3.5 % per year. In Western Europe the consumption was 83,000 t in 2001 compared to 58,000 t 1998 for these substances.[1,2,3]

The chlorinated organophosphate esters tris-(chloro*iso*propyl) phosphate (TCPP), tris-(dichloro*iso*propyl) phosphate (TDCP) and tris-(chloroethyl) phosphate are predominantly used as flame retardants in polyurethane foams. As TCEP was found to be carcinogen in animal experiments the production was phased out around 1990 in Europe. It was substituted by TCPP. Although TDCP is carcinogen as well, it is still used as flame retardant for special applications. The market share is in comparison to TCPP small, though.

The non-chlorinated alkylphosphates tri-*n*-butylphosphate (T*n*BP), tri-*iso*-butylphosphate (T*i*BP), triphenylphosphate (TPP), ethylhexyldiphenylphosphate (EHDPP) and tris-(butoxyethyl) phosphate (TBEP) are predominantly used as plasticisers. Other applications are as additives to hydraulic fluids, in floor polishes and as flame retardants. An over view on the usage of each substance is given in Table 1.

All selected organophosphate esters have been identified and quantified in the indoor environment. The chlorinated alkylphosphates are emitted from consumer products such as furniture upholstery and mattresses as well as from polyurethane foams and plates used for construction[4,5]. Thus they have been detected in several studies in indoor air[6,7,8,9,10]. As TPP is used as alternative to halogenated flame retardants in electronic devices this substance was detected in indoor air as well[11,12]. Due to their boiling points the selected organophosphate esters belong to the semi volatile organic compounds (SVOC). These substances are mostly bound to airborne particles[13]. Thus these substances were detected in household dust as well[14,15].

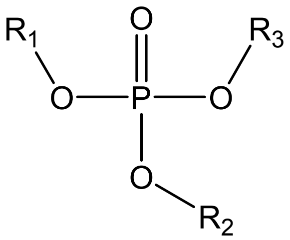
Table 1 Application of the selected organophosphate esters

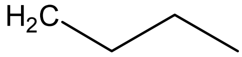
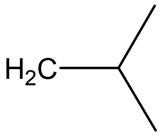
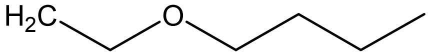
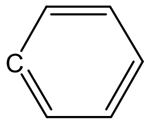
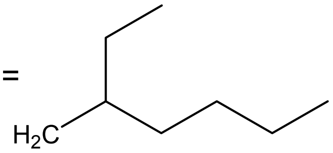
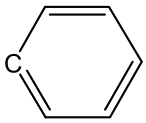
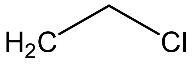
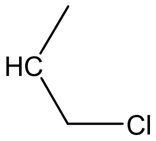
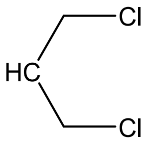
Substance	Application
Tri-*iso*-butylphosphate	Lubricant, plasticiser, pore size regulation in concrete[16]
Tri-*n*-butylphosphate	Solvent for cellulose esters, lacquers and natural gums; plasticiser in the manufacture of plastics and vinyl resins; antifoam agent for concrete; additive to hydraulic fluids[17]
Tris-(chloroethyl) phosphate	Flame retardant (mainly for rigid polyurethane foam, minor use in flexible polyurethane), PVC compounds, cellulose ester compounds and coatings[18]
Tris-(chloro*iso*propyl) phosphate	Flame retardant in rigid and flexible polyurethane foams in divers consumer products (upholstery, mattresses) and building insulation
Tris-(dichloro*iso*propyl) phosphate	Flame retardant in rigid and flexible polyurethane foam, other plastics and resins, acrylic latexes
Tris-(butoxyethyl) phosphate	Plasticiser in synthetic rubbers, plastics and lacquers; floor polishes[19]
Triphenylphosphate	Flame retardant (electronic devices); additive to hydraulic fluids[20]
Ethylhexyldiphenylphosphate	Plasticiser in divers plastics (PVC, PUR, NBR, cellulose acetate)[21]

The description of the emission pathway of these products and the fate in the aquatic environment were the objectives of this study.

The structural formula of the selected organophosphates is given in Table 2. TCPP is an isomeric mixture. Thus only the main isomer tris- (methyl, 2-chloroethyl) phosphate (tris-(chloro*iso*propyl) phosphate) is displayed.

Table 2 Structural formula of the selected organophosphate esters



Tri-*n*-butylphosphate (T*n*BP)	$R_1 = R_2 = R_3$			
Tri-*iso*-butyl-phosphate (T*i*BP)	$R_1 = R_2 = R_3$			
Tris-(butoxyethyl) phosphate (TBEP)	$R_1 = R_2 = R_3$			
2-ethylhexyldiphenylphosphate (EHDPP)	$R_1 = R_2$		$R_3 =$	
Triphenylphosphate (TPP)	$R_1 = R_2 = R_3$			
Tris-(2-chloroethyl) phosphate (TCEP)	$R_1 = R_2 = R_3$			
Tris-(methyl,2 -chloroethyl) phosphate (TCPP)	$R_1 = R_2 = R_3$			
Tris-(2-chloro-(1chloromethyl)-ethyl) phosphate (TDCP)	$R_1 = R_2 = R_3$			

Toxicology of phosphororganic flame retardants and plasticisers

The acute oral toxicity (LC_{50} rats) for the chlorinated and non-chlorinated flame retardants and plasticisers is moderate[17-20]. It ranges from 1 to 6 g/kg bodyweight for the different substances. For aquatic organism the 96h-LC_{50} values, e.g., in rainbow trout, ranged from 0.36 mg/L to 250 mg/L[17-20]. A comparison of these data is quite difficult as there are large differences for the divers organisms tested. Thus Leisewitz *et al.* proposed a guideline value of 0.1 µg/L for TCPP in surface waters[22]. Almost nothing is known on the effect on humans. T*n*BP has been reported to have a slight inhibitory effect on human plasma cholinesterase in an *in vitro* study and for TPP a significant reduction of in red blood cell cholinesterase has been observed.

It has been shown that TDCP and TCEP were carcinogen in animal experiments (F344/N rats and B6C3F1 mice)[,23,24,25]. No data concerning carcinogenicity are available for TCPP. Recently it was focused on toxicological issues of the chlorinated substances TCEP and TCPP as these compounds were included in the second and the fourth EU priority list respectively[26,27]. It was demonstrated that TCPP and TCEP were not mutagenic, cytotoxic or genotoxic and no estrogenic or anti-estrogenic potential were observed[28]. From the non-chlorinated organophosphate esters T*n*BP is supposed to be neurotoxic. The same effect was observed for TPP but it was supposed that the technical mixture that was tested contained tricresylphosphate as impurity. It was believed that this substance caused the neurotoxic effect and not TPP itself.

Because of the release of flame retardants in the indoor environment under normal conditions of use on the one hand and of toxicological risks such as carcinogenicity and neurotoxicity on the other hand, an indoor guideline value of 0.005 mg/m³ (precautionary value) and 0.05 mg/m³ (effect related value) for TCEP and some other organophosphate ester flame retardants was suggested[29]. Moreover Sagunski *et al.* (1997) have derived an ADI-value 40 µg/Kg day for TCEP[30].

1 Organophosphate ester flame retardants and plasticisers in wastewater treatment plants

1.1 *Introduction to STPs*

TCEP and TCPP have been identified in municipal wastewater and thus in influents of STPs, too (van Stee *et al.*[31], 1999), but they have rarely been quantified. As little is known on the concentrations and the elimination of organophosphates in wastewater treatment processes it is crucial to obtain information on the concentrations of these substances in influents of sewage treatment plants as well as their elimination from wastewater. Recently Marklund *et al.*[32] (2005) determined organophosphate ester flame retardants and plasticisers in influent and effluent samples of several sewage treatment plants in Sweden. Although the elimination rates for selected organophosphate esters were determined, this study was only indicative as samples were taken as weekly averages. Own studies described in this work demonstrate that assured results on the elimination of the selected organophosphates TCPP, TCEP, TDCP, T*i*BP, T*n*BP, TPP, TBEP and EHDPP are only obtained from a sampling over a certain period of time.

As the treated wastewater is normally discharged into rivers, the elimination behaviour of these substances influences the water quality of the receiving water. This is important as very often this water is used for the production of drinking water[33]. Additionally it is of special interest to get information on the elimination of organophosphate esters during different steps of the wastewater treatment process. In two studies wastewater samples from the various steps in five different STPs were analysed. In the first study samples of two STPs with preceding and simultaneous denitrification respectively were taken before and immediately after the activated sludge tanks as well as from the effluent of the final filtration unit before the treated wastewater is discharged into the receiving river. To obtain information on the efficiency of the STPs in removing organophosphates it is required to study elimination rates over a certain period of time. In the second study the elimination efficiencies of three STPs that differed from each other by inhabitant equivalent values, wastewater inflow and treatment technique (activated sludge plant, trickling filter) were determined.

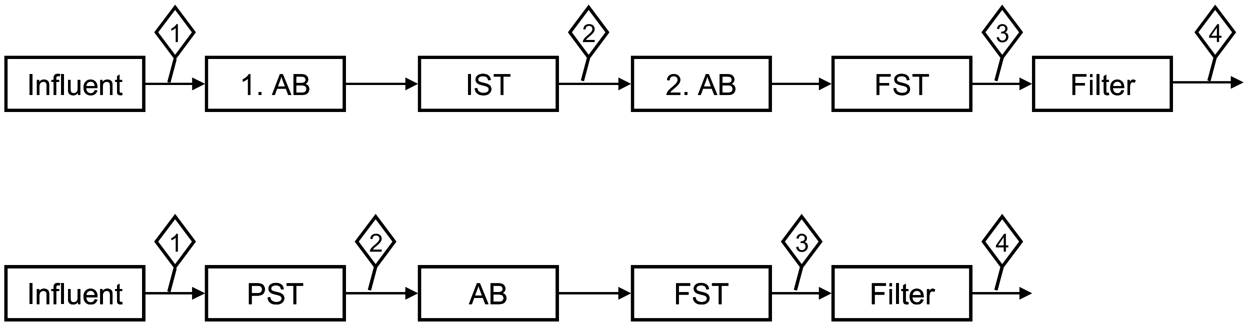
1.2 *Elimination of organophosphate esters on different steps in the wastewater treatment process*

1.2.1 Experimental to multistep analysis in STPs

In this study samples from different stages of the wastewater treatment process have been analysed from two sewage treatment plants in North Rhine- Westphalia (NRW) in spring 2003.

The sewage treatment plant A is provided with a two-stage biological treatment, i.e., two aeration basins and a downstream biological filtration unit (compare Figure1.1). Sampling point no 1 was located at the main collector prior to the sand trap and the screening plant. The process water from the sludge dewatering is added before the sampling point. The first aeration basin for the raw wastewater, which is in this case highly charged with TOC, is followed by an intermediate settling tank (IST) before the partially purified water enters the second aeration basin with preceding denitrification. At sampling point no 2 samples were collected from the effluent of the IST. Samples of the effluent of the final sedimentation tank (FST) were taken at sampling point no 3. The FST is located after the second aeration basin. Before the treated wastewater is discharged into river Rhine it is finally filtered through a biological filter. The filter bed consists of gravel at the bottom and sand at the top. The flow of the treated wastewater and air for the aeration of the filter is from the bottom to the top. Sampling point no 4 was located at the effluent of the STP after the final filtration unit. Sampling points no 2 and no 3 were chosen to provide information about the elimination of the analysed compounds at different stages of the wastewater treatment process whereas sampling points 1 and 4 provide data on the elimination efficiency of organophosphates from wastewater.

Figure 1.1 Scheme of the two sewage treatment plants with the respective sampling points



AB: aeration basin
IST: intermediate settling tank
FST: final sedimentation tank
PST: primary settling tank

STP B is a single stage activated sludge plant with downstream contact filtration (Figure 1.1). The wastewater flows into the primary settling tank (PST) before it enters the aeration basin with simultaneous denitrification. Samples were taken of the influent immediately after the screening plant and the sand trap (sampling point no 1) and of the effluent of the PST (sampling point no 2). After the biological purification step the wastewater is separated from the sludge in the final sedimentation tank (FST). Sampling point no 3 was located at the effluent of the FST. Finally the wastewater passes through the contact filtration unit before it is fed in the receiving water, the river Rhine. The final filter unit is constructed similar to the one in the STP A. Sampling point no 4 was located at the effluent of the final filtration.

The comparison of the concentrations at 1 and 2 displays effects of the PST, while the difference between 2 and 3 demonstrates the efficiency of the aeration basin. Sampling point no 3 in comparison to sampling point no 4 was intended to provide data on effects of the contact filtration.

Both STPs are rather large with wastewater volumes of 109,000 m^3 d^{-1} at the STP B respectively 220,000 m^3 d^{-1} at the STP A. The corresponding inhabitant equivalent values are 1,090,000 for B and 1,100,000 for A.

The samples were automatically taken as 24-hour composite samples. The samples were refrigerated at 4 ^{o}C during this 24 h interval. They were transported to the laboratory immediately after sampling and extracted within 24 hours after arrival. The samples were generally extracted on the same day by solid phase extraction using DVB-hydrophobic Speedisks (Mallinckroth Baker, Griesheim Germany; 45 mm diameter). When it was not possible to extract the organophosphates immediately, the samples were stored at 4°C overnight.

A solid-phase extraction manifold (IST Grenzach Wyhlen, Germany) with PTFE stopcocks and needles was used. Before the extraction the SPE-cartridges were rinsed successively with methyl *tert*. butyl ether (MTBE) and toluene. Afterwards the disks were conditioned with methanol and water. The water samples were passed through the disks at a flow rate of 200 mL/min (vacuum). The analytes were successively eluted with MTBE and toluene and an aliquot of internal standard T*n*BP d_{27} solution was added to the eluate. The residual water was removed from the organic phase by freezing the samples overnight at –20°C. The samples were concentrated using a rotary evaporator at 60°C and 60 mbar to a final volume of 1 mL. Because of matrix interferences a clean up of the extracts was necessary, especially for the samples taken of STP-influents. For these purposes a clean up using silica gel (F60, Merck Darmstadt, Germany) was established. 1 g of dried silica gel (105°C, 24h) was put into an 8 mL glass column between two PTFE frits. After conditioning with *n*-hexane, 1 mL of the sample extract was applied to the column. After a cleaning step with 8 mL *n*-hexane/MTBE (9:1 v/v) the analytes were eluted twice with 8 mL ethyl acetate. Due to the fact that not all interferences were eliminated another internal standard (parathion-ethyl d_{10}) was added at this stage to the eluate. Afterwards the volume of the samples was reduced to 1 mL using a rotary evaporator. The solvent was exchanged to toluene and the extract was concentrated to a final volume of 1 mL for GC-MS analysis.

The samples were analysed on a gas chromatography system with mass spectrometric detection ("Trace" Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. The PTV (1 µl injection volume) was operated in splitless mode with the following temperature program: 90°C [0.1 s] $\rightarrow$ 14.5°C s^{-1} $\rightarrow$ 280°C $\rightarrow$ 5°C s^{-1} $\rightarrow$ 320°C [5 min] (cleaning phase). The GC separation was performed using a DB-5MS column (J&W Scientific, Folsom, CA, USA); length: 30 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 90°C [2 min] $\rightarrow$ 10°C min^{-1} $\rightarrow$ 280°C [15 min] using He (5.0) as carrier gas with a flow of 1.5 mL min^{-1}. The mass spectrometer was used with electron impact ionisation with 70 eV ionisation energy. The MS was operated in selected ion monitoring (SIM) mode with the detector (photo multiplier) set to a voltage of 500 V.

The different organophosphate esters were detected by means of their mass spectral data and retention time. For quantitative measurements the method has been validated. Recovery rates ranged from 75% to 90% with 5-13% RSD. Full quality data for the method was obtained from three replica extractions of spiked HPLC water at six different concentrations (5, 10, 50, 100, 500, 1500 ng/L). The whole set of parameters is given in Table 1.1.

Table 1.1 Quality assurance data fort he applied method

Compound	Analytical Ion [amu]	Verifier Ion [amu]	Recovery Rate [%]	RSD [%]	LOD [ng/L]
T*i*BP	155	211	78	6	1.3
T*n*BP	155	211	87	7	1.2
TCEP	249	251	83	8	6.1
TCPP	277	279	80	4	1.0
TDCP	381	379	81	5	7.0
TPP	325	326	90	7	1.3
TBEP	199	125	75	10	1.1

Furthermore municipal wastewater was extracted with the described method and parallel per liquid-liquid extraction with toluene. Both methods gave comparable results.

1.2.2 Results and discussion to multistep analysis in STPs

1.2.2.1 STP A

Measurements of the influent samples showed a considerable day-to-day variation in the concentrations of the various organophosphorus compounds. The concentrations ranged from 570-5,800 ng/L TCPP and 2,400-6,100 ng/L TBEP. Analysis of the temporal trends revealed that variations on a weekly basis occurred for TCPP, only. It seemed that on weekends the load of TCPP in this wastewater treatment plant was lower than on working days. Compared to samples from the influent (1), concentrations in samples of the effluent (4) were found to be 1,700-6,600 ng/L TCPP and 290-790 ng/L TBEP. These measurements revealed that the non-chlorinated and chlorinated organophosphate esters were eliminated at different rates in wastewater treatment with activated sludge. While the elimination of the non-chlorinated organophosphate ester TBEP ranged from 82 % to 93 % the chlorinated organophosphates, e.g., TCPP seemed not to be removed at all. A comparison of the highest input and output levels of the chlorinated flame retardants showed that they were of the same order of magnitude. Figures 1.2 and 1.3 give an overview over the measured concentrations of TBEP and TCPP at the different sampling points during the experiment at STP A. The results for all organophosphates are given in Table 1.2.

Table 1.2 Concentrations of the different organophosphate esters in the influent and effluent of STP A and elimination rates calculated on a daily basis

Analyt	max. Influent (1) [ng/L]	max. Effluent (4) [ng/L]	mean Influent (1) [ng/L]	mean Effluent (4) [ng/L]	Elimination [%]
TiBP	2200	290	1300	160	86 ± 6
TnBP	5500	2300	1200	520	67 ± 16
TCEP	640	410	290	350	none
TCPP	5800	6600	2000	3000	none
TDCP	180	180	100	130	none
TBEP	6100	790	3700	440	88 ± 4
TPP	290	250	130	70	57 ± 24

Figure 1.2 Concentrations of TCPP in ng/L during the experiment at different steps of the wastewater purification in STP A (WE = weekend)

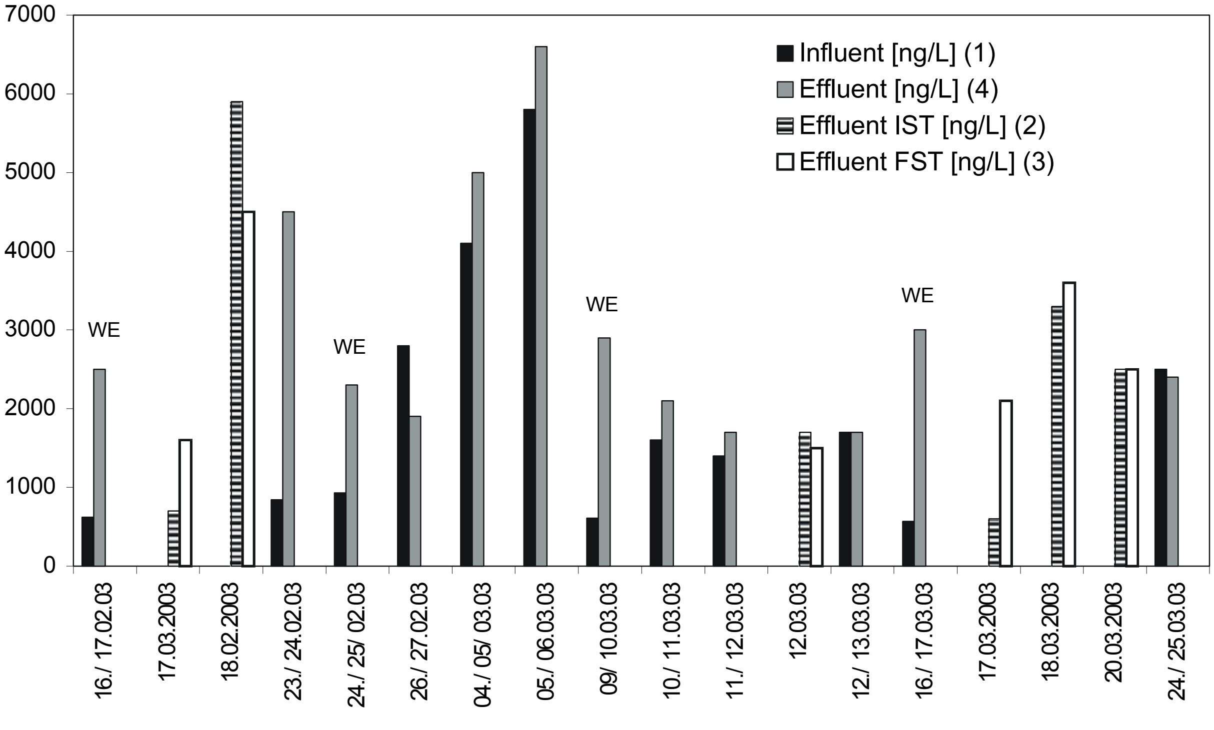
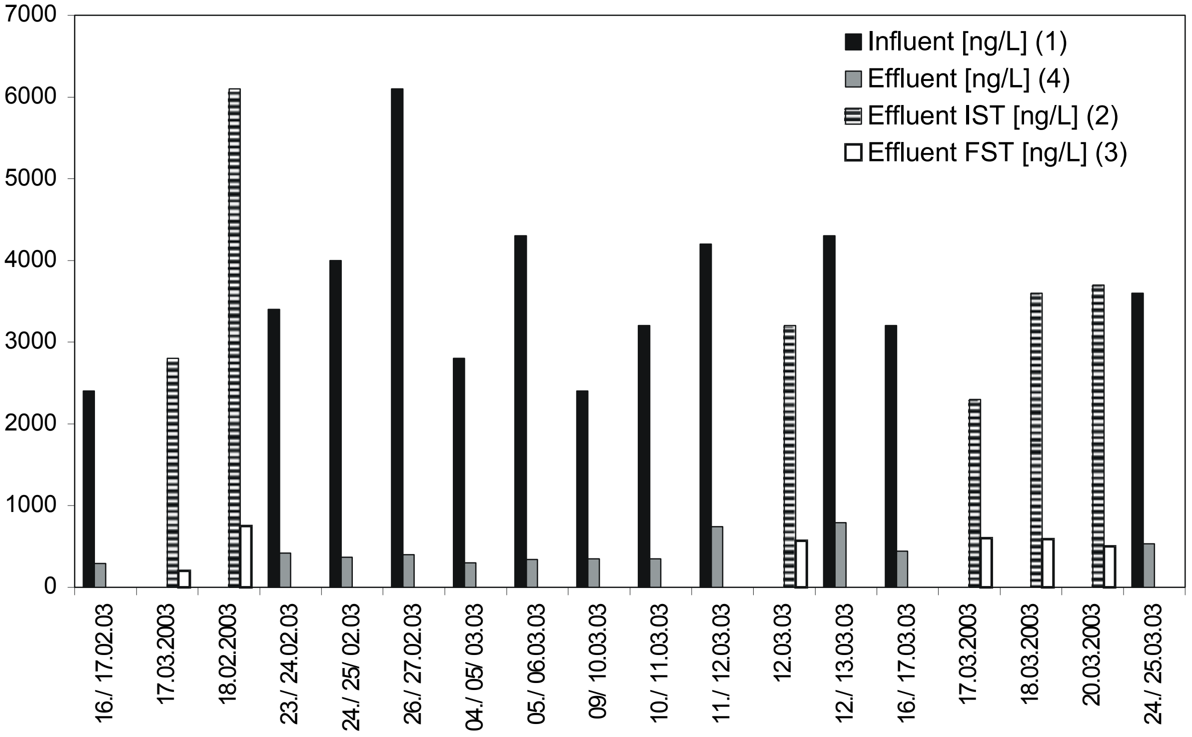


Figure 1.3 Concentrations of TBEP in ng/L during the experiment at different steps of the wastewater purification in STP A



The concentrations of the different organophosphates at sampling point no 2 were of the same order of magnitude as for the influent (1) of the STP. The concentrations ranged from 600-5,900 ng/L TCPP and 2,300-6,100 ng/L TBEP in the effluent of the intermediate settling basin (2). These data show that the first aeration step did not contribute to the elimination of the alkylated organophosphates such as TBEP. At STP A the first biological cleaning step is designed for the fast reduction of dissolved organic carbon (e.g. fats and saccharides) with an average sludge age of one day. Thus an elimination of xenobiotics by means of biodegradation in this step of the wastewater treatment was not expected. The concentrations of the various organophosphates in the effluent of the final sedimentation (3) were of the same order of magnitude as for the effluent (4). They ranged, e.g., from 1,500-4,500 ng/L for TCPP and 250-750 ng/L for TBEP. The elimination rates calculated on a daily basis for the second aeration basin ranged from 74-93 % for TBEP whereas the chlorinated organophosphates (TCPP, TCEP and TDCP) were not eliminated at all. The results for the elimination of all organophosphates in the STP A are given in Table 1.3.

Table 1.3 Concentrations of organophosphate esters at diverse steps of wastewater purification of STP A and elimination rates calculated on a daily basis

Analyt	max. Effluent IST (2) [ng/L]	max. Effluent FST (3) [ng/L]	mean Effluent IST (2) [ng/L]	mean Effluent FST (3) [ng/L]	Elimination [%]
TiBP	2300	370	1600	300	79 ± 8
TnBP	4600	670	1100	260	53 ± 25
TCEP	380	430	260	350	none
TCPP	5900	4500	2500	2600	none
TDCP	180	180	100	110	none
TBEP	6100	750	3600	540	84 ± 6
TPP	140	54	93	36	60 ± 20

Furthermore the mean elimination rates for the whole wastewater treatment process were compared to the elimination rates achieved from the second aeration basin. For T*i*BP, T*n*BP and TBEP the elimination rates for the entire process were slightly higher (2 to 7 %, compare Tables 1.2 and 1.3) than those calculated between the effluent of the intermediate settling (no 2) and the effluent of the final sedimentation (no 3). Considering the variability of the elimination rates there was no difference between the elimination rates achieved between sampling points no 1 and no 4 and between sampling points no 2 and no 3. This led to the conclusion that neither the first aeration basin nor the final filtration but the main aeration basin contributed to the elimination of the non- chlorinated organophosphate esters.

1.2.2.2 STP B

In general similar data and conclusions were obtained from STP B. A huge day-to-day variability in the concentrations of the different organophosphates was detected. On the other hand, no effect of weekends for TCPP was observed in this STP. The concentrations ranged from 460-850 ng/L TCPP and 1,800-8,000 ng/L TBEP in the influent and 680-1,000 ng/L TCPP and 65-1,200 ng/L TBEP in the effluent. An overview of all organophosphates is given in Table 1.4.

Table 1.4 Concentrations of the different organophosphate esters in the influent and effluent of STP B and elimination rates calculated on a daily basis

Analyt	max. Influent (1) [ng/L]	max. Effluent (4) [ng/L]	mean Influent (1) [ng/L]	mean Effluent (4) [ng/L]	Elimination [%]
TiBP	1500	130	840	78	86 ± 10
TnBP	370	160	260	100	55 ± 15
TCEP	250	470	180	370	none
TCPP	940	1100	650	820	none
TDCP	250	310	110	150	none
TBEP	8000	1200	4000	400	89 ± 9
TPP	140	31	81	20	75 ± 10

Based on these data the following elimination rates were calculated on a daily basis for the non- chlorinated organophosphates: 72-95 % T*i*BP, 32-76 % T*n*BP, 73-98 % TBEP and 56-87 % TPP. As in the STP A the chlorinated organophosphates were not eliminated at all. Figures 1.4 and 1.5 give an overview over the measured concentrations of TBEP and TCPP at the different sampling points during the experiment at STP B. The concentrations of the flame retardants in the effluent of the primary settling tank (2) (260-780 ng/L TCPP and 1,100-1,900 ng/L TBEP) were within the same range of magnitude as in the influent (1). This indicated that the primal sedimentation step did not contribute to the elimination of the non-halogenated organophosphates. The results for the other organophosphates are displayed in Table 1.5.

In the effluent of the final settling basin (3) the concentrations ranged from 300-910 ng/L TCPP and 46-130 ng/L TBEP. From these data, elimination rates for this partial process for each day were calculated, i.e., 69-91% for T*i*BP, 0-40% for T*n*BP, 88-98% for TBEP and 9-47% for TPP. Mean values calculated from these elimination rates revealed that the elimination rates for all organophosphates except for TBEP were slightly lower in that part of the cleaning process than for the entire wastewater treatment process. Considering the variability for the elimination rates there was no difference between the elimination rates achieved between sampling points no 1 and no 4 in comparison to the results from sampling sites no 2 and no 3. Thus neither the final filtration step nor the primary sedimentation tank contributed to the elimination of the non- chlorinated organophosphates.

Table 1.5 Concentrations of the different organophosphate esters at different steps of the wastewater purification of STP B and elimination rates calculated on daily basis

Analyt	max. Effluent PST (2) [ng/L]	max. Effluent FST (3) [ng/L]	mean Effluent PST (2) [ng/L]	mean Effluent FST (3) [ng/L]	Elimination [%]
TiBP	1800	270	980	78	83 ± 10
TnBP	400	180	240	100	40 ± 23
TCEP	250	660	310	560	none
TCPP	780	1400	950	820	none
TDCP	120	440	62	310	none
TBEP	2200	130	1700	91	94 ± 4
TPP	100	63	54	38	40 ± 6

Figure 1.4 Concentrations of TCPP in ng/L during the experiment at different steps of the wastewater purification at STP B

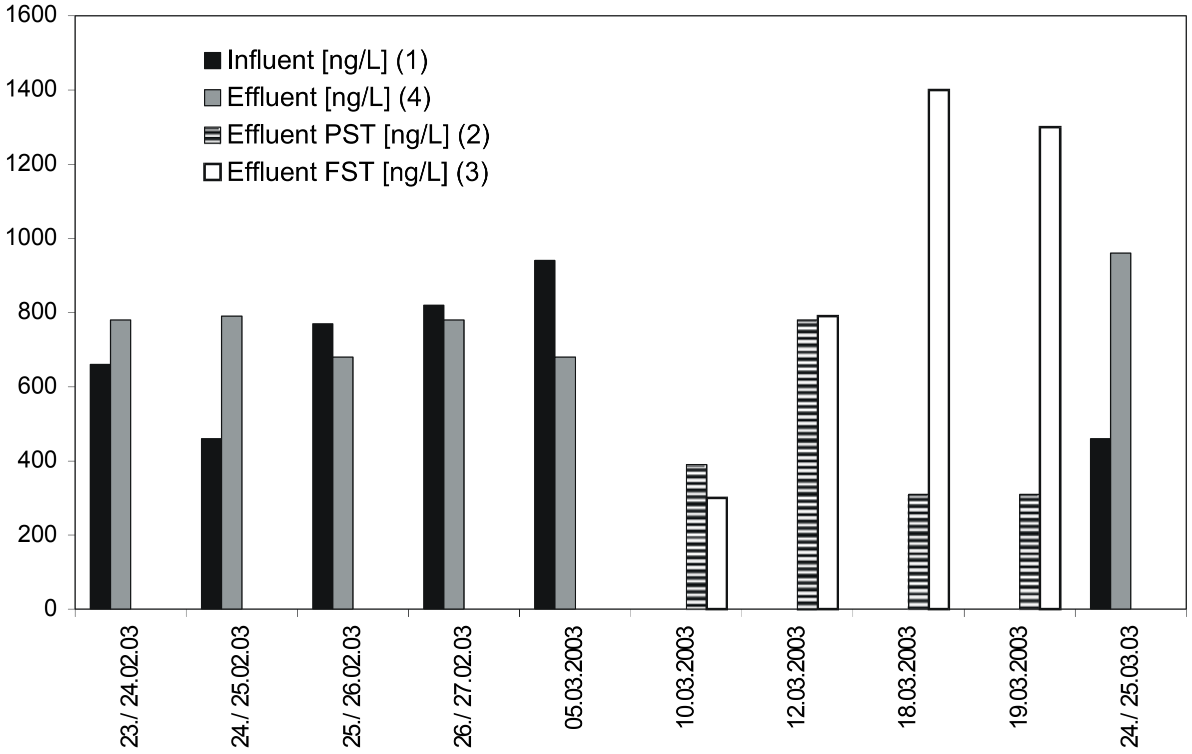
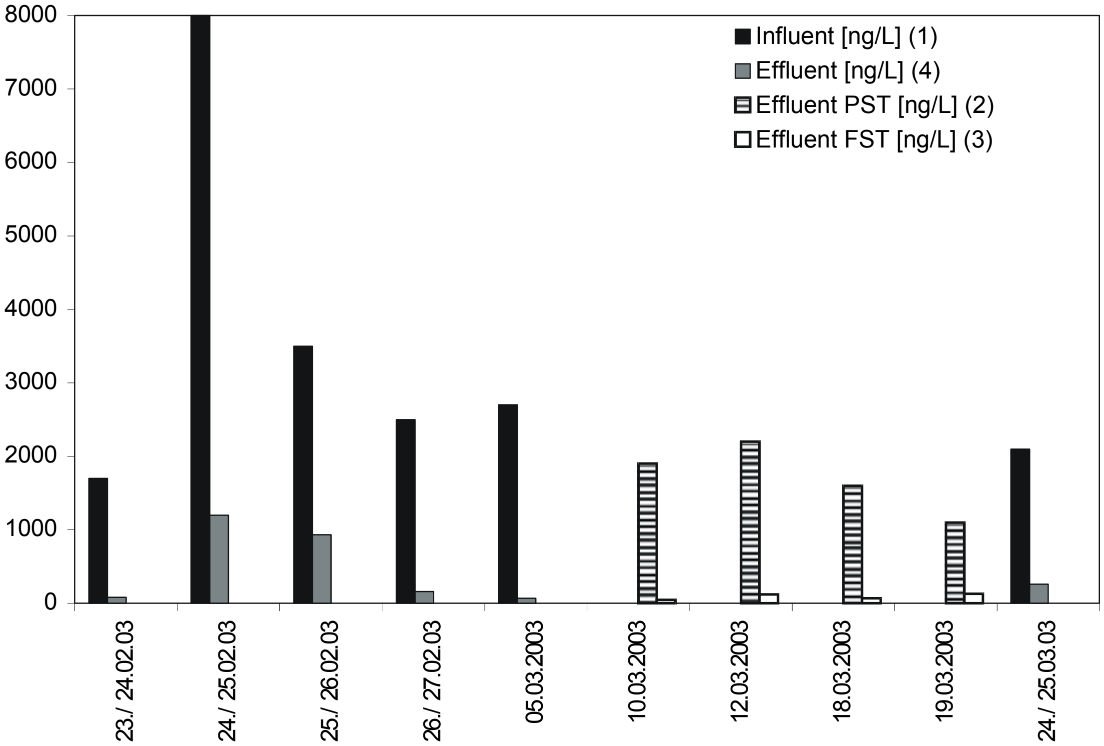


Figure 1.5 Concentrations of TBEP in ng/L during the experiment at different steps of the wastewater purification at STP B



The studies on STP A and B give a first overview on the elimination of the selected organophosphate esters in the wastewater treatment process. Whereas the elimination rates from 55-89 % were observed for the non-chlorinated alkylphosphates in both STPs, no elimination was observed for the chlorinated flame retardants TCPP, TCEP and TDCP.

1.3 *Comparison of the elimination of organophosphate esters in STPs with different wastewater treatment techniques*

1.3.1 Materials and Methods to comparison of different STP techniques

For confirmation purposes three more STPs in the Ruhr catchment area have been sampled over a period of four weeks each. This was of special interest because the river Ruhr is very important for the drinking water supply of over 5 million inhabitants in this area. STPs C and D are activated sludge plants. In STP E a trickling filter process is used for wastewater treatment. Whereas STP C with 250,000 inhabitant equivalent values and a wastewater volume of 70,000 m³/d is only slightly smaller than STPs A and B, STPs D and E are comparably small with inhabitant equivalent values of 32,000 for STP D and 64,000 for STP E. The corresponding wastewater volumes are 13,000 m³/d for STP D and 12,000 m³/d for STP E. Figures 1.6-1.8 give details on the wastewater treatment in the respective wastewater treatment plants.

Figure 1.6 Wastewater treatment at STP C (activated sludge plant, 250,000 inhabitant equivalent values)

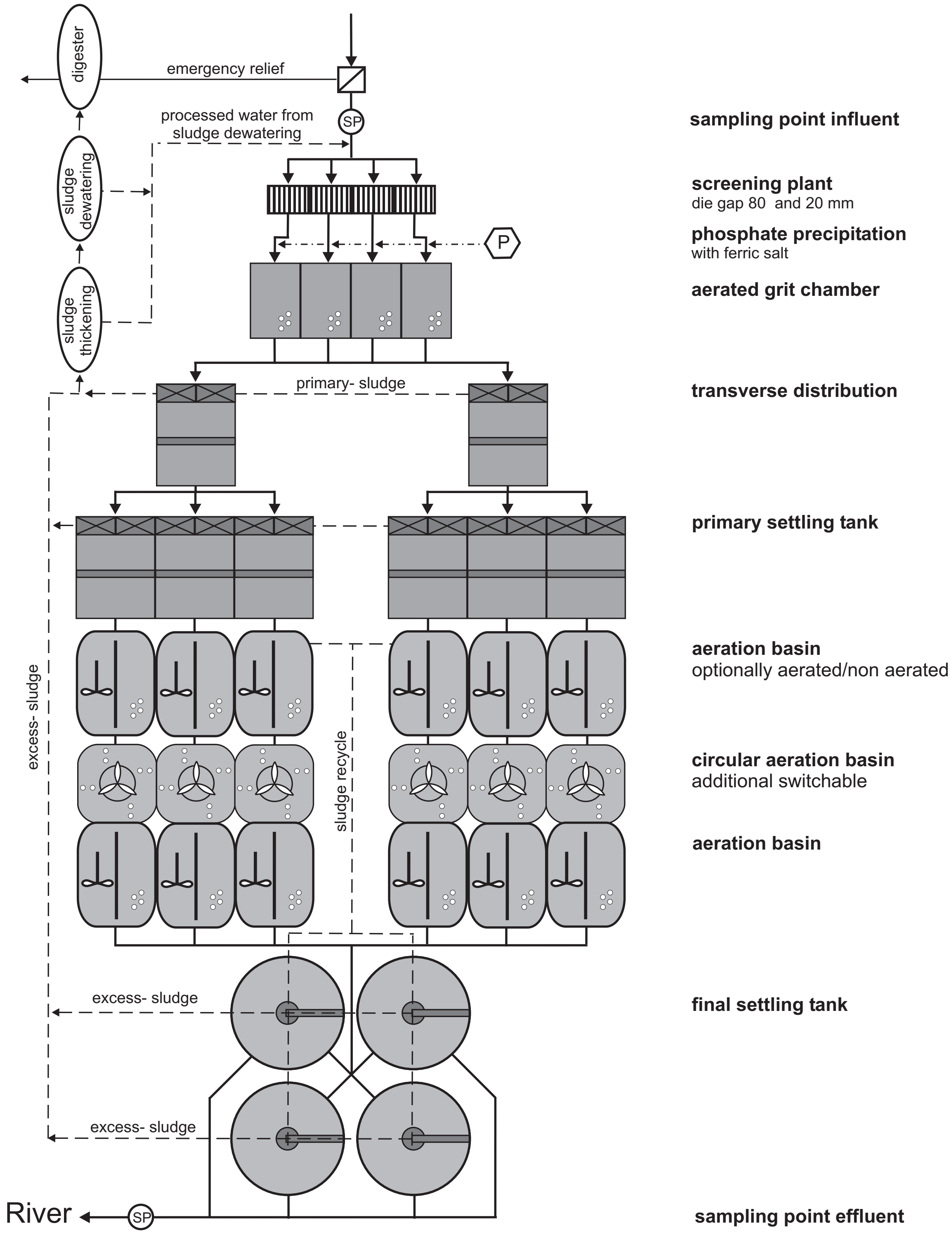


Figure 1.7 Wastewater treatment at STP D (activated sludge plant, 32,000 inhabitant equivalent values)

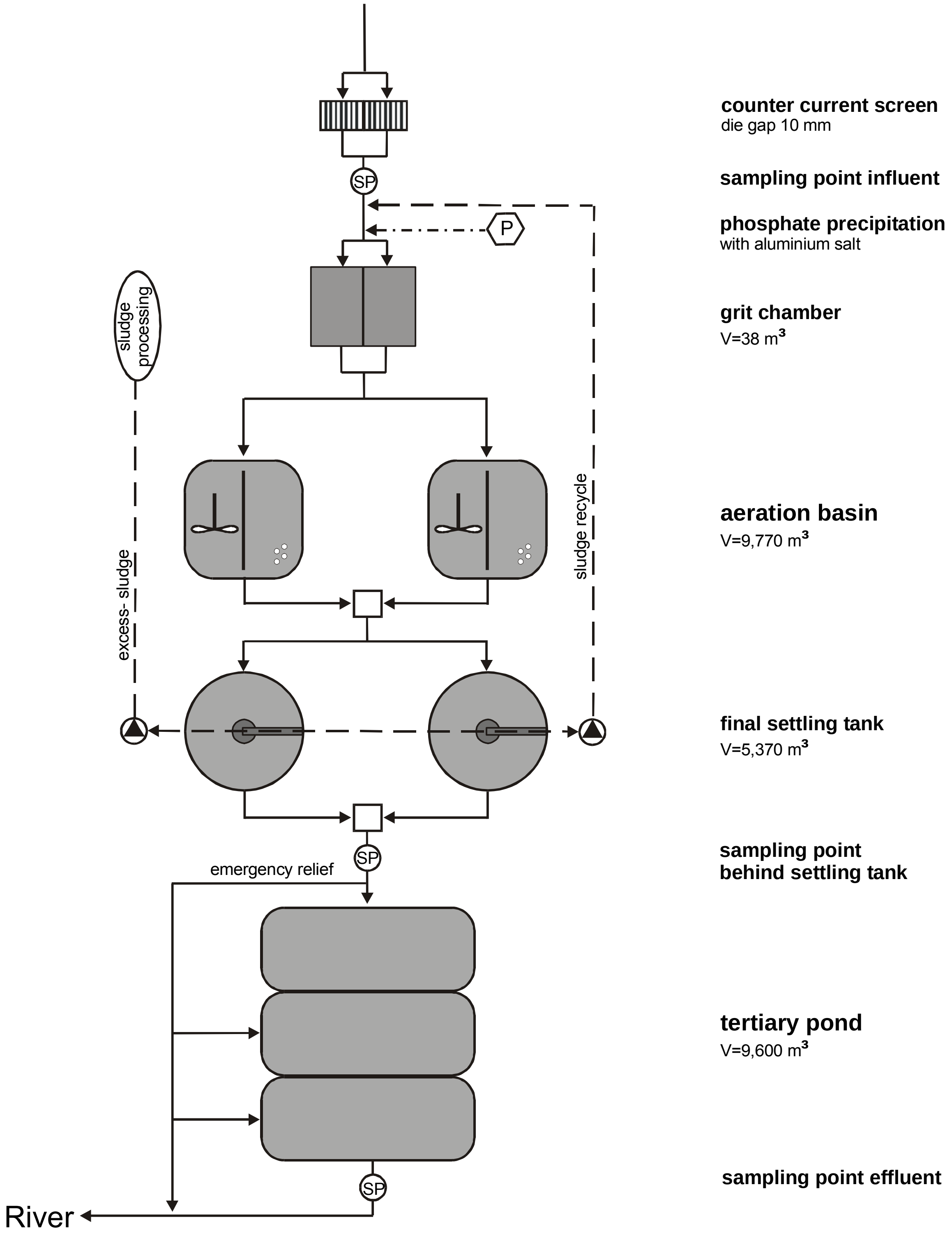
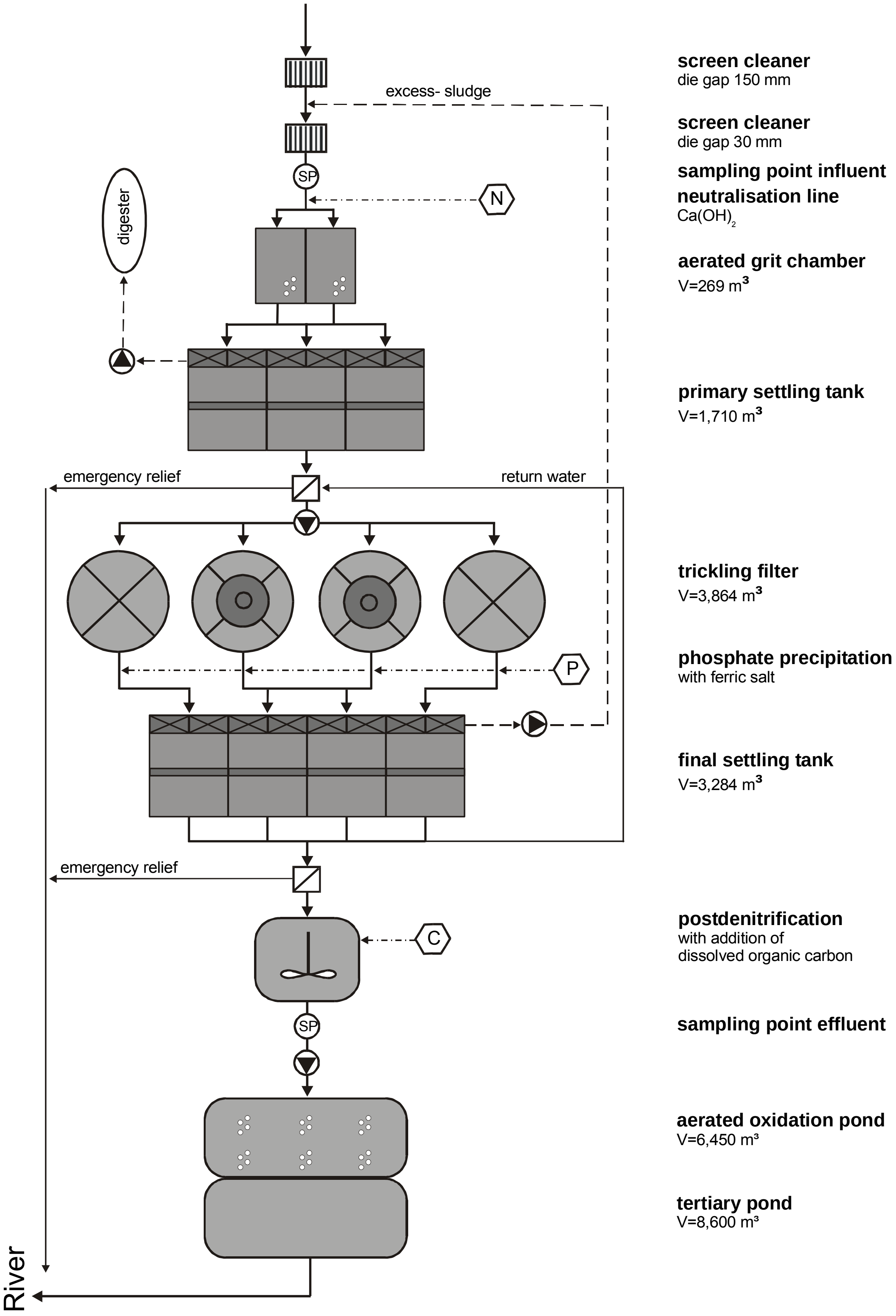


Figure 1.8 Wastewater treatment at STP E (trickling filter, 64,000 inhabitant equivalent values)



Samples were taken of the influent and the effluent of each STP. In contrast to the first study samples were taken daily. At STPs C and D samples from the outflow of the sludge dewatering were taken as well. From these samples it was supposed to obtain information if an additional treatment of the process water flow lowers the concentrations of the different organophosphates in the effluents, especially for TCPP, TCEP and TDCP as these substances were not eliminated in the wastewater treatment process. Whereas in STP C anaerobic sludge stabilisation is used in STP D the excess sludge is stored in a sludge pond (aerobic sludge stabilization). Due to the different sludge treatment there might be differences concerning the concentrations of the selected organophosphates in the process water from the sludge dewatering as well. In STP C the digested sludge is stored in a settling tank for thickening before it is centrifuged. Thus samples were taken from the effluent of the settling tank and from the effluent of the centrifuge dewatering. In STP D samples were taken from the back flow of supernatant water from the sludge pond.

For the evaluation of the efficiency of the wastewater treatment concerning the organophosphate esters, the loads of theses substances in the effluent were compared to the loads after wastewater treatment, i.e., the effluent of the respective treatment plant.

The samples were taken as 24-hour composite samples. Samples from treatment plant C were transported to the laboratory immediately after sampling and extracted on the same day. Samples from waterworks D and E were transported every 2-3 days to the laboratory. During this interval they were stored at 4 °C. For the determination of the organophosphates 1 L of each water sample was extracted with 10 mL toluene after adding an aliquot of internal standard solution (T*n*BP d_{27}, TPP d_{15}). The extraction (30 min) was performed by vigorous stirring with a PTFE coated magnetic stirrer. After a sedimentation phase of 20 min the organic phase was separated from the aqueous one and the residual water was removed from the organic phase by freezing the samples overnight at –20 ^{o}C. The samples were concentrated with a Syncore concentration unit (Büchi, Essen, Germany) at 60 ^{o}C and 60 mbar to a final volume of 1 mL. The samples were analysed on a gas chromatography system with mass spectrometric detection (DSQ Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. The PTV (1 µl injection volume) was operated with the following temperature program: 115 °C [0.05 min, 20 mL min^{-1}

He] → 12 °C s^{-1} (splitless) → 280 °C [1.2 min] → 1 °C min^{-1} → 300 °C [7 min] (cleaning phase)

The GC separation was performed using a DB5-MS column (J&W Scientific, Folsom, CA, USA); length: 15 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 100 °C [1 min] → 30 °C min^{-1} → 130 °C → 8 °C min^{-1} → 220 °C → 30 °C min^{-1} → 280 °C [7 min] using He (5.0) as carrier gas with a flow of 1.3 mL min^{-1}. The mass spectrometer was used with electron impact ionization with 70 eV ionization energy. The MS was operated in selected ion monitoring (SIM) mode. Full quality data of the method is given in Table 1.6.

Table 1.6 Quality assurance data of the applied method

Compound	Analytical Ion [amu]	Verifier Ion [amu]	Recovery Rate [%]	RSD [%]	LOQ [ng/L]
T*i*BP	211	155	128	13	10
T*n*BP	211	155	100	11	10
TCEP	249	251	28	12	10
TCPP	277	279	92	10	3
TDCP	379	381	108	13	3
TBEP	199	299	103	7	30
EHDPP	251	362	94	11	3
TPP	325	326	101	14	3

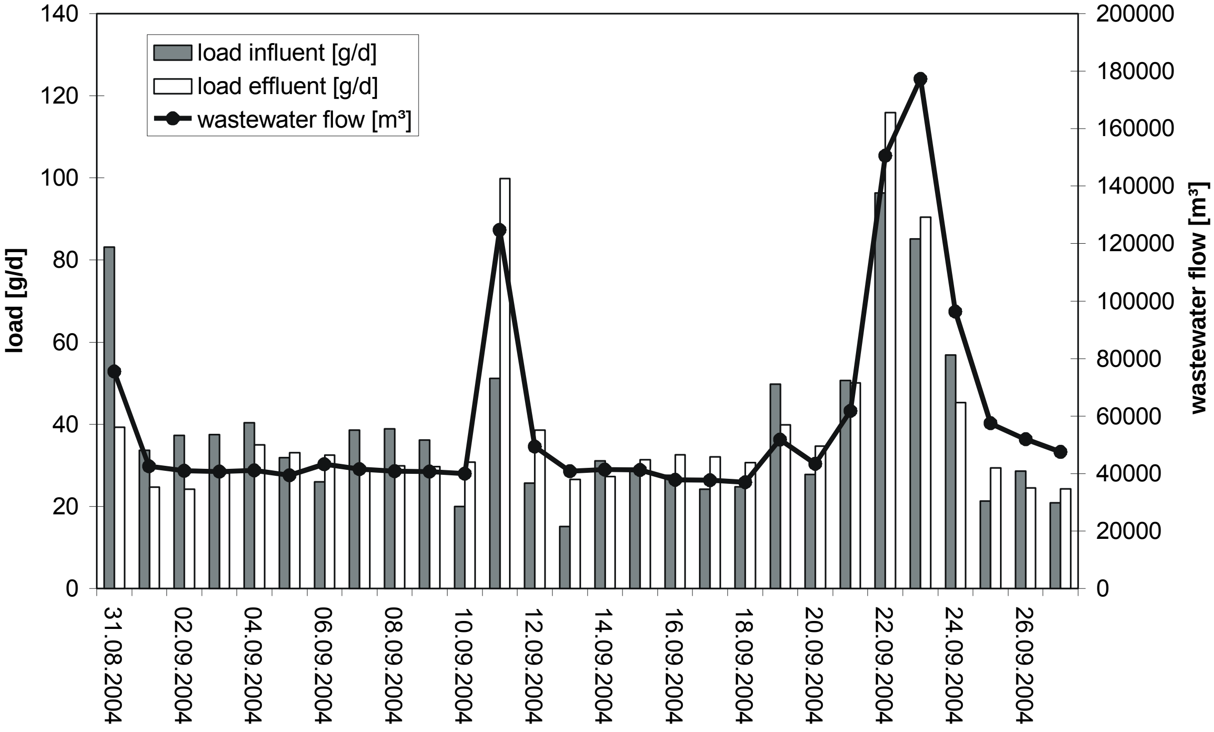
1.3.2 Results and discussion to comparison of different STP techniques

The advantage of these measurements was that on the one hand samples were taken daily over a period of four weeks and on the other hand the sampling was independent from weather effects especially rainfall because of comparing the loads of each compound in the influent and effluent of the respective STP instead of referring just to concentrations.

1.3.2.1 STP C

At STP C the daily load of TCPP in the influent and effluent was approximately 40 g/d except from rainfall. In this case it rose up to 100-120 g/d (compare Figure 1.9). Similar results were obtained for TCEP and TDCP although the loads were significantly lower than for TCPP (8-11 g/d TCEP and ~ 5 g/d TDCP on dry weather conditions, 27-36 g/d TCEP and 14-57 g/d TDCP during rainfall).

Figure 1.9 Loads of TCPP at STP C in the influent and effluent during the experiment



In contrast to TCPP and TCEP a significant elimination was observed for TDCP if elimination rates are calculated on the basis of the influent and effluent loads over the complete sampling period. However the day to day variation of the elimination rates was high (details are given in Table 1.7).

Table 1.7 Influent and effluent loads of the selected chlorinated organophosphates given from day to day (maximum values during rainfall) mean values and elimination rates (elimination rates for normal wastewater flow) in STP C

analyte	load influent [g/d]	load effluent [g/d]	mean influent [g/d]	mean effluent [g/d]	Elimination rate [%]	day to day elimination [%]
TCPP	15-40 (max. 96)	24-35 (max. 116)	39	40	none	0 ± 35
TCEP	5.6-16 (max. 36)	7.7-11 (max. 32)	13	12	none	0 ± 28
TDCP	4.2-11 (max. 56)	4.1-6.2 (max. 27)	11	8.3	26	12 ± 49 (30 ± 16)

Comparing the loads with the concentrations it is noticeable that during rainfall the concentrations, e.g., for TCPP decreased in influent samples whereas the loads increased. The observed dilution and the higher wastewater volume were not proportional (compare Figure 1.10). This indicates that other sources for these substances are relevant during rainfall. On the one hand run off water from streets and, especially for TCPP, from construction sites should be discussed as possible point sources and on the other hand the remobilisation of sediment from the sewer might contribute to the emission of the alkylphosphates. For other substances like TPP no effect on the concentrations due to rainfall was detected (compare Figure 1.10). The fact that the concentrations were stable during rainfall for some of the organophosphates whereas a dilution effect was observed for others indicates the existence of a multitude of emission sources and pathways for the particular substances.

Figure 1.10 Concentrations of TCPP and TPP in influent samples during at STP C in comparison to the wastewater inflow

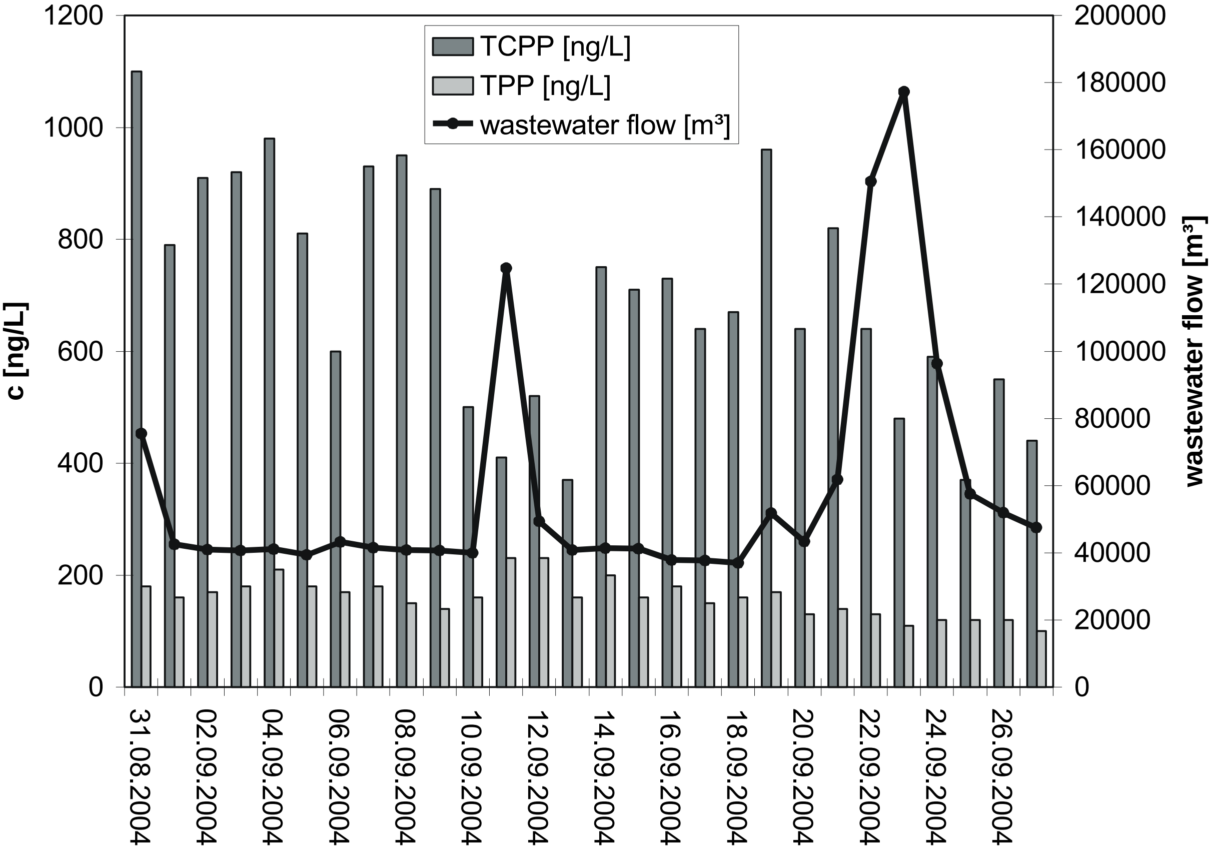


Figure 1.11 shows the daily elimination rates of TDCP in comparison to the respective wastewater flow. Whereas elimination was observed for TDCP for periods without rainfall and a constant wastewater flow no elimination was detected during

rainfalls. Thus elimination rates for TDCP in “dry periods” were found to be 30 % ± 16 % (compare Table 1.7). A correlation of the wastewater flow and the elimination efficiency of this STP concerning TCPP and TCEP was not observed according to the accuracy of the analytical method. Apparently other parameters must influence the elimination efficiency as well as for some days the elimination rates for TDCP are low at a “normal” wastewater flow as well.

Figure 1.11 Elimination rates and wastewater flow for T*i*BP in STP C

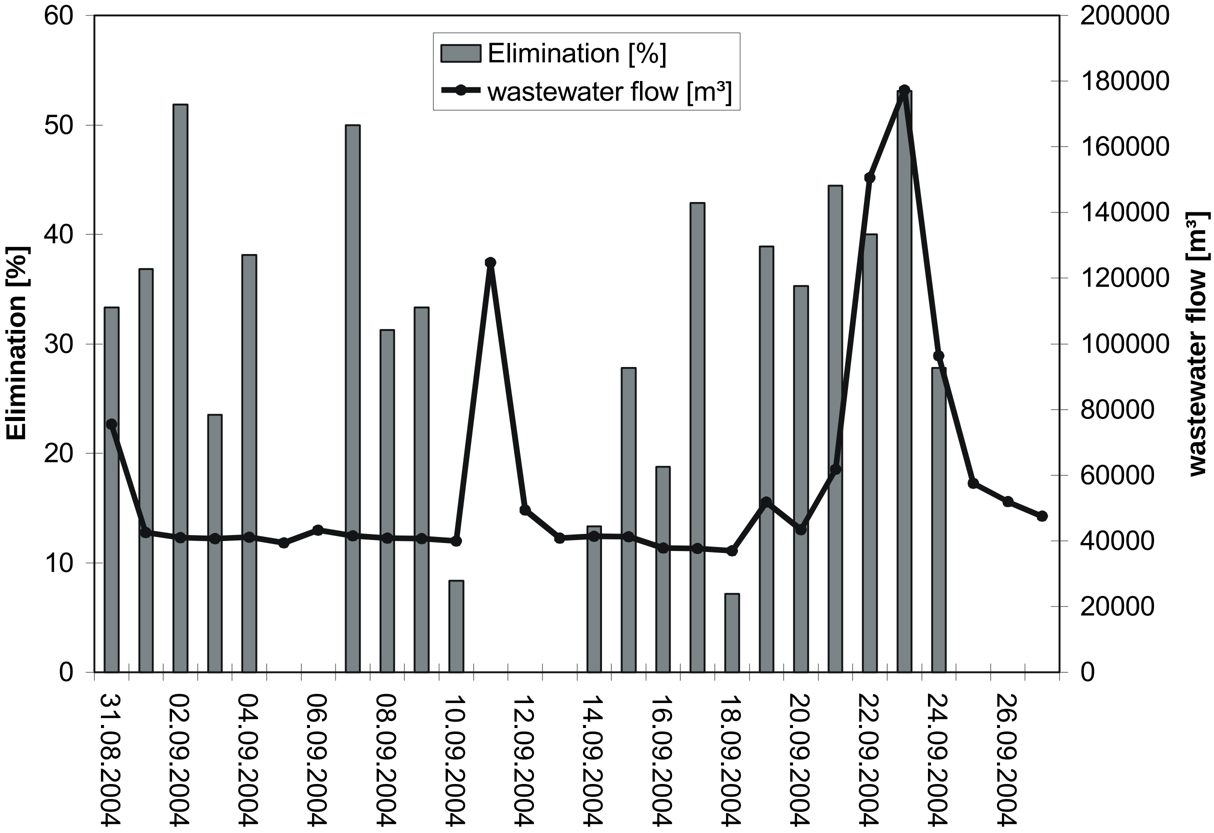
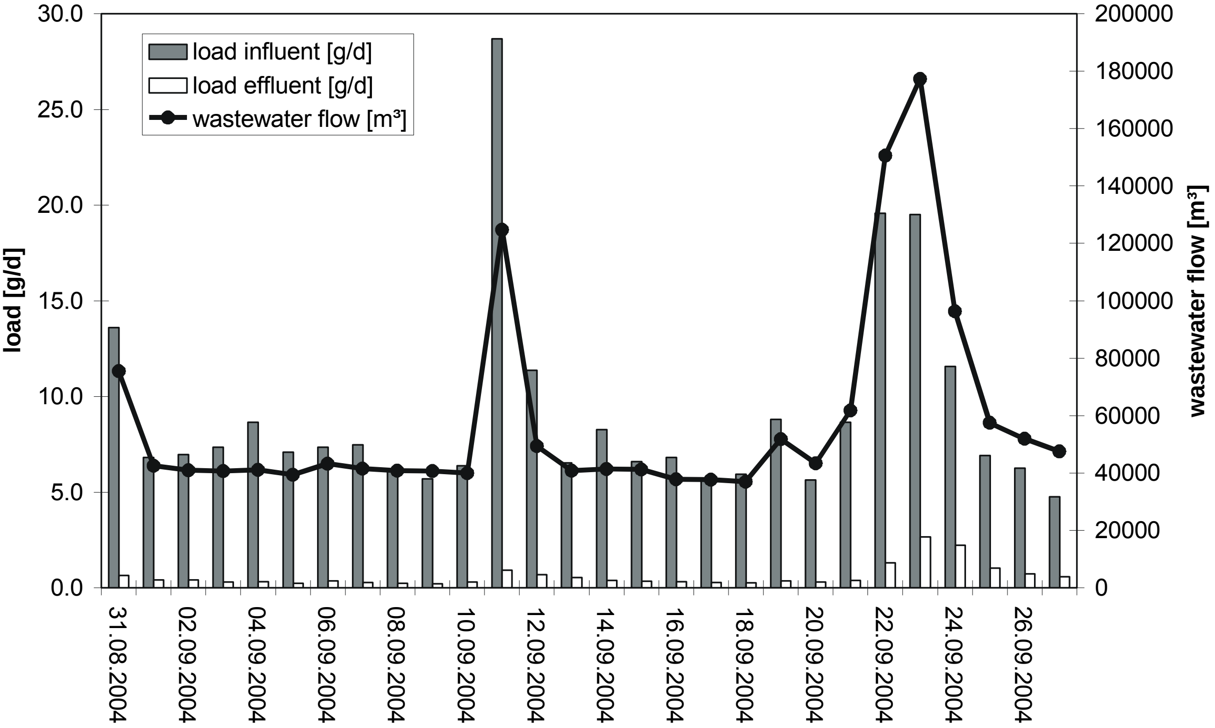


Figure 1.12 shows the loads of TPP in the influent and effluent of STP C during the experiment. As observed for the chlorinated organophosphates the day to day variance is low (3.8-6.7 g/d). With increasing wastewater flows significantly higher loads were observed (29 g/d). Similar results were observed for T*i*BP, T*n*BP, EHDPP and TBEP though the daily concentrations of TBEP were about ten times higher than of the other organophosphates (160-660 g/d, 1,600 g/d during rainfall). It is also noticeable that the calculated loads from effluent samples were lower than in the respective influent samples. Thus TPP was effectively eliminated in this STP.

Figure 1.12 Loads of TPP at STP C in the influent and effluent during the experiment

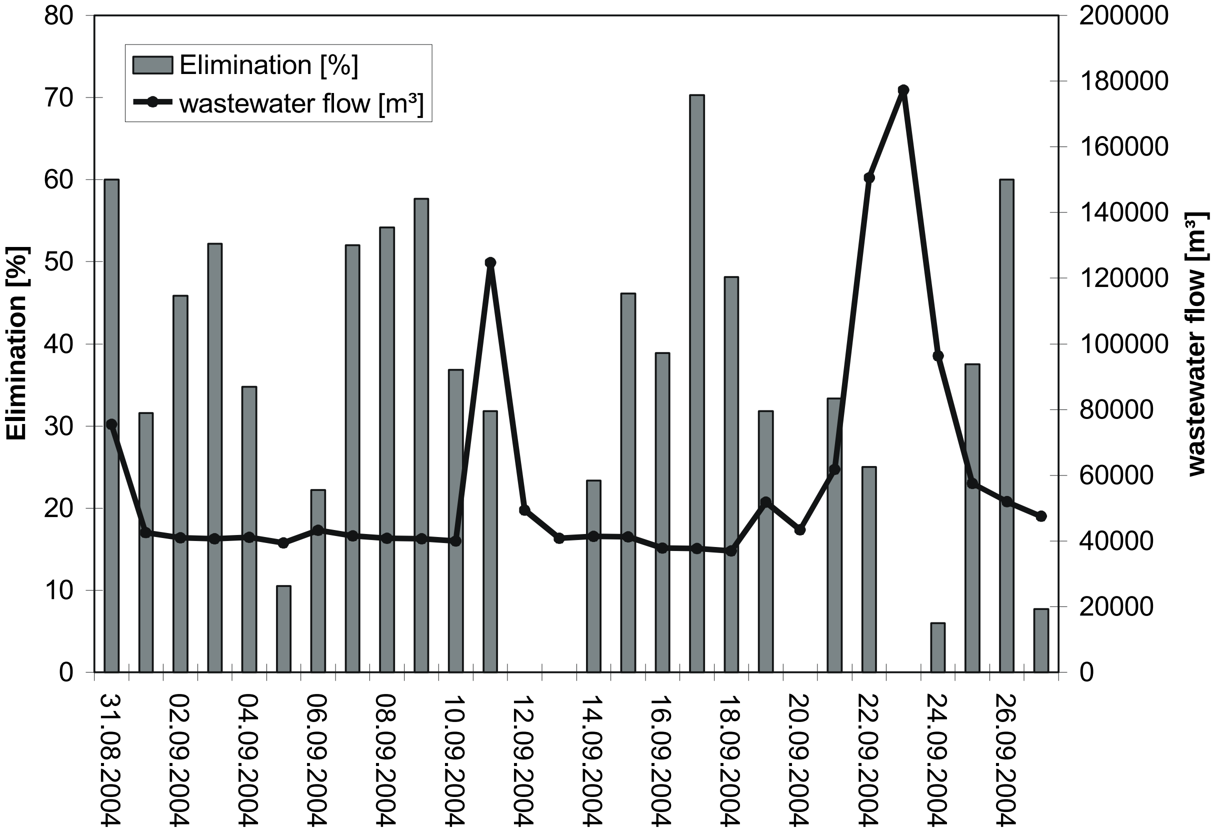


Similar results were obtained for the other non-chlorinated although the elimination efficiency for T*i*BP and T*n*BP was more influenced by the wastewater flow than TPP. For both substances no elimination was observed during rainfall (compare Figure 1.13 for T*i*BP). Thus elimination rates for T*i*BP and T*n*BP calculated for dry periods were higher and day to day variance lower (T*i*BP 37 ± 18 %, T*n*BP 71 ± 15 %) than for the complete sampling period (T*i*BP 29 ± 32 %, T*n*BP 68 ± 21 %). For TBEP and EHDPP concentrations in effluent samples were below LOQ. Estimated elimination rates were < 99 % for TBEP and EHDPP based on the respective limit of detection. Details are given in Table 1.8.

Table 1.8 influent and effluent loads of the selected chlorinated organophosphates given from day to day (maximum values during rainfall) mean values and elimination rates (elimination rates for normal wastewater flow) in STP C

analyte	load influent [g/d]	load effluent [g/d]	mean influent [g/d]	mean effluent [g/d]	Elimination rate [%]	day to day elimination [%]
T*i*BP	5-11 (max. 27)	3.8-6.7 (max. 19)	11	7.1	34	29 ± 32 (37 ± 18)
T*n*BP	5-18 (max. 26)	1.4-4.5 (max. 9.6)	11	2.9	73	68 ± 21 (71 ± 15)
TBEP	160-660 (max.1600)	< LOQ (max. 18)	430	< LOQ	> 99	n.d.
TPP	5.7-8.6 (max. 29)	0.2-0.4 (max. 2.7)	9.1	0.6	93	93 ± 4
EHDPP	1.4-4.5 (max. 8.6)	< LOQ	11	< LOQ	> 99	n.d.

Figure 1.13 Elimination rates and wastewater flow for T*i*BP in STP C

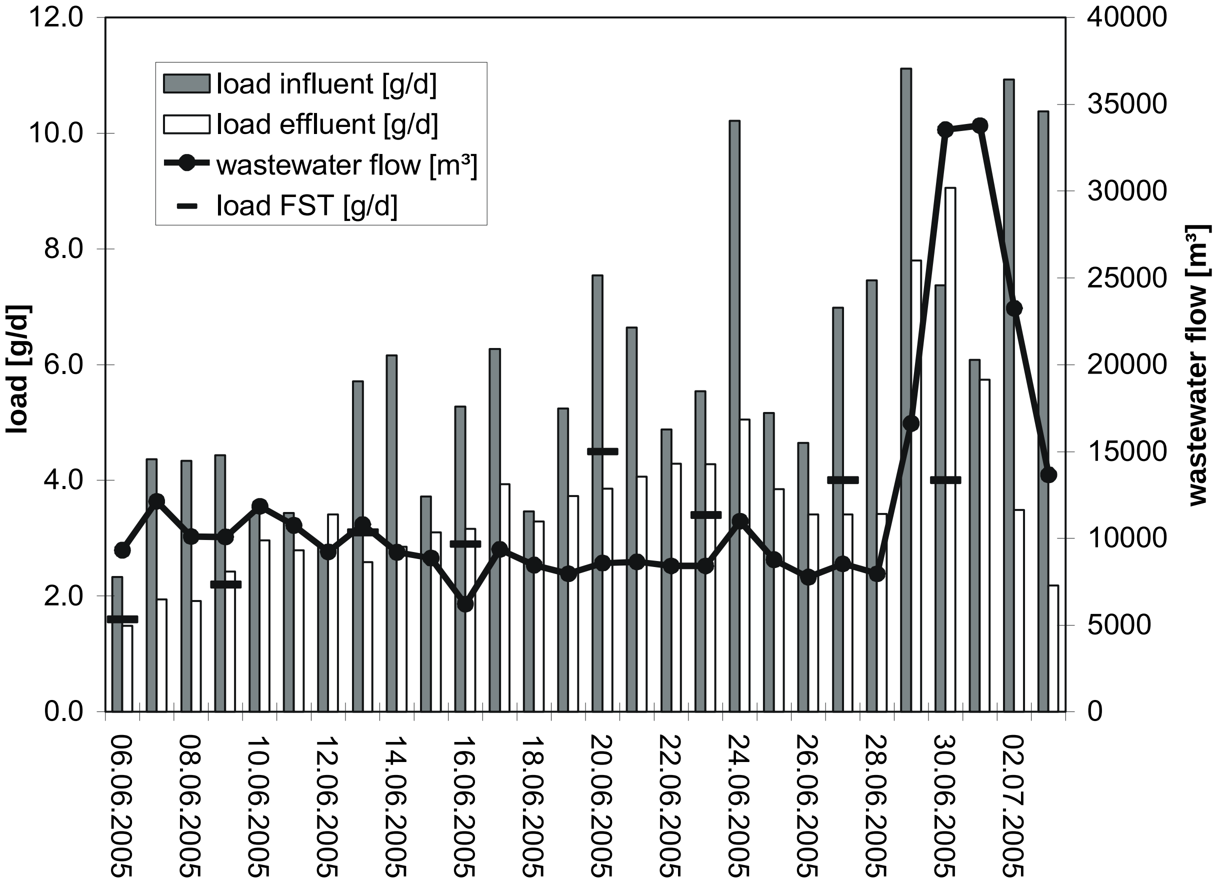


1.3.2.2 STP D

In contrasts to the sewage treatment plants mentioned above, STP D is located in a more or less rural area upstream of the highly industrialised area of the Ruhr megalopolis. With an inhabitant equivalent value of 32,000 and a wastewater flow of 13,000 m³ this STP is comparably small. After the final sedimentation the treated wastewater flows through a tertiary pond before it is discharged into the receiving water. Samples of the effluent of this pond were taken daily whereas grab samples of the effluent of the final sedimentation tank were analysed twice a week.

As expected the loads for all selected organophosphate esters were lower than in the large STP mentioned above. They ranged from 2.3-10 g/d in the influent and from 1.5-5.1 g/d in the effluent for TCPP. Higher values were determined for TBEP (13-140 g/d (influent), 9.9-24 g/d (effluent). Figures 1.14 and 1.15 show that the loads of TCPP and TBEP varied significantly from day to day whereas they were almost stable at STP C. Moreover the variance seems not to be associated to the wastewater flow although higher loads of organophosphates were detected during rainfall except for TCPP and TBEP. For those two substances the concentrations in influent samples decreased with increasing wastewater flow whereas they were almost stable for the other selected organophosphate esters. A comparison of the data achieved from the effluent of the final sedimentation tank and the effluent of the tertiary pond showed no differences. Thus the tertiary pond did not contribute to the elimination of the selected organophosphates.

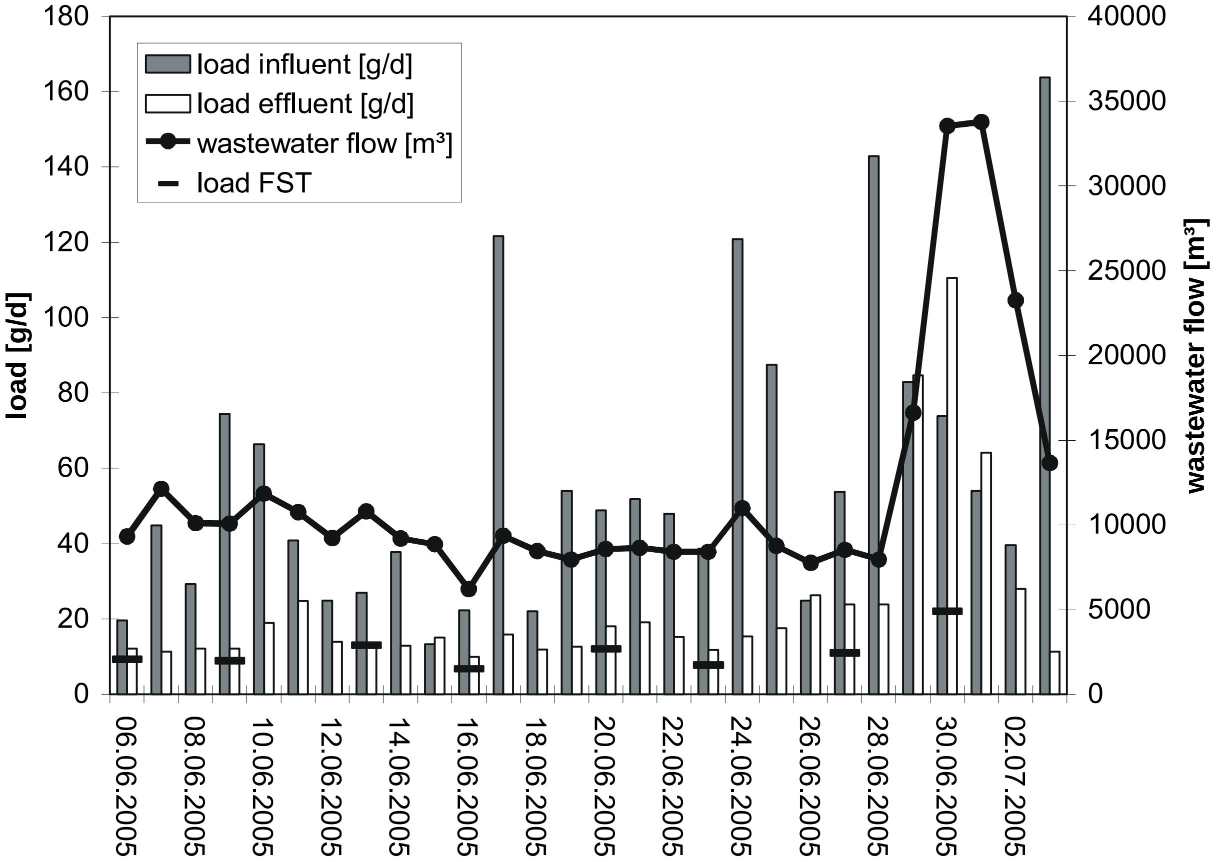
Figure 1.14 Loads of TCPP at STP D in the influent and effluent during the experiment (FST: effluent final sedimentation tank)



Surprisingly TCPP was eliminated significantly in this STP. The elimination rate was 38 % based on the influent and effluent loads over the sampling period. Comparing the daily elimination rates it seems that in this STP the elimination efficiency is associated to the wastewater flow as no elimination for TCPP was observed for the increased values at the end of the sampling period (34 ± 23 % respectively 36 ± 20 % (dry weather flow). In contrast to TCPP no elimination was observed for TCEP and TDCP according to the accuracy of the analytical method.

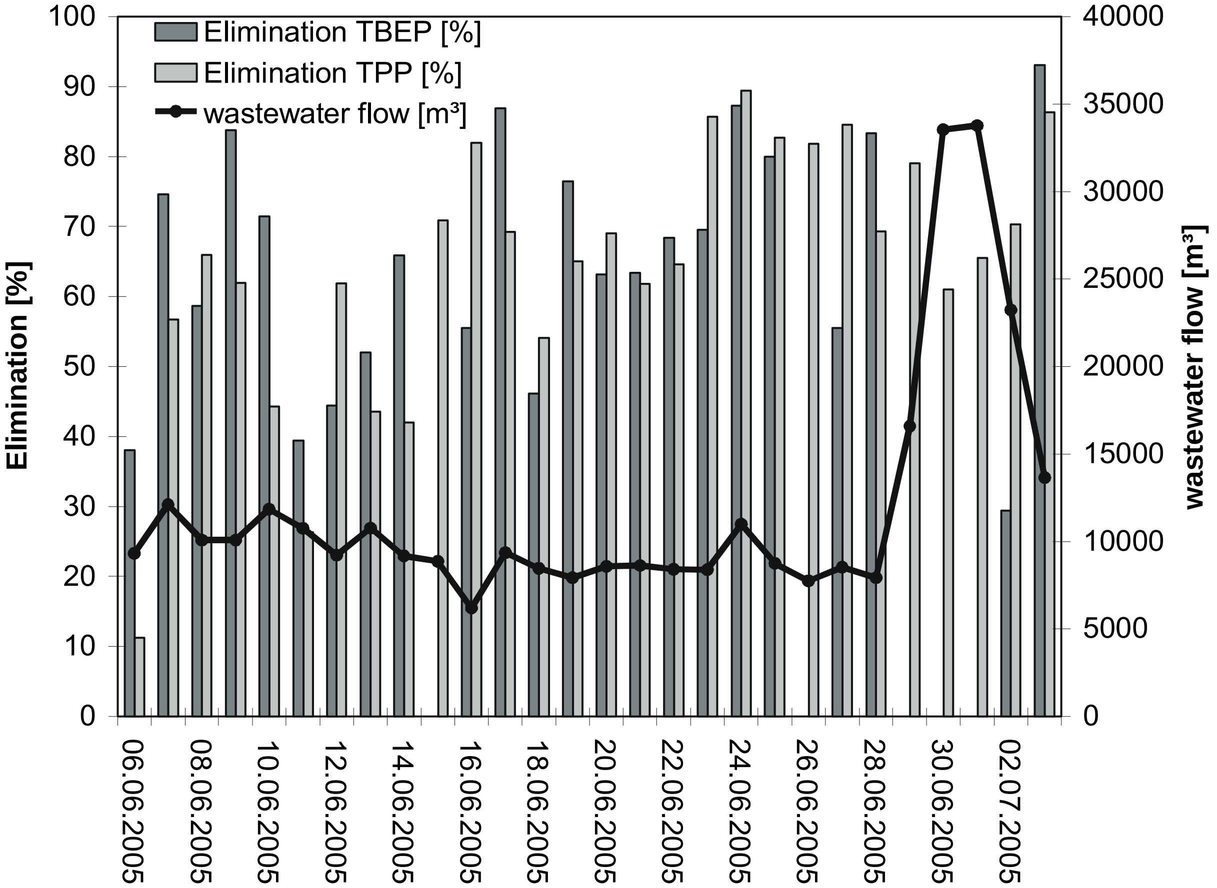
Similar results were observed for TBEP. The elimination rate was 59 % based on the influent and effluent loads over the sampling period. As for TCPP the elimination efficiency is linked to the wastewater flow. Observed elimination rates were 50 ± 36 % for the complete sampling period and 59 ± 25 % for dry weather flow respectively. In contrast to the other STPs no elimination was observed for T*i*BP and T*n*BP. For T*n*BP an elimination rate of 16 % was observed over the complete sampling period, but according to the variety of the elimination efficiency of the STP and the accuracy of the analytical method this was not significant.

Figure 1.15 Loads of TBEP at STP D in the influent and effluent during the experiment (FST: final sedimentation tank)



For TPP similar elimination rates were determined as for TBEP although it seemed that the elimination of TPP was less effected by rainfall and increased wastewater flows than the one of TBEP. Whereas elimination rates for TPP decreased barely with the increasing wastewater flow at the end of the experiment, no elimination was observed for TBEP during rainfall (compare Figure 1.16).

Figure 1.16 Comparison of elimination efficiency and wastewater flow for TPP and TBEP in STP D



For EHDPP concentrations of effluent samples were below LOQ. Thus it was not possible to calculate daily elimination rates. An overview on the results is given in Tables 1.9 and 1.10.

Table 1.9 Influent and effluent loads of the selected chlorinated organophosphates given from day to day (maximum values during rainfall), mean values and elimination rates (elimination rates for dry weather flow) in STP D

analyte	load influent [g/d]	load effluent [g/d]	mean influent [g/d]	mean effluent [g/d]	Elimination rate [%]	day to day elimination [%]
TCPP	2.3-10 (max. 11)	1.5-5.1 (max. 9.1)	5.9	3.7	38	34 ± 23 (36 ± 20)
TCEP	0.62-2.2 (max. 2.6)	0.78-1.9 (max. 3.7)	1.6	1.4	none	3 ± 36
TDCP	0.63-1.3 (max. 4.4)	0.56-1.6 (max. 4.7)	1.4	1.3	none	7 ± 33

Table 1.10 Influent and effluent loads of the selected non-chlorinated organophosphates given from day to day (maximum values during rainfall), mean values and elimination rates (elimination rates for dry weather flow) in STP D

analyte	load influent [g/d]	load effluent [g/d]	mean influent [g/d]	mean effluent [g/d]	Elimination rate [%]	day to day elimination [%]
T*i* BP	1.0-7.4 (max. 7.4)	1.5-4.5 (max. 13)	4.0	7.1	none	0 ± 100
T*n* BP	1.1-6.7 (max. 9.6)	1.0-4.4 (max. 6.8)	3.2	2.9	none	0 ± 70
TBEP	13-143 (max. 164)	9.9-26 (max. 111)	58	< LOQ	59	50 ± 36 (59 ± 25)
TPP	0.58-2.1 (max. 2.1)	0.11-0.85 (max. 0.85)	1.2	0.6	65	65 ± 18
EHDPP	0.14-1.1 (max. 1.1)	<LOQ-0.11 (max. 0.11)	0.4	< LOQ	< 99	n.d.

1.3.2.3 STP E

STP E is located in the same area as STP D. In contrast to the other STPs mentioned before this wastewater treatment plant is not an activated sludge plant. Wastewater is treated with trickling filters and post denitrification. During the sampling extensive civil works were carried out. Concerning the wastewater volume STP E is comparable to STP D (12,000 m³ and 13,000 m³ respectively) whereas the corresponding inhabitant values are with 64,000 twice as much as in STP D.

In contrast to STPs C and D there was an extremely high variance of the daily wastewater volumes with a short period of dry weather at the beginning of the sampling campaign. The loads of the selected organophosphates were in the same range as in STP D. For the chlorinated organophosphates they ranged from 1-5 g/d in the influent. Surprisingly the highest value was observed for TDCP (11 g/d). In the effluent the respective loads were in the same order of magnitude with again the highest loads for TDCP (10 g/d). As in the STPs mentioned before, the daily loads correspond with the wastewater flow although in this STP the correspondence between loads and wastewater inflow was different for each substance. Whereas for TCPP and TBEP the amounts increased only slightly for TPP a significant correlation was observed (compare Figure1.18). This was also reflected by the measured concentrations in influent samples (compare Figure 1.17). For TCPP and TBEP the concentrations decreased almost in the same ratio as the wastewater inflow increased whereas the concentrations for TPP, T*n*BP, T*i*BP and TCEP were not influenced by the wastewater volume at all. For TDCP an increase of the amounts was observed, though.

Figure 1.17 Concentrations of TCPP and TPP in influent samples during at STP E in comparison to the wastewater inflow

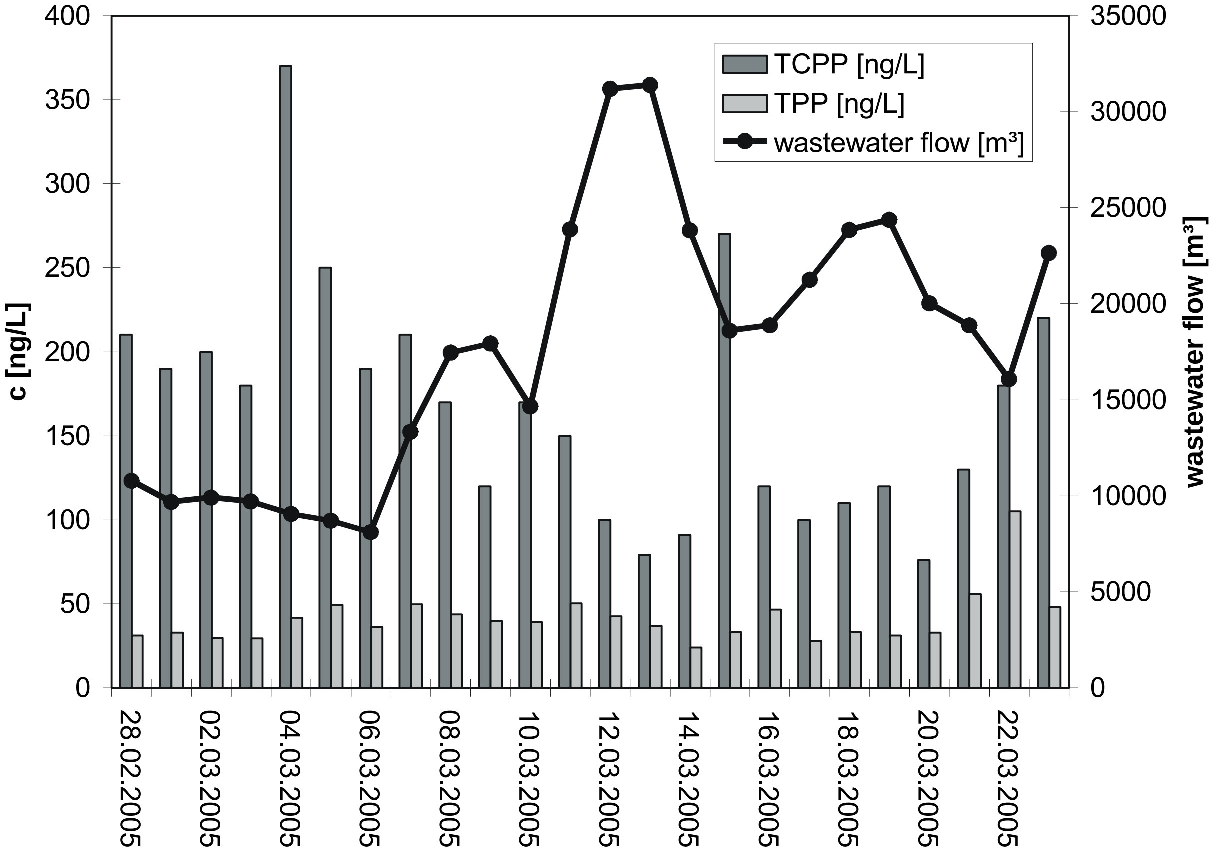
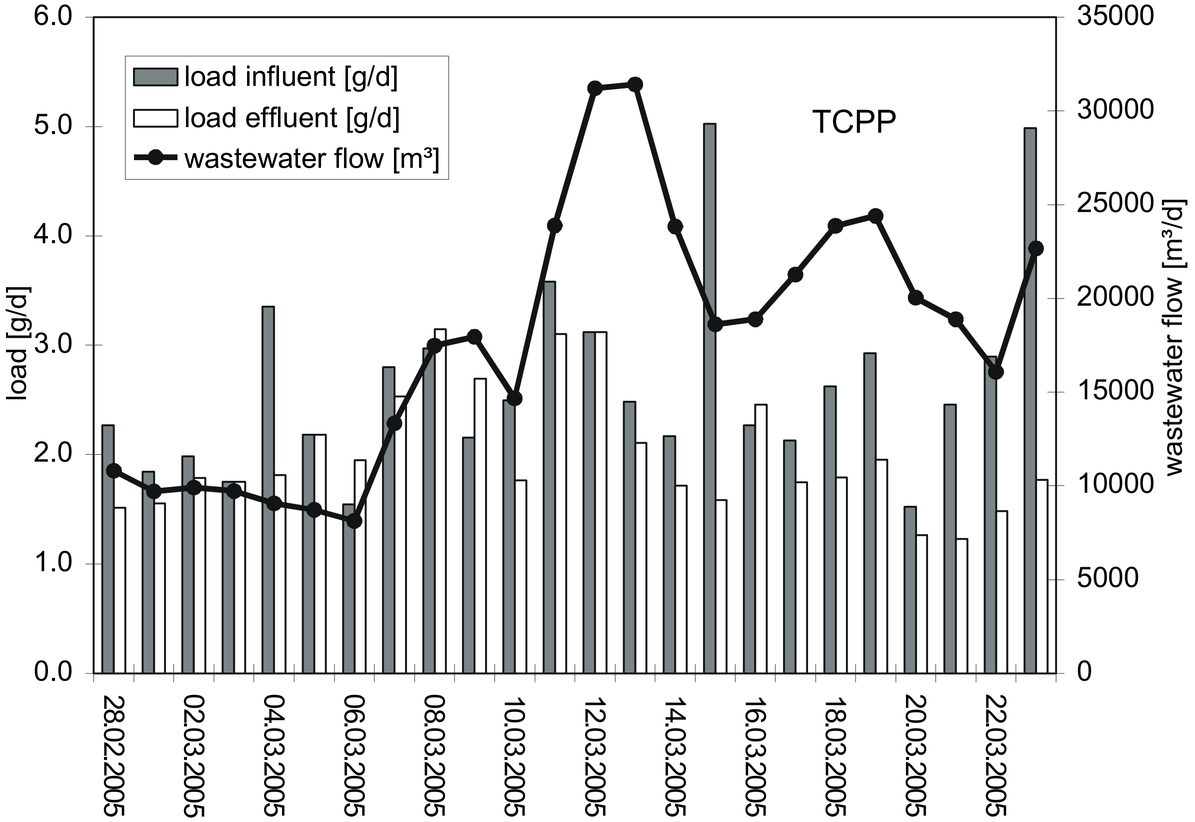
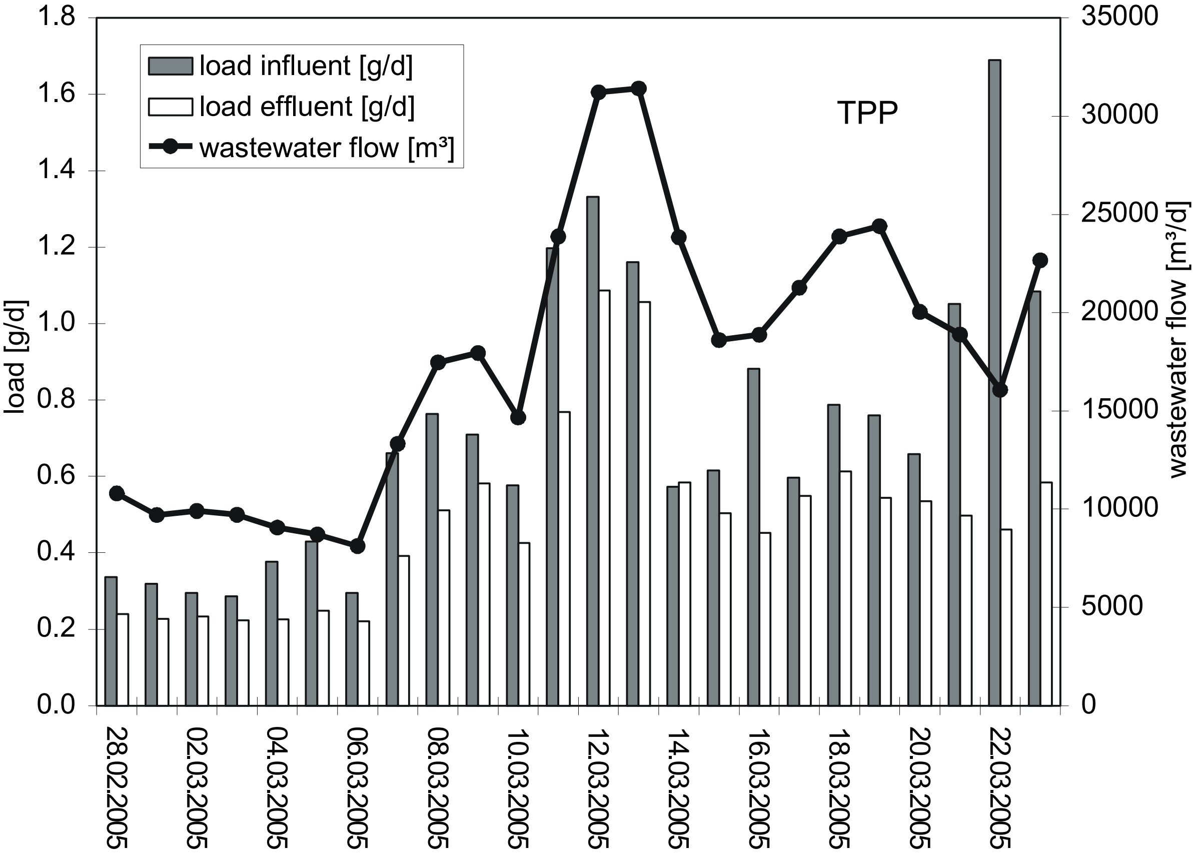


Figure 1.18 Loads of TCPP and TPP at STP E in the influent and effluent during the experiment





Comparing influent and effluent loads over the complete sampling period a slight reduction of TCPP was observed. It seemed that the elimination efficiency decreased with an increasing wastewater flow but on most days influent and effluent loads were the same considering the accuracy of the analytical method. For TDCP and TCEP no elimination was observed.

The highest loads of the non-chlorinated organophosphates in the influent of this STP were again observed for TBEP. They ranged from 26-85 g/d during the dry weather period at the beginning of the sampling and rose up to 120 g/d during the increased wastewater flow. For T*i*BP and T*n*BP they ranged from 0.5-1.5 g/d and from 0.29-0.43 g/d for TPP respectively.

For all selected non-chlorinated organophosphates the respective values were lower in effluent samples except for T*i*BP. In this case the loads were significantly higher in the effluent than in the influent. They ranged from 8.6-37 g/d in the effluent. Due to the fact that extensive civil works were carried out during the experiment a considerable part of the T*i*BP might stem from the concrete utilised for the construction as this substance is used to regulate the pore size in concrete. Thus it was not possible to determine any elimination for T*i*BP. On the basis of the influent and effluent loads elimination rates were found to be 22 % for T*n*BP, 27 % for TBEP and 33 % for TPP. For all substances the daily variance was high. Figure 1.19 shows the elimination rates for TPP and TBEP in comparison to the wastewater flow. For both substances decreasing elimination efficiencies were observed for an increase of the wastewater flow. However it seemed that the elimination of TPP was less affected by the water flow than TBEP, especially at the beginning of the experiment (06.03.2005-09.03.2005) as no elimination was observed for TBEP. Moreover the trickling filter process was apparently adapted to the higher wastewater volumes at the end of the sampling period as the elimination rates somewhat stabilised especially for T*n*BP (compare Figure 1.20). This finding holds also for TBEP and TPP. The day to day variance was still high for those two substances though. Figures 1.19 and 1.20 also clarify that the adaptation of the trickling filter process to the increased wastewater volumes concerning to the elimination efficiency strongly depends on the respective substance. Whereas elimination rates for T*n*BP stabilised after nine days for TBEP and TPP some kind of stabilisation was observed only at the end of the experiment. An overview of the results is given in Tables 1.11.

Figure 1.19 Elimination rates of TPP and TBEP in comparison to the wastewater flow during the experiment at STP E

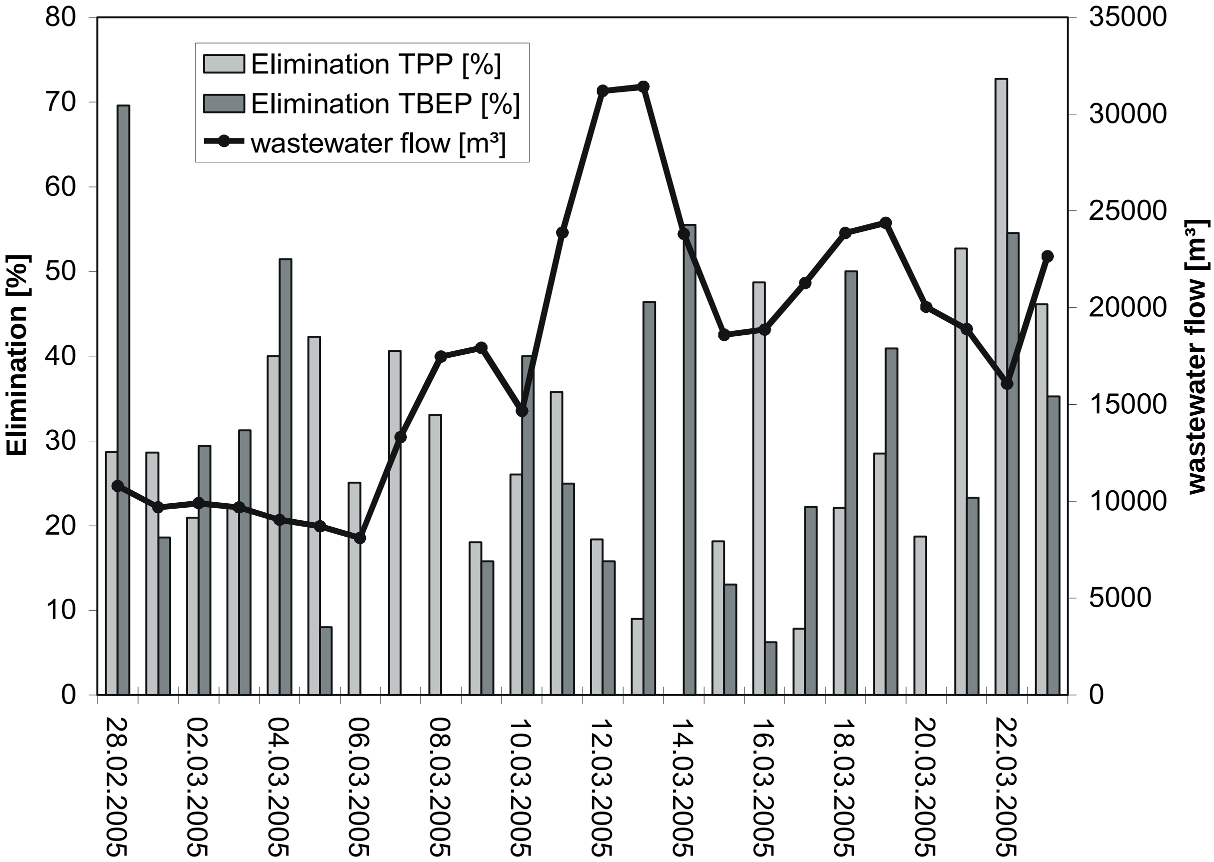
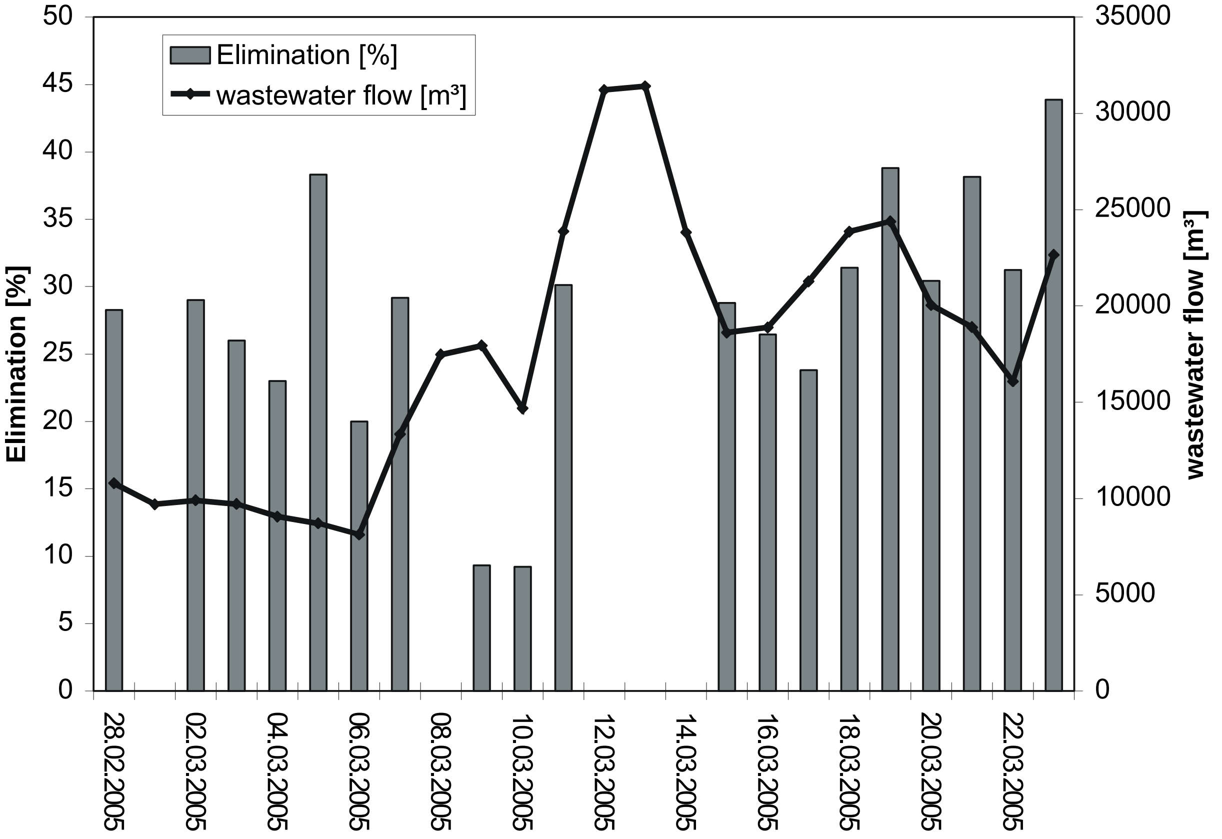


Table 1.11 Influent and effluent loads of the selected chlorinated organophosphates given from day to day, maximum values, mean values and elimination rates (elimination rates for normal wastewater flow) in STP E

analyte	load influent [g/d]	load effluent [g/d]	mean influent [g/d]	mean effluent [g/d]	Elimination rate [%]	day to day elimination [%]
TCPP	1.5-3.4 (max. 5.0)	1.5-2.2 (max. 3.1)	2.6	2.0	24	19 ± 25
TCEP	0.85-2.3 (max. 3.1)	1.1-1.5 (max. 4.1)	1.8	2.2	none	0 ± 37
TDCP	0.41-1.1 (max. 13)	1.1-1.9 (max. 10)	2.5	2.8	none	0 ± 86
T*i*BP	0.47-1.4 (max. 2.6)	16-24 (max. 37)	0.93	17	none	none
T*n*BP	0.77-1.1 (max. 2.2)	0.62-0.79 (max. 1.9)	1.3	1.0	22	20 ± 18 (27 ± 11)
TBEP	26-63 (max. 110)	26-40 (max. 64)	54	39	27	18 ± 40 (33 ± 18)
TPP	0.29-0.43 (max. 1.7)	0.22-0.25 (max. 1.1)	0.73	0.49	33	29 ± 16

Figure 1.20 Elimination efficiency and wastewater flow for T*n*BP in STP E



1.3.3 Comparison of the Concentrations of the selected organophosphate esters in influent and effluent as well as from samples of the sludge dewatering

Before excess sludge from STPs is disposed or used as fertiliser on agricultural areas the sludge is dewatered by centrifuging or sludge pressing. At STP C samples were taken from the effluents of the centrifuge and the settling tank for digestive sludge respectively. STP D has no sludge dewatering devices and excess sludge is stored in sludge ponds. Thus at this STP D samples were taken from the back flow of supernatant water from the sludge pond. Presently the water from sludge dewatering is fed to the influent of STPs (compare, e.g., figure 1.6). Thus the inflow concentrations might increase if considerable amounts of the selected organophosphates are determined in these partial streams. As especially the chlorinated organophosphates were hardly eliminated in the wastewater treatment it was the objective of this sampling to study if concentrations and loads respectively can be reduced in influents and effluents of STPs by an additional treatment of the process water. Table 1.12 gives an overview on the mean values of the influent and effluent concentrations of the selected organophosphates as well as the concentrations measured in the effluent of the respective sludge dewatering processes at STP C and D. This Table displays that the concentrations for both STP were very similar throughout the sampling. This indicates that the differences in the loads are connected to the different wastewater volumes.

Table 1.12 Mean values of the concentrations in ng/L of the selected organophosphate ester in the influent and effluent of STPs C and D as well as from the effluent of the respective sludge dewatering processes (Cen: centrifuge; ST: settling tank for digestive sludge; SPo: sludge pond)

Analyte	STP C				STP D		
	Influent [ng/L]	Effluent [ng/L]	Effluent Cen [ng/L]	Effluent ST [ng/L]	Influent [ng/L]	Effluent [ng/L]	Effluent SPo [ng/L]
T*i*BP	200	120	94	260	380	340	280
T*n*BP	200	52	120	190	300	230	140
TCEP	230	220	290	320	150	120	110
TCPP	700	700	2100	2700	560	350	400
TDCP	180	140	170	280	120	100	150
TPP	160	9.6	24	10	110	38	28
TBEP	7700	210	1800	6200	5500	1900	5300
EHDPP	60	< 10	100	130	39	< 10	28

The same results were observed for the amounts of the organophosphates in process water from sludge dewatering. Moreover the concentrations in these samples were in the same range as for influent samples. As the process water from the sludge dewatering is discharged into the influent it is of special interest to estimate if a reduction of these substances in process waters optimizes the elimination efficiency of the respective STP. Except for TCPP, in both STPs the concentrations were in the same order of magnitude. An estimation on the loads for the respective substances is difficult as the sludge dewatering is a discontinuous process. For STP C the water flow of the effluent of the centrifuge is about 2400 m^3/d and from the effluent of the settling tank 500 m^3/d though. This means that the process water volume is less than approximately 5 % of the wastewater inflow in STP C. For STP D data in the water flow from the sludge pond were not available but similar ratios can be expected. This indicates that the concentrations as well as the loads in the influent of the STPs are not influenced significantly by process water as the amounts in process water were in the same range as in influent samples. Only for TCPP significantly higher concentrations were observed in samples of the sludge dewatering in STP C. As TCPP was not eliminated in this STP an additional treatment of process water might be useful to reduce the loads in effluent samples. For STP D the treatment of process water might reduce the effluent loads in general as the elimination efficiency is lower than in the large STP.

1.4 *Conclusions on the elimination of organophosphate esters in sewage treatment plants*

Whereas the elimination rates for the respective substances were comparable at the STPs A and B and the type of construction did not influence the elimination efficiency, the current study of STPs showed significant differences between the diverse wastewater treatment plants. Moreover changes in the wastewater flow due to rainfall are an important factor as they influence the elimination efficiency. At all STPs that were studied, the elimination rates decreased with an increase of the wastewater volume. In Table 1.13 the elimination rates of the selected organophosphate esters at the respective STPs are summarised. Apparently the elimination efficiency is higher at the large STPs A, B and C than in the smaller STPs D and E. The lowest elimination rates were detected for STP E (trickling filter process). On the one hand the trickling filter process might be less effective then the activated sludge process on the other hand the wastewater volume was almost three times as high as under dry weather conditions during the complete sampling period. Moreover it was obvious that the trickling filters needed several days to adapt to the increased wastewater volumes. The fact that the elimination rates determined for dry weather flow and after adaptation to the higher wastewater volumes were, e.g., comparable for T*n*BP, might show that the trickling filter process was indeed less effective than the activated sludge process. It was surprising that the chlorinated flame retardant TCPP was eliminated in STPs D and E whereas no elimination was observed at STP A-C although the elimination efficiency at these plants was in general higher. Neither TDCP nor TCEP were eliminated in both STPs. Kawagoshi *et al.*[34] (2002) performed long term degradation experiments on TCPP. In these studies it was found that this compound was not eliminated. It is discussed that TCPP is partly bound to particles as lower results for the respective organophosphates from the same samples where observed for SPE in comparison to the LLE if, after sedimentation of particles, only the aqueous phase was extracted. Otherwise both methods give the same results if the complete sample is extracted. Bester (2005) studied the concentrations of TCPP in influent and effluent samples as well as digested sludge over a period of five days (dry weather). In this period 350 g TCPP left the plant with the wastewater effluent while about 480 g were exported with the sludge. TCPP is hardly eliminated in the wastewater treatment process and thus no elimination due to sorption to sludge is supposable. The amounts of TCPP in the sludge were comparable with those of the effluent, though. Thus this study also indicates that TCPP is to some extend bound to particles.

Not all the samples in STPs D and E were extracted the same day after sampling. Thus TCPP was possibly mobilised from particles during storage. In this context two types of particles should be discussed. On the one hand there are particles from the technosphere, e.g., plastic particles. In this case the TCPP is not extractable by LLE as it is dissolved in the polymer material. On the other hand TCPP might be sorbed to particles from the biosphere from which TCPP would be extractable by LLE. As demonstrated by Bester it seems that polymer particles might be more relevant as TCPP is because of its low log K_{OW} supposable not bound to particles from the biosphere. It might be possible that TCPP is mobilised from, e.g., degrading polyurethane particles during these somewhat longer storage periods. Thus higher concentrations in influent samples would be observed than for comparable samples that were extracted almost immediately after sampling. For effluent samples the amounts would not change during storage as particles are removed during wastewater treatment. Thus in comparison to effluent samples a reduction of TCPP would be observed for influent samples that were stored for a certain period of time.

Table 1.13 Summarisation of the elimination rates for the selected organophosphates; for STPs C,D and E elimination rates given as mean values on basis of influent and effluent loads over the complete sampling period as well as the day to day elimination for dry weather flow; n.d.: not detectable due to construction at STP E

STP	characteristics of STP	Elimination [%]							
		T*i*BP	T*n*BP	TPP	TBEP	EHDPP	TCEP	TCPP	TDCP
A	two-stage activated sludge plant; 220,000 m³/d, 1,100,000 IEV	86 ± 6	67 ± 16	57 ± 24	88 ± 4	n.d.	none	none	none
B	single stage activated sludge plant; 109,000 m³/d, 1,090,000 IEV	86 ± 10	55 ± 15	75 ± 10	89 ± 9	n.d.	none	none	none
C	single stage activated sludge plant; 70,000 m³/d, 250,000 IEV	34 (37 ± 18)	73 (71 ± 15)	93 (93 ± 4)	> 99	> 99	none	none	26 (30 ± 16)
D	single stage activated sludge plant; 13,000 m³/d, 32,000 IEV	none	none	65 (65 ± 18)	59 (59 ± 25)	> 99	none	38 (36 ± 20)	none
E	trickling filter; 12,000 m³/d, 64,000 IEV	n.d.	22 (27 ± 11)	33 (29 ± 16)	27 (33 ± 18)	n.d.	none	24 (19 ± 25)	none

1.5 *Emission sources of organophosphorus flame retardants and plasticisers to sewer systems*

1.5.1 Identification of point or non-point sources in wastewater collection systems

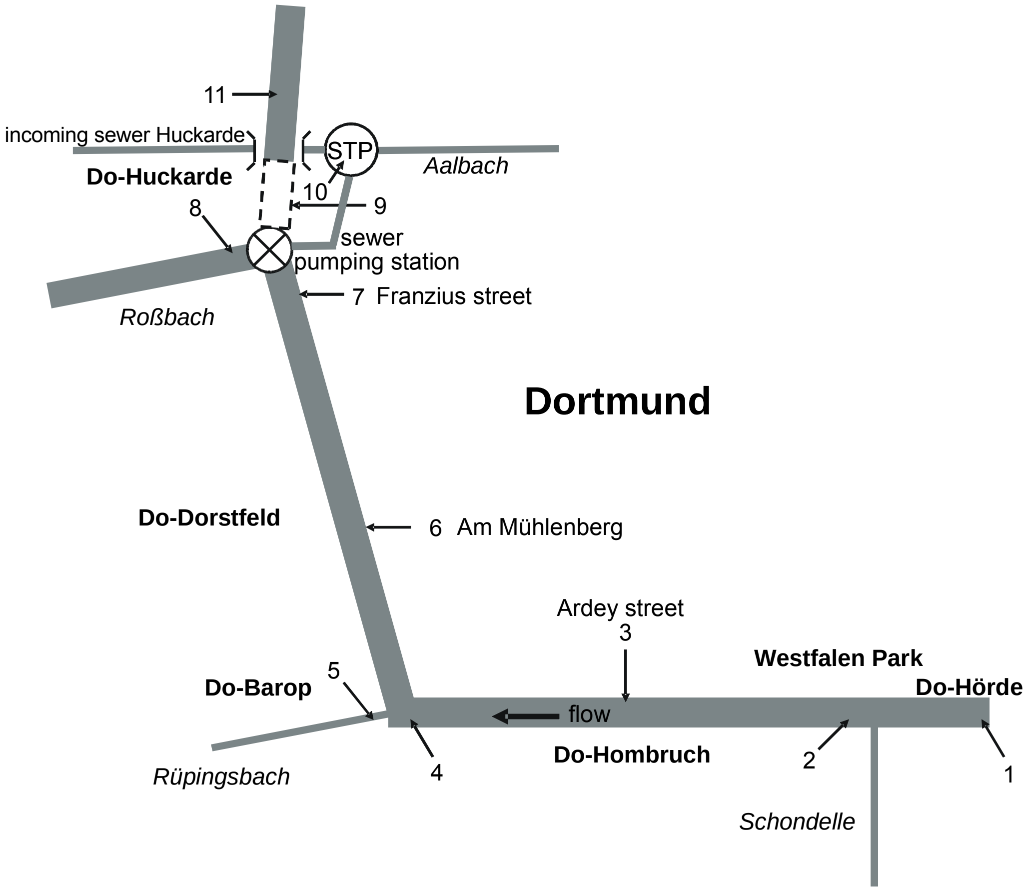
The objective of the sampling of the sewer system was to clarify if the selected organophosphate esters are emitted by point or non-point sources. To detect point sources for the chlorinated and non-chlorinated alkylphosphates grab samples were taken from the sewer system of the City of Dortmund (Figure 1.21). Most of the city's wastewater is discharged to the river Emscher and some of its "tributaries" like the Roßbach and Aalbach. The tributary Aalbach was not accessible for sampling at that time, though. This sample area was chosen because most parts of the sewer system of Dortmund were open sewage canals. Thus sampling was comparatively simple as there was no need to climb down into the underground parts of the sewer system.

The first sampling point was the stormwater overflow in the southern part of Dortmund. The sampling followed the route of the main canal (Emscher) and covered also several tributaries from diverse parts of the City. As the water of the Emscher is treated in a large wastewater treatment plant samples from the inflow and the outflow were analysed as well. The last sampling point is located downstream of the STP effluent. Location and characteristics of the chosen sampling points are given in Table 1.14. All samples were taken on one day during a dry period in June 2003. The sampling was repeated in December 2003 for selected sampling points. The samples were extracted by liquid-liquid extraction with toluene and measured with the GC-MS-system described in chapter 1.2.

Table 1.14 Location and characteristics of the chosen sampling points as well as the measured concentrations of the different organophosphate esters in ng/L in June (respectively December 2003)

Sample	Sample characteristics	Analyt c [ng/L]						
		TiBP	TnBP	TCEP	TCPP	TDCP	TBEP	TPP
1	Emscher: stormwater overflow	42	6	n.d.	9	n.d.	3	11
2	Emscher, post discharge Schondelle-channel	2500	190	220	660	48	7400	48
3	Emscher downstream Schondelle, Ardey street	540	150	370	1300	56	5800	51
4	Emscher, upstream Rüpingsbach, Am Mühlenberg	2200	150	140	690	88	7200	62
5	Rüpingsbach	520	150	190	610	39	1700	69
6	Emscher downstream Rüpingsbach	670	160	270	520	64	7900	64
7	Emscher at Franzius street, upstream Roßbach	250 (230)	92 (310)	180 (180)	440 (230)	51 (38)	2200 (7500)	78
8	Roßbach	1400 (380)	190 (110)	480 (61)	550 (100)	120 (670)	5300 (220)	87 (18)
9	Emscher wastewater overflow of STP, almost no water	49	18	190	250	29	140	36
10	Pumpingstaion Huckarde at STP	110	240	90	280	21	140	35
11	Emscher after wastewater treatment	270 (260)	75 (100)	740 (170)	1400 (170)	89 (78)	350 (2400)	78 (26)

Figure 1.21 Sampling points of the river Emscher sampling



In the stormwater overflow (1) the concentrations of the selected organophosphate ester flame retardants and plasticisers were in the low ng/L-range. Marklund *et al.*[35] (2005) connected the emission of organophosphate esters into the environment to traffic as the concentrations of these substances were higher in snow directly located at streets and decreased with increasing distance. Thus it was not expected to detect considerable amounts of these substances as the samples were taken during a period of dry weather. The situation changed dramatically at sample point two. At this point the river Emscher is already canalised. Moreover the wastewater of the southern suburbs of the City of Dortmund is discharged to the Emscher via the Schondelle-channel near this sampling location. The detected amounts ranged from 48 ng/L to 7,400 ng/L for the non-chlorinated alkylphosphates and from 48 ng/L to 660 ng/L for the chlorinated substances. At the following sampling points varying amounts for the respective substances were detected but they were all in the concentration ranges as expected for wastewater. Moreover no distinct distribution pattern was observed for the diverse substances. Right before sample point 9 the Emscher and the Roßbach are pumped underground to the STP in the North of Dortmund. The sample at this point is taken from the stormwater overflow of the sewer system. Thus significantly lower concentrations were detected for the organophosphate esters as the remaining pools were mostly fed by rainwater from several weeks before. The comparison of sample points 7 and 8 (before wastewater treatment) and sample 11 (after wastewater treatment) gives hints on the elimination efficiency of the wastewater treatment plant at this location. As expected the non-chlorinated organophosphate esters were partly eliminated as, e.g., the concentration for TBEP was 7,400 ng/L in the Emscher before and 350 ng/L after wastewater treatment. No elimination was observed for the chlorinated flame retardants. In December 2003 the sampling was repeated at sample points 7, 8 und 11 after heavy rainfall. Obviously the concentrations for some of the organophosphate were on the one hand lower due to dilution effects, e.g., in the Roßbach on the other hand not all the wastewater was treated at the STP but discharged directly to the Emscher. This was indicated by the turbidity of the treated water and on the high concentration for TBEP (2,400 ng/L). An overview on the results is given in Table 1.14. These results also indicate that the emission of these substances cannot be traced back to specific point sources in the wastewater collection system.

Organophosphate esters have been detected in leachate and leakage water from waste disposal landfills in several studies[36,37,38]. As these landfills are connected to the public sewer system if they have no wastewater treatment plant, they may contribute to the discharge of these compounds as well.

1.5.2 Experiments for the identification of relevant non-point sources

As the organophosphorus flame retardants and plasticisers have been detected in indoor dust (e.g., Marklund et. al, 2003) other emission sources for these substances might be water from cleaning floors. Thus point samples from three locations were analysed for the selected organophosphate esters. The results are given in Table 1.15. Whereas floors one and two were cleaned with normal household cleaning agents, the laminate was mopped with a special cleaning agent for this kind of floors.

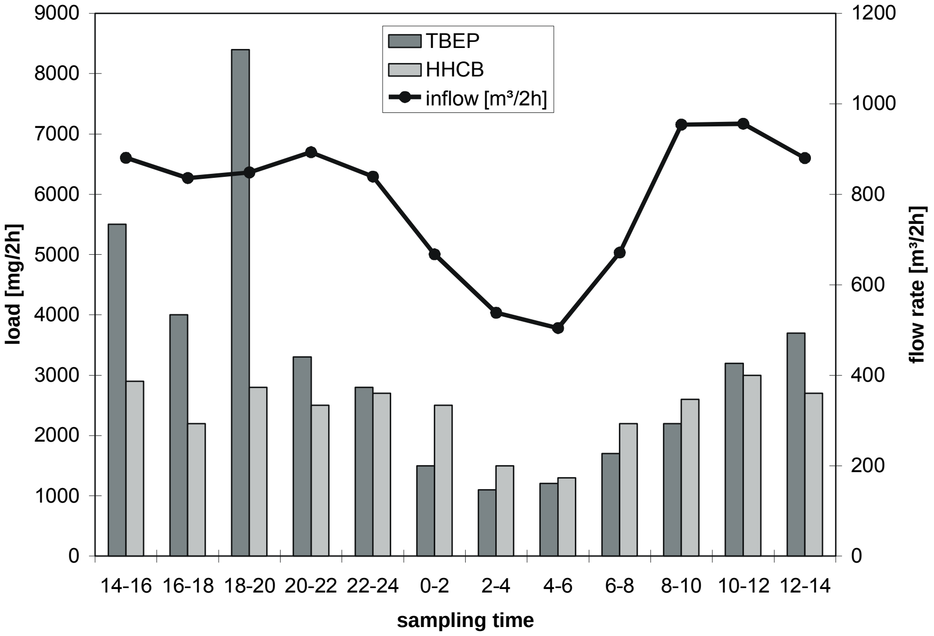
Table 1.15 Results of the „cleaning experiment"

Sample	TiBP	TnBP	TBEP	TPP	TCEP	TCPP	TDCP
PVC 1	670 ng/L	92 ng/L	0,1 mg/L	310 ng/L	1.3 µg/L	480 ng/L	480 ng/L
Laminate	3400 ng/L	1500 ng/L	11 mg/L	540 ng/L	4.7 µg/L	330 ng/L	n.d.
PVC 2	1700 ng/L	2000 ng/L	0.026 mg/L	50 ng/L	23 µg/L	440 ng/L	350 ng/L

Table 1.15 shows that the concentrations determined ranged from the lower ng/L-range for TPP up to amounts of 10 mg/L for TBEP. Due to the fact that the measuring method was only calibrated for concentrations up to 20,000 ng/L the data achieved for TBEP are only indicative. About 8 % of an average use of 129 L per capita and day are used in Germany for cleaning purposes[39,40]. This means that about 10 % of municipal wastewater consists of water that was used for cleaning purposes (dilution approximately 1:10). Thus floor cleaning might contribute to the loads in wastewater if the detected amounts in the respective samples are about an order of magnitude higher than in municipal wastewater itself. The very high concentrations of TBEP in the samples indicate that the source "floor sweeping" seems to be relevant for the loads in wastewater. The achieved data base is only indicative as huge variation was determined for the concentrations for T*i*BP, T*n*BP, TPP, TCEP and TDCP. From some samples it might be concluded that sweeping is a relevant source, while from others it seems to be rather negligible. The

concentrations of TCPP that were detected in these samples were not relevant to explain the concentrations in wastewater, though. Thus other sources for the emission of this substance are more important. Prösch *et al.*[41], e.g., discussed contaminated textiles as sources for TCPP in wastewater. In this study the concentrations of TCPP were measured in wash water of cotton clothes (8 x 8 cm) that were exposed in rooms and cars. An estimation of the TCPP quantities from washing procedures in comparison to loads detected in municipal wastewater showed that washing water contributes significantly to the total loads. Eriksson *et al.*[42], (2003) detected TCEP and TPP in grey wastewater and state that these substances stem from contaminated clothes as well. Grey wastewater refers to wastewater from households, business complexes, hotels, schools etc. where no contribution of toilettes or heavily polluted process water is included. Another hint that these substances are emitted from households gives a 24-h characteristic curve for these substances. At STP D samples were taken in intervals of two hours over a period of 24 hours. Figure 1.22 displays the loads for TBEP and the musk fragrance HHCB. The emission of HHCB is directly connected to households as this substance is, e.g., used in shower gels. Apparently the loads of TBEP and HHCB decrease during the night and thus they are correlated to the wastewater flow. Similar results were obtained for the other selected organophosphate ester.

Figure 1.22 Comparison of the inflow loads for TBEP and HHCB over a period of 24 hours for STP D



The studies for the detection of point and non-point sources indicate that the selected phosphororganic flame retardants and plasticisers are emitted from a multitude of sources.

1.6 *Degradation experiments in batch reactors*

Complementary to the elimination of organophosphorus flame retardants and plasticisers in the wastewater treatment process, batch degradation experiments were accomplished. Therefore activated sludge from a wastewater treatment plant was spiked with the selected organophosphate esters. One batch experiment was held under aerobic conditions while the second one was conducted under alternating conditions, i.e., it was switched from aerated to nonaerated conditions in 1 hour intervals.

1.6.1 Materials and Methods for degradation of organophosphates in batch reactors

For the batch experiments 4 L of activated sludge from a municipal wastewater treatment plant was spiked to a final concentration of 10,000 ng/L of the non-chlorinated alkylphosphates T*n*BP, T*i*BP, TPP, TBEP and EHDPP and the chlorinated organophosphorus flame retardants TCPP, TCEP and TDCP, each. The dry mass concentration was 3 g/L in the respective experiments.

For determination of the respective organophosphate esters 100 mL of the spiked sludge was extracted with 5 mL toluene after adding 100 µl of internal standard solution by vigorous stirring with a PTFE coated magnetic stirrer for 30 min. After a sedimentation phase of 20 min the aqueous phase was separated from the organic one and the residual water was removed from the organic phase by freezing the samples overnight at –20 ^{o}C. The samples were concentrated with a concentration unit (Büchi Syncore, Büchi, Essen, Germany) at 60 °C and 60 mbar to 1 mL.

On the first day of the experiments samples were taken hourly, on the second three times (in the morning, at noon and in the evening) and on the following days once in the morning. The first sample was taken after the sewage sludge was spiked with the chlorinated and non-chlorinated phosphorus flame retardants and plasticisers.

For the quantification of the organophosphorus flame retardants and plasticisers a gas chromatography- mass spectrometry system was used (for details compare chapter 1.4.1).

1.6.2 Results and discussion to degradation of organophosphate esters in batch reactors

1.6.2.1 Results for the aerobic degradation experiment

The measurements of the first five samples showed that a homogenous distribution of the substances was reached after five hours. Thus the highest concentration was used as starting point for a possible degradation process. Figure 1.23 shows the concentrations of T*n*BP during the degradation experiment. After 220 hours the concentration was below LOQ. Moreover this substance shows a typical first order degradation curve. The corresponding equation (1)[43] is:

$$c = c_0 \bullet e^{-k \cdot t} \tag{1}$$

with c_0 as starting concentrations, k as slope and t as time.

Figure 1.23 Degradation curve of T*n*BP (aerobic experiment)

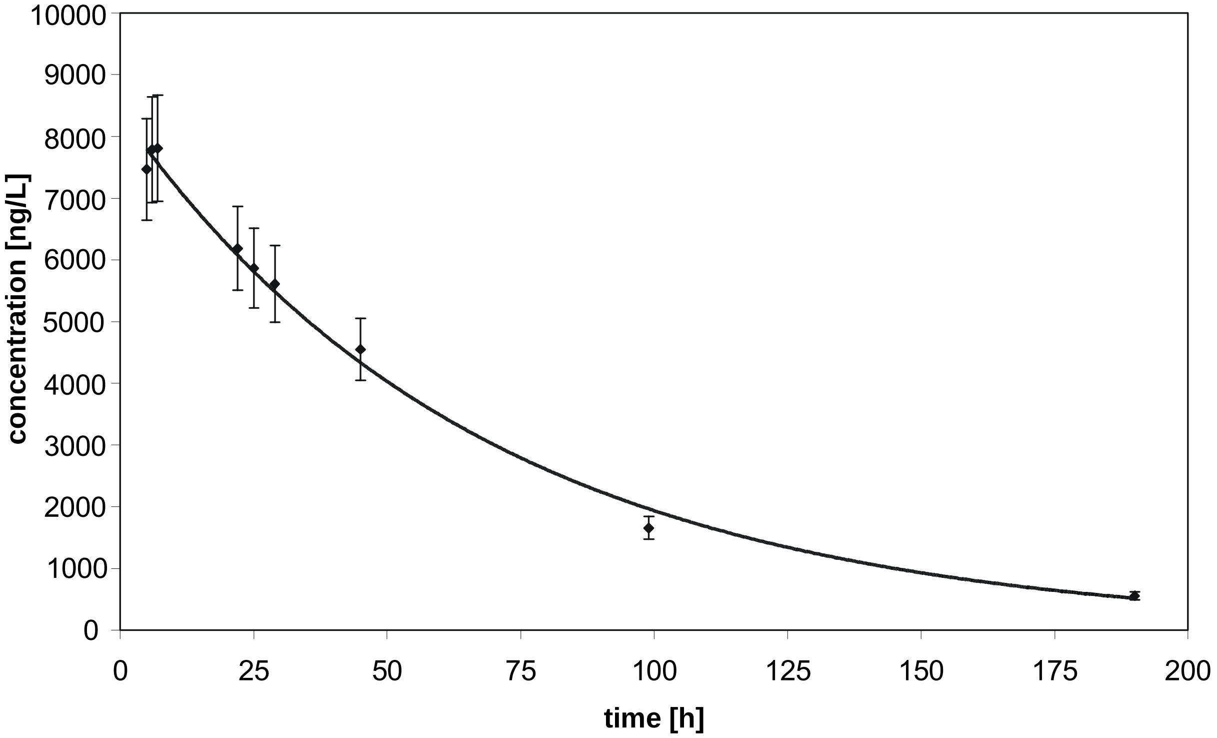
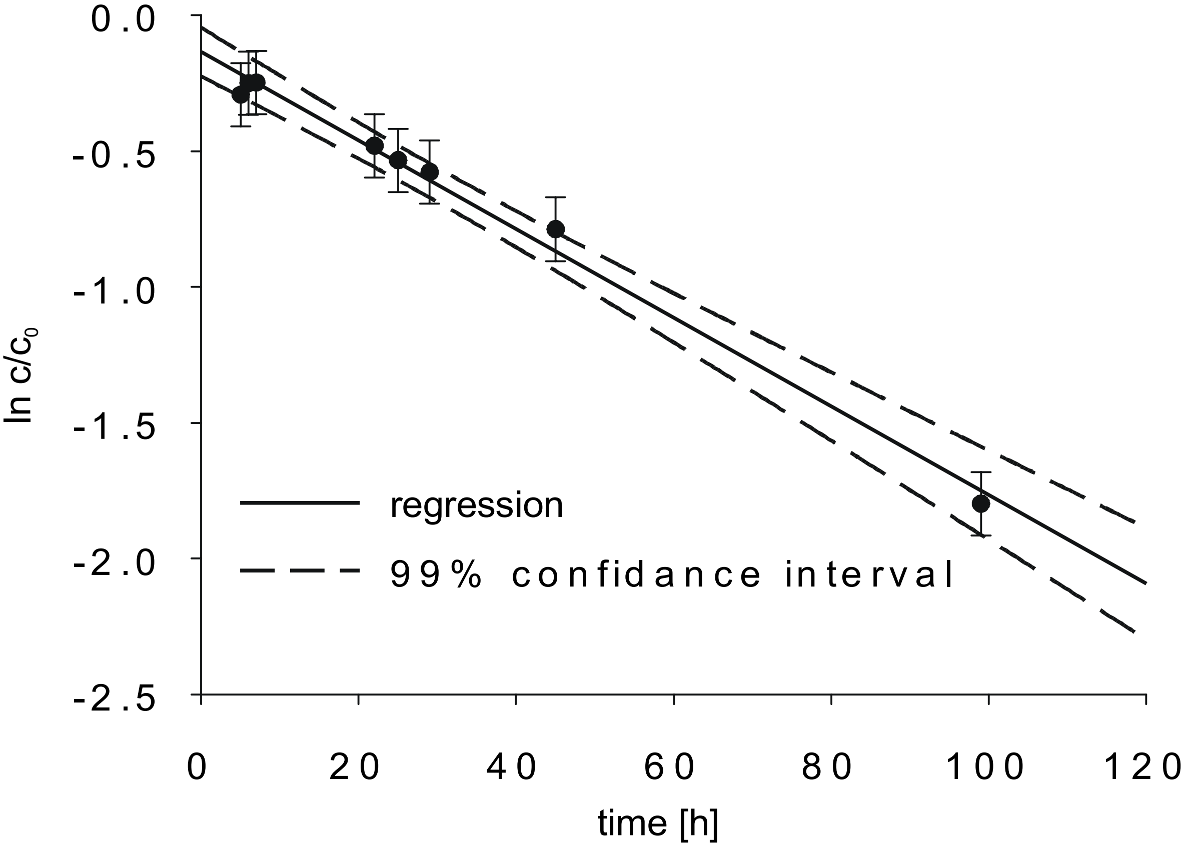


Figure 1.24 shows the natural logarithm of the concentration c divided by the starting concentration c_0 (ln c/c_0) versus time (t) plot. This plot provides a straight line with a very good regression. This confirms the assumption that the elimination of T*n*BP follows a first order degradation. From the slope of the regression line k the half-life ($t_{½}$) of this substance can be calculated from the equation (2):

$$t_{½} = \frac{\ln 2}{k} \qquad (2)$$

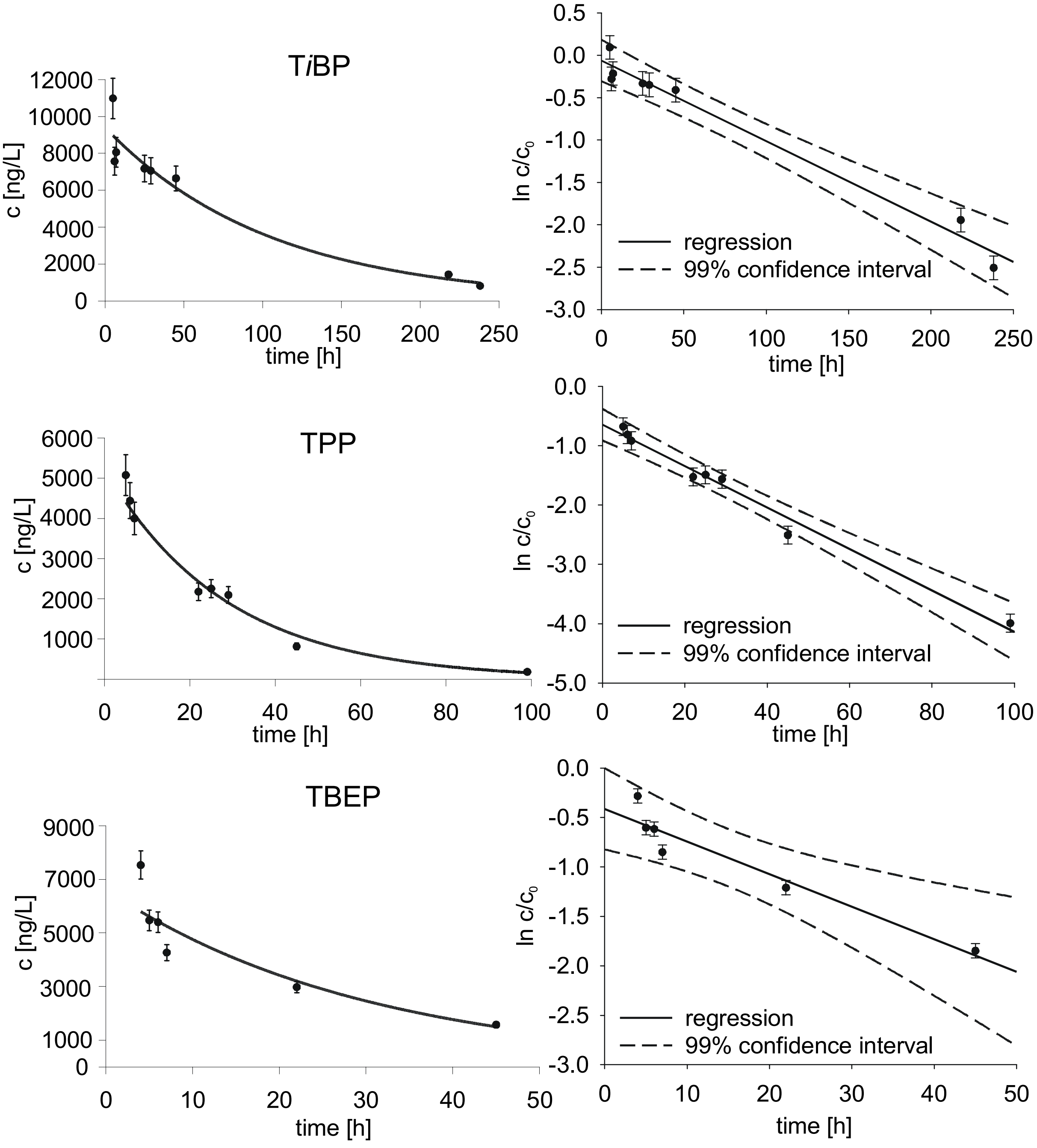
with $t_{½}$: half-life; k: slope

Figure 1.24 ln(c/c_0) versus time plot of T*n*BP (aerobic) Experiment



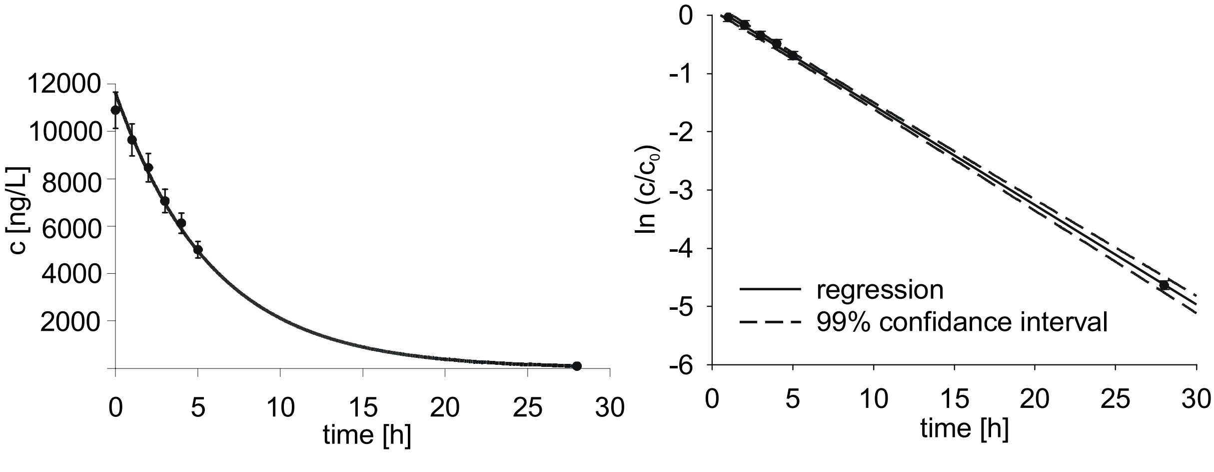
The calculated half-life for T*n*BP was 47 h. For T*i*BP and TPP similar plots were obtained (compare Figure 1.25) with good regressions for the concentration vs. time plots and the ln c/c_0 vs. time plots respectively. Due to matrix interferences that were significantly higher for those substances the respective regression lines were not as good as for T*n*BP though. Moreover TPP revealed a faster degradation as T*i*BP and T*n*BP. After 99 h the concentration in the sample extract was below the LOQ. Thus less data were received for the calculation of the respective half-life and the uncertainty of the result was slightly higher. For TBEP a first order degradation was observed as well (compare Figure 1.25). As TBEP also degraded very fast, the concentration in the sample extract was below the LOQ after 45 h, less data were achieved to study the elimination. The respective half-lives were 73 h for T*i*BP, 20 h for TPP and 21 h for TBEP.

Figure 1.25 Degradations curves of T*i*BP, TPP and TBEP as well as the respective ln (c/c_0) vs. time plot (aerobic experiment)



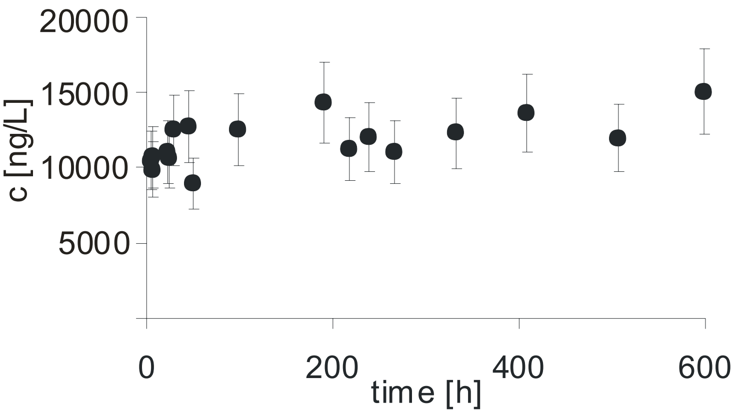
Because of the observed problems with the homogenous distribution of the organophosphate esters within the batch the experiment was repeated. Instead of spiking the sewage sludge directly, 2 L of tap water were spiked with the respective substances. After vigorous stirring 2 L of sewage sludge from a different STP as in the first experiment were added. The final concentrations of the respective flame retardants and plasticisers were 10,000 µg/L. As in the experiment described above the degradation was operated under aerobic conditions. Five samples were taken hourly and extracted with the described method. The last sample was extracted the next day after 28 h. In contrast to the first experiment a homogenous distribution of the substances was observed directly. Figure 1.26 displays the degradation curve for TBEP and the ln (c/c_0) vs. time plot. As in the first experiment a first order degradation was observed for TBEP with very good regressions for the different plots. The calculated half-life was in this case only 4 h. For the other non-chlorinated organophosphate esters similar plots as for TBEP were achieved. For T*i*BP only a slight reduction of the concentrations was observed during this experiment. Due to the poor regression of the first order degradation the calculated half-life is only indicative. The corresponding half-lives were 28 h for T*i*BP, 23 h for T*n*BP and 24 h for TPP.

Figure 1.26 Degradations curve for TBEP as well as the corresponding ln (c/c_0) vs. time plot (aerobic experiment)



For the chlorinated organophosphorus flame retardants TCEP, TCPP and TDCP no degradation was observed in both experiments as the measured concentrations for the respective substance was constant according to the accuracy of the analytical method. An example is given in Figure 1.27. Similar results were obtained for TCEP and TDCP.

Figure 1.27 Concentrations of TCPP in the first experiment (aerobic experiment)



An overview on the results for both experiments is given in Table 1.16.

Table 1.16 Overview on the results of both permanently aerated experiments. Results for T*i*BP from the second experiment are only indicative

Analyte	Experiment 1			Experiment 2		
	slope (k)	R²	half-life [h]	slope (k)	R²	half-life [h]
T*i*BP	0.0095	0.976	**73 ± 5**	0.025	0.524	**28**
T*n*BP	0.015	0.994	**47 ± 2**	0.030	0.995	**23 ± 1**
TBEP	0.033	0.923	**21 ± 3**	0.17	0.999	**4 ± 0.1**
TPP	0.035	0.983	**20 ± 1**	0.029	0.978	**24 ± 2**
TCEP	no elimination observed			no elimination observed		
TCPP	no elimination observed			no elimination observed		
TDCP	no elimination observed			no elimination observed		

Table 1.16 also displays that the elimination depends on conditions like dry mass concentrations. Whereas in the first experiment the undiluted activated sludge was used, the sludge in the second one was diluted 1:1 (v/v) with tap water. Other parameters as enzyme activity, oxygen content or temperature were not controlled. In the first experiment identical half-lives for TBEP and TPP were observed whereas in the second one TBEP was degraded significantly faster. Another important factor that apparently influences the half-lives for the particular alkylphosphates is the origin

of the used sludge. In the respective experiments sludge from two different STPs was used. The oxygen content in combination with the biological oxygen demand (BOD) and the dissolved organic carbon (DOC) respectively might influence the elimination of these substances as well, as T*i*BP, T*n*BP and TBEP were degraded faster in the second experiment than in the first one (compare figure 1.16). In the second aerated experiment the sewage sludge was diluted 1:1 (v/v) with tap water. Thus the DOC as well as the BOD might be lower in this system in comparison to the first experiment with undiluted sludge, especially in the beginning.

1.6.2.2 Results for the aerobic/anaerobic degradation experiment

For this experiment sludge from the same STP was used as in the first degradation experiment. As in the first aerated experiment a homogenous distribution of the analytes within the batch was observed after five hours. Figure 1.28 shows that for T*n*BP a significant reduction of the starting concentration was observed after 99 hours whereas in the permanently aerated experiment a noticeable degradation was detected already after 22 hours. The elimination of T*n*BP still follows a first order kinetic but the degradation processes was significantly slower than in the permanently aerated experiment. Similar results were obtained for T*i*BP. The elimination of TPP seems to be influenced by the changing conditions as a higher degradation rate was observed for the aerobic/anaerobic experiment. Due to the comparable poor linear regression of the ln c/c_0 vs. time plot for TBEP the calculated half-life is only indicative. Thus regarded to the uncertainty of the calculated half-life only a slight reduction of the degradation kinetic was observed. For the chlorinated flame retardants TCEP, TCPP and TDCP no elimination was observed. An overview on the results (half-life, linear regression coefficient (R^2) and slope (k) are given in Table 1.17.

Figure 1.28 Degradations curve for T*n*BP as well as the corresponding ln (c/c$_0$) vs. time plot of the aerobic/anaerobic experiment

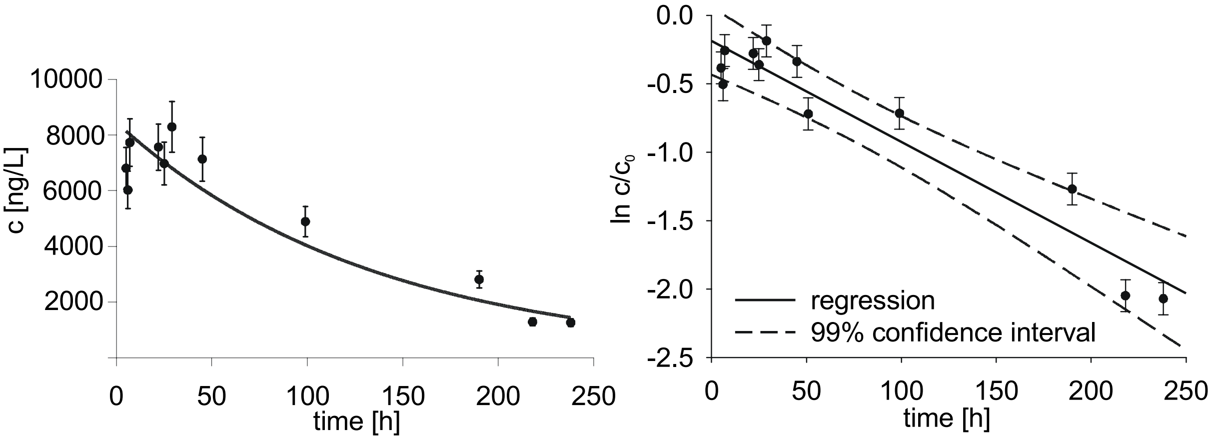


Table 1.17 Overview on the results of the aerobic/anaerobic experiment. Results for TBEP are only indicative

analyte	slope (k)	R²	half-life [h]
T*i* BP	0.0048	0.936	**144 ±16**
T*n* BP	0.0074	0.913	**94 ± 9**
TBEP	0.020	0.891	**34 ± 9**
TPP	0.063	0.993	**11 ± 1**
TCEP	no elimination observed		
TCPP	no elimination observed		
TDCP	no elimination observed		

The comparison between the aerobic and aerobic/anaerobic experiment applying the same sewage sludge indicates that the non-chlorinated alkylphosphates are degraded faster under a permanently aeration. Apparently under anaerobic conditions no elimination might be observed for T*i*BP and T*n*BP and to some extend for TBEP as half-lives in the aerobic/anaerobic experiment are twice as long as in the aerobic one. Moreover T*n*BP was degraded faster than T*i*BP. A similar elimination behaviour was noticed for those two substances in STPs C, D and E. TPP was eliminated faster in the aerobic/anaerobic than in the aerobic experiment. This might give hints to different elimination mechanism. In the same experiments the elimination behaviour of the polycyclic musk fragrances HHCB and AHTN were studied as well. As for TPP a faster degradation was observed in the aerobic/anaerobic experiment. The two experiments demonstrate that the differences of the elimination efficiency of the non-chlorinated alkylphosphates T*i*BP, T*n*BP and TBEP in STPs might depend on the residence time in the aeration tank under aerobic conditions. For the reduction of nitrogen loads in wastewater, simultaneous denitrification is applied inter alia for wastewater treatment. To some extend the conditions in this process are comparable to the conditions in the aerobic/anaerobic experiment as it is carried out alternating between aerobic and anaerobic conditions within the aeration tank. As the respective substances are degraded faster under aerobic than under aerobic/anaerobic conditions, elimination rates for T*i*BP, T*n*BP and TBEP might be lower in STPs with simultaneous denitrification than in other STPs operating with separated denitrification under similar conditions such as the residence time or the concentrations of dry solids. Furthermore the elimination efficiency for these substances in STP might be increased by extended aeration.

1.6.3 Identification of Metabolites

As possible degradation pathway of the alkylphosphates the dealkylation is proposed for the respective organophosphate esters. Anderson *et al.*[44] studied the fate of triphenylphosphate in soil. Diphenylphosphate (DPP) was detected as main metabolite whereas monophenylphosphate (MPP) was not identified. Chapman *et al.*[45] identified bis-(2-chloroethy) phosphate (BCEP) and 2-chloroethanol as main metabolites of TCEP in studies on the metabolism of TCEP by human and rat liver preparations. Similar degradation products were thus expected for the other selected organophosphate esters. The respective sludge samples were analysed for possible metabolites at the end of the degradation experiment (after 600 h).

For the detection and identification of possible metabolites of the respective organophosphate esters, 100 mL from each sludge were extracted by solid phase extraction using DVB-hydrophobic Speedisks (Mallinckroth Baker, Griesheim Germany; 45 mm diameter). The samples were passed through the disks at a flow rate of 200 mL/min (vacuum). The Elution was successively performed with 8 mL *n*-hexane, MTBE, ethyl acetate and acetone each. The residual water was removed from the organic phase by freezing the samples overnight at –20°C. The volume of the dried extracts was reduced to 1 mL with a Syncore concentration unit (Büchi, Switzerland) at 60 °C. After adding 10 mL of toluene the extracts were concentrated to a final volume of 1 mL.

For the determination of possible metabolites the extracts were fractionated with dried silica. 1 g of dried silica (105 °C, 24 h) was filled in an 8 mL glass column between two PTFE-frits. After conditioning with 8 mL *n*-hexane, 1 mL of the sample extract was applied to the column. The elution was performed with 8 mL *n*-hexane, *n*-hexane/MTBE (95:5 v/v, 90:10 v/v, 80:20 v/v, 70:30 v/v and 50:50 v/v respectively), MTBE, ethyl acetate and acetone each. Each fraction was concentrated to 1 mL. After adding 10 mL of toluene, the volume was reduced to a final volume of 1 mL and the samples were devided into two sub samples of 0.5 ml each.

For GC-MS analysis 100 µl TMSH solution (Macherey–Nagel, Düren, Germany) were added to 0.5 mL of the sample extracts for derivatisation (2 h, 70 °C) as it was expected that possible metabolites are more polar than the respective organophosphate. Possible metabolites are hydrolysis products (dialkylated/arylated and monoalkylated/arylated phosphate esters) of the respective compounds are discussed.

The samples were analysed on a gas chromatography system with mass spectrometric detection (DSQ Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. The PTV (4 µl injection volume) was operated with the following temperature program: 115 °C [0.05 min, 20 mL min^{-1} He] $\rightarrow$ 12 °C s^{-1} (splitless) $\rightarrow$ 280 °C [1.2 min] $\rightarrow$ 1 °C min^{-1} $\rightarrow$ 300 °C [7 min] (cleaning phase)

The GC separation was performed using a DB5-MS column (J&W Scientific, Folsom, CA, USA); length: 15 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 100 °C [2 min] $\rightarrow$ 5 °C min^{-1} $\rightarrow$ 280 °C [7 min] using He (5.0) as carrier gas with a flow of 1.3 mL min^{-1}. The mass spectrometer was used with electron impact ionization with 70 eV ionization energy. The MS was operated in scan mode (scan range 95-600 amu, scan rate 555.3 amu/s, 1.072 scans/s).

Some of the metabolites are commercially available (dibutylphosphate (DBP), diphenylphosphate (DPP)). Bis-(butoxyethyl) phosphate (BBEP), bis-(chloroethyl) phosphate (BCEP) and bis-(chloro*iso*propyl) phosphate (BCPP) were synthesized from phosphorus oxytrichloride and the respective alcohols.

Each of the respective fractions was analysed for the respective methylated dialkylphosphate. Only in the ethyl acetate fraction of the aerated degradation experiment methylated BCEP was detected. This was surprising as the measured concentrations during the experiment were almost stable. The identification was performed by comparing the mass spectral data and retention time of the chromatogram of the synthesised BCEP (reference) and of the sample (ethyl acetate fraction). Figures 1.29 and 1.30 display the identification of BCEP. Apparently the retention time and the mass spectrum of the synthesised BCEP are concordant with the data obtained from the sample. Thus BCEP is adequately identified. An interpretation on the mass fragment is given in chapter 8.2.1

Figure 1.29 Comparison of the retention times of BCEP obtained from the reference and the chromatogram of the ethyl acetate fraction

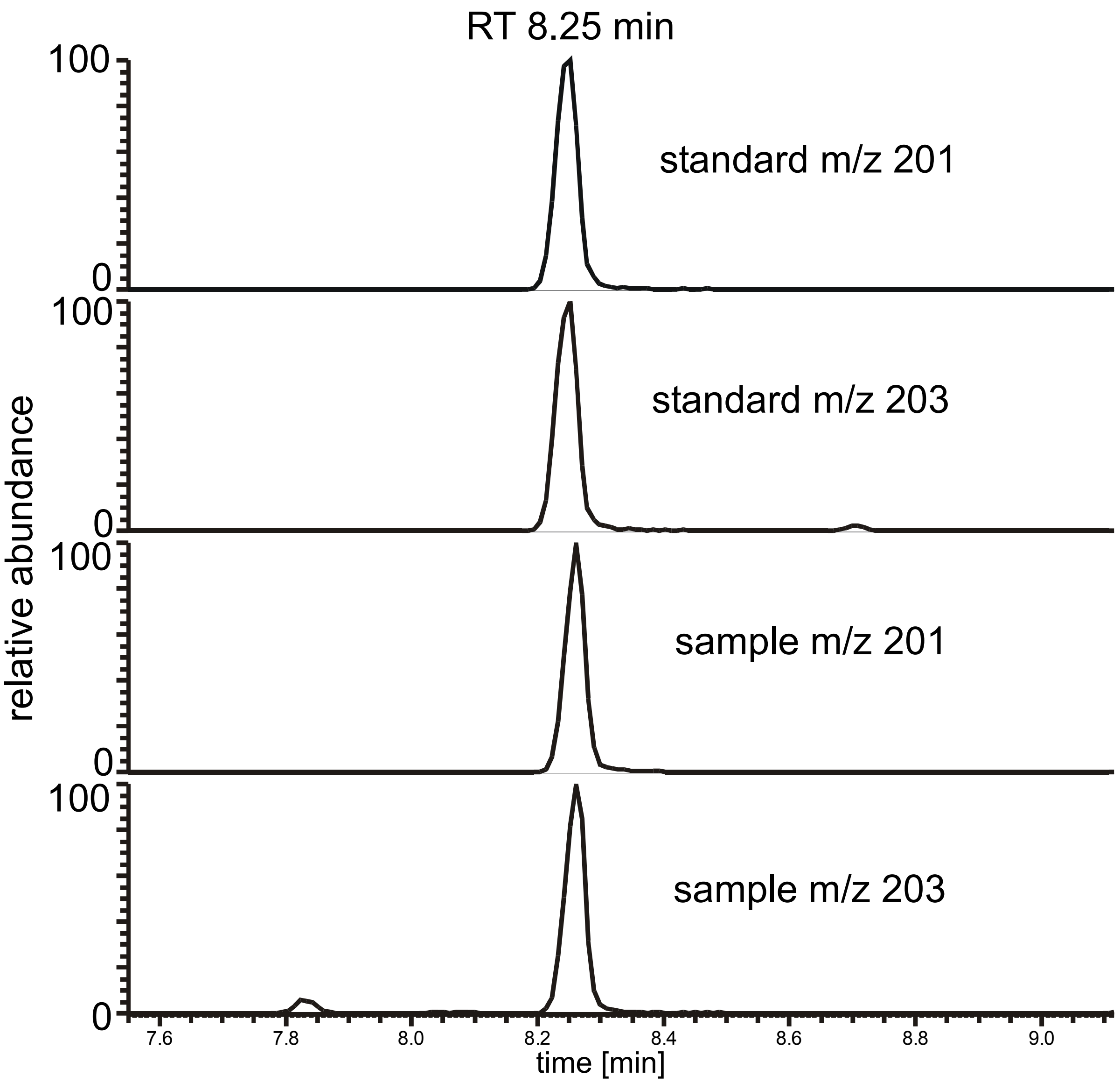
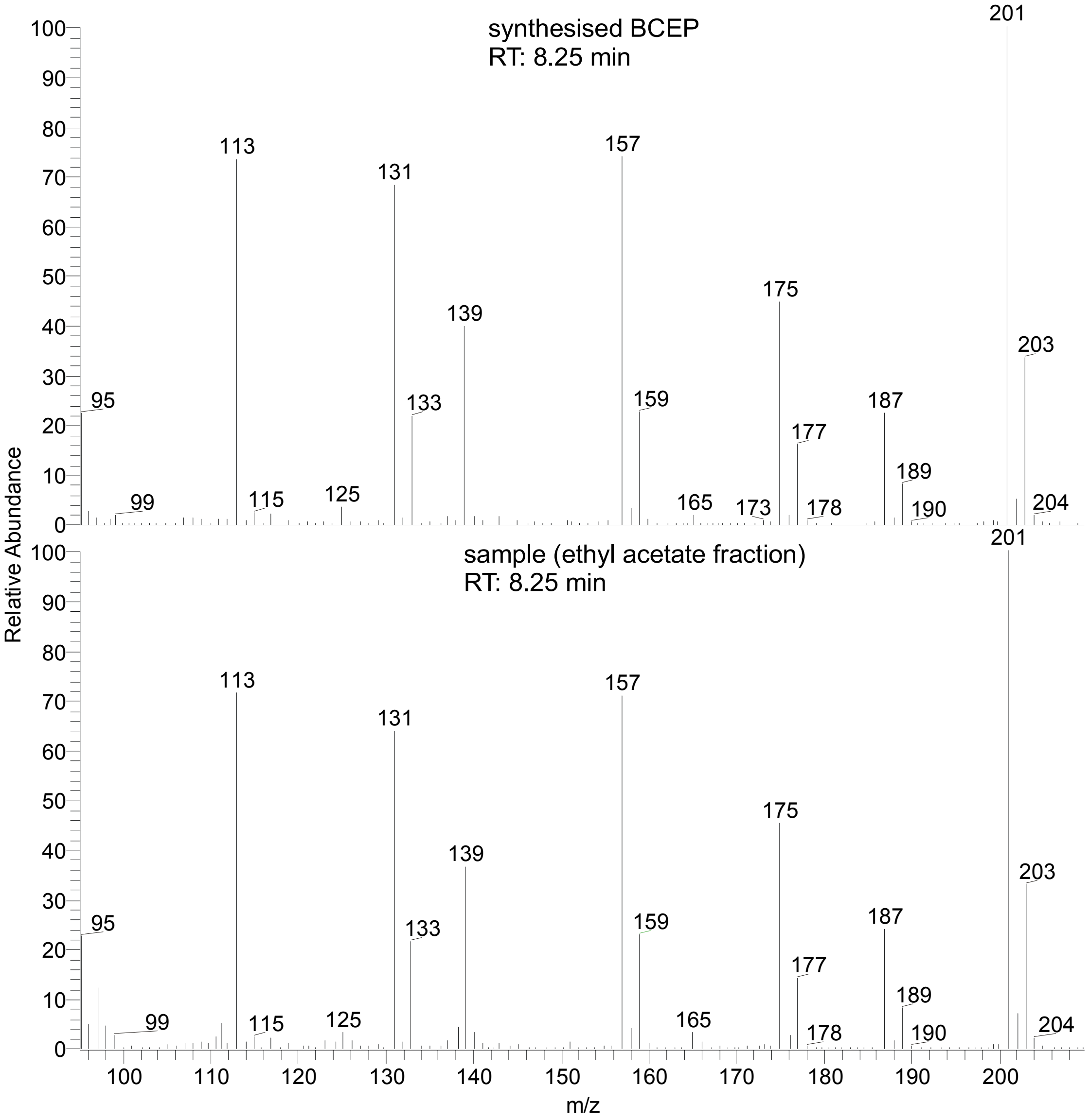


Figure 1.30 Comparison of the mass spectral data of BCEP obtained from the reference and the chromatogram of the ethyl acetate fraction



No metabolites of the other selected organophosphates were identified. This might have two reasons. On the one hand the respective organophosphates were not degraded under the conditions of the experiments. This may be the case especially for TCPP and TDCP as these substances are very persistent. On the other hand the hydrolysis to the mono-alkylated organophosphates and the complete ester cleavage to phosphate and the respective alcohol should be discussed. This is considered especially for the non-chlorinated organophosphate esters. The concentrations for most of the non-chlorinated organophosphates were below the respective LOQ after 100 h in the aerated and 250 h in the aerobic/anaerobic experiment respectively.

This means that after 600 h most of these substances might be degraded to the mono-alkyltaed organophosphates or have completely been hydrolysed.

1.7 *Conclusions on the behaviour of organophosphate esters in STPs*

While the chlorinated organophosphates such as TCPP, TCEP and TDCP were hardly eliminated in the wastewater treatment process (trickling filters and activated sludge), the non-chlorinated derivatives, i.e., T*i*BP, T*n*BP, TBEP, TPP and EHDPP were partially eliminated.

Additionally an extremely high day-to-day variability was detected for the inflow concentrations of all organophosphates in STPs A and B, while other compounds such as musk fragrances or triclosan, which were analysed from the same samples, remained constant throughout the weeks. In the case of TCPP lower concentrations were detected on weekends in STP B. The studies at STP C, D and E have demonstrated that the concentrations and loads of the selected organophosphates were strongly related to the wastewater flow. It was also demonstrated that the selected organophosphate esters are emitted by a multitude of sources.

The elimination mostly occurred in the main aeration basin, which may be attributed to sorption to sludge as well as biodegradation processes. The degradation experiments in batch reactors demonstrated that except from TPP the half-lives for the non-chlorinated alkylphosphates were lower under aerobic than under aerobic/anaerobic conditions. This indicates that different degradation processes are relevant for the elimination of T*i*BP, T*n*BP and TBEP on the one hand and TPP on the other hand. Moreover these experiments showed that the elimination process is influenced by many parameters such as the dry mass concentration or the origin of the sludge. In the aerated degradation experiment BCEP was identified as metabolite of TCEP after 600 h of incubation.

At STPs A and B the efficiency of the treatment process for the organophosphate esters was comparable. Thus the type of construction (single stage or double stage biological treatment) of the STP was not relevant for the elimination of these substances.

The elimination efficiency corresponds to the wastewater inflow. Lower elimination rates were observed for increased wastewater flows because of rainfall at STPs C, D and E.

In the observed STPs the elimination efficiency for the non-chlorinated organophosphate esters was apparently lower for the trickling filter process than for the activated sludge process.

Additional treatment of process water from sludge dewatering might reduce the effluent loads of the samples especially for smaller STP with lower elimination rates as the larger ones although the process water flow is low in comparison to the total wastewater inflow of STPs.

2 Organophosphorus flame retardants and plasticisers in surface waters

2.1 *Introduction to surface waters*

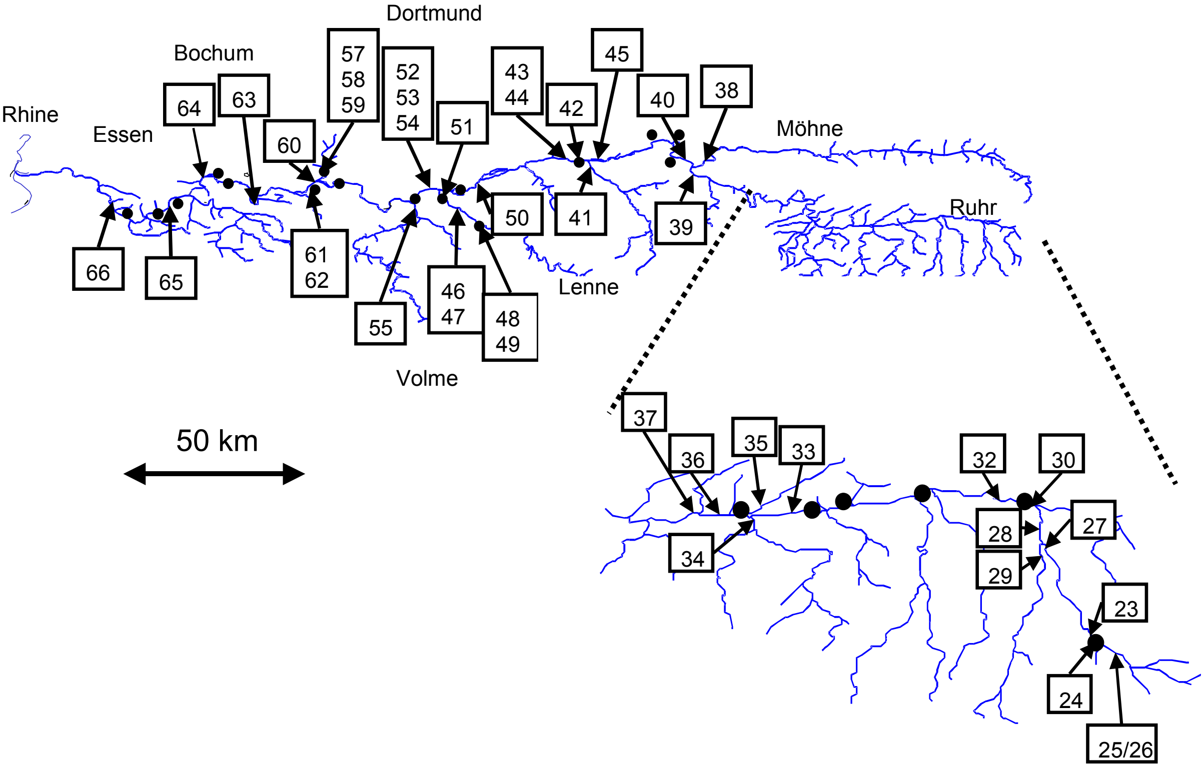
Some of the organophosphorus flame retardants and plasticisers, especially TCPP, have been identified in surface waters before. But only in a few studies they have been quantified properly (Kolpin *et al.*[46], 2002, Fries and Püttmann[47], 2001). The way of introduction of these compounds into surface water is supposed to occur via sewage treatment plants as discussed by Fries and Pittman (2003)[48] as well as by Bester[49] (2005) and Meyer *et al*[50] (2004) (compare preceding chapter as well).

The experimental area of the Ruhr was chosen as this river supplies several million inhabitants of the Ruhr megalopolis with water for drinking water extraction. On the other hand this river is used to discharge the wastewater from two million inhabitants. It is protected since the third decade of the last century by sewage treatment plants and additionally wastewater is preferably introduced not into the Ruhr but into other rivers such as the river Emscher wherever possible.

The river Ruhr is a small river (in comparison to e.g. the Rhine or the Elbe) with 2.2 billion m^3 water flow annually near the mouth (Hattingen). The spring is located in the moderately populated "Sauerland" area. It passes several lakes until it reaches the industrial Ruhr area in which it feeds into the purification plants that supply drinking water to about 5 million inhabitants.

After the river has passed those plants that are located near the cities Dortmund (near sample station 50), Bochum (in the vicinity of sample station 56) and Essen (near sample station 63), it reaches the river Rhine (compare Figure 2.1). Several other tributaries (such as the River Möhne) are also used to control the water flow in the Ruhr in a way that the water extraction plants can operate continuously.

Figure 2.1 Sample stations in the river Ruhr system with the respective sewage treatment plants indicated as •



2.2 *Materials and Methods*

During the sampling in September 2002 the water flow of the river Ruhr was about 25-28 m^3/s, which is less than the average. This was due to the fact that the sampling period was in the middle of a dry period with no rainfall at all. This period was chosen, to be able to perform back calculations. Rainfall can hardly be calculated as the documentation on rainfall is done with low spatial resolution. The exact location and a characterisation of sampling sites are shown in Table 2.1.

Table 2.1 Location and characterisation of the selected sampling sites

Code	Characteristics	km	Date
23	Effluent of STP Niedersfeld (4000 inhabitants)	211	17.09.02
24	Plume of STP Niedersfeld	211	17.09.02
25/26	Ruhr upstream of STP Niedersfeld	213	17.09.02
27	Ruhr upstream of tributary Neger		17.09.02
28	Ruhr downstream of tributary Neger, concrete plant (no visible effluent)		17.09.02
29	Tributary Neger		17.09.02
30	River Ruhr		17.09.02
31	Field blank		17.09.02
32	River Ruhr		17.09.02
33	Dam/Lock, River Ruhr (Heinrichstal)		17.09.02
34	Tributary Henne		17.09.02
35	Tributary Gebke		17.09.02
36	STP Meschede 1 (downstream of Tributaries Henne and Gebke)		17.09.02
37	STP Meschede 2		17.09.02
38	Tributary Möhne	140	17.09.02
39	Downstream of STP Wildshausen-Arnsberg (98,000 inhabitants) upstream of Möhne	145	17.09.02
40	Downstream of tributary Möhne	138	17.09.02
41	Tributary Hönne	117	17.09.02
42	Ruhr downstream of STP Menden-Bösperde (120,000 inhabitants)	116	17.09.02
43	Plume of STP Menden-Bösperde	115	17.09.02
44	Plume of STP Menden-Bösperde	114	17.09.02
45	River Ruhr upstream of tributary Hönne and STP Menden-Bösperde	118	17.09.02
46/47	Tributary Lenne (Motorway) (upstream Hagen STPs)	93	19.09.02
48	Effluent of STP Hagen Fley (17,000 inhabitants)	92	19.09.02
49	Tributary Lenne upstream of STP Hagen Fley (17,000 inhabitants)	94	19.09.02
50	River Ruhr at Schwerte upstream of Tributary Lenne and STPs Hagen	95	19.09.02
51	Effluent STP Hagen Boele 17000 inhabitants (44,000 inhabitants)	92	19.09.02
52/53/54	Ruhr downstream of STP Hagen and Tributary Lenne	90	19.09.02
55	Tributary Volme	86	19.09.02
56	Ruhr upstream of STP Ölbachtal, downstream of STP Witten (120,000 inhabitants)	69	19.09.02
57/58/59	Effluent of STP Ölbachtal (160,000 inhabitants)	68	19.09.02
60	Lake Kemnaden, bight into which the effluent of STP Ölbachtal discharges (leisure boat harbour)	67	19.09.02
61	Lake Kemnaden after introduction of the effluent of STP Ölbachtal downstream of no 60	66	19.09.02
62	Lake Kemnaden after introduction of the effluent of STP Ölbachtal downstream of no 61	65	19.09.02
63	Ruhr downstream of lake Kemnaden downstream of STP Hattingen (75,000 inhabitants)	60	19.09.02
64	Ruhr downstream of STP Burgaltendorf, Steele and Rellinghausen (serving 36,000, 54,000 and 51,000 inhabitants respectively	56	19.09.02
65	Western end of lake Baldeney, downstream of STP Kupferdreh (73,000 inhabitants)	37	19.09.02
66	Downstream of STP Kettwig and STP Werden (22,000 and 29,000 inhabitants)	18	19.09.02

1 L of each water sample was immediately extracted with 10 mL toluene after adding an aliquot of internal standard solution (T*n*BP d_{27}). The extraction (30 min) was

performed by vigorous stirring with a teflonised magnetic stirrer. After a sedimentation phase of 20 min the organic phase was separated from the aqueous one and the residual water was removed from the organic phase by freezing the samples overnight at –20 °C. The samples were concentrated with a rotary evaporator at 60 °C and 60 mbar to a final volume of 1 mL.

As TCEP was not recovered very well by liquid liquid extraction an alternative solid phase extraction utilising DVB-hydrophobic Speedisks (Mallinckroth Baker, Griesheim, Germany) with 45 mm diameter was established. A solid-phase extraction manifold (IST Grenzach Wyhlen, Germany) with PTFE stopcocks and needles was used. Before the extraction the SPE-cartridges were rinsed successively with methyl *tert.* butyl ether (MTBE) and toluene. Afterwards the disks were conditioned with methanol and water. The water samples were passed through the disks with a flow rate of 200 mL/min. Successively, the analytes were eluted with MTBE and toluene and an aliquot of Internal Standard T*n*BP d_{27} solution was added to the eluate. The residual water was removed from the organic phase by freezing the samples overnight at –20°C. The samples were concentrated with a rotary evaporator at 60°C and 60 mbar to a final volume of 1 mL.

The samples were analysed on gas chromatography system with mass spectrometric detection (“Trace” Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. The PTV (1 µl injection volume) was operated in splitless mode with the following temperature program: 90°C [0.1 s] $\rightarrow$ 14.5°C s^{-1} $\rightarrow$ 280°C $\rightarrow$ 5°C s^{-1} $\rightarrow$ 320°C [5 min] (cleaning phase). The GC separation was performed using a DB-5MS column (J&W Scientific, Folsom, CA, USA); length: 30 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 90°C [2 min] $\rightarrow$ 10°C min^{-1} $\rightarrow$ 280°C [15 min] using He (5.0) as carrier gas with a flow of 1.5 mL min^{-1}. The mass spectrometer was used with electron impact ionisation with 70 eV ionisation energy. The MS was operated in selected ion monitoring (SIM) mode with the detector (photo multiplier) set to a voltage of 500 V.

The different organophosphates were detected by means of their mass spectral data and the respective retention time. Both methods were validated for quantitative measurements. Recovery rates were 89 to 107 % with 11-29 % RSD (see Table 2.2). Only TCEP was not recovered very well by this LLE procedure and standard deviations were high. Thus all presented data for TCEP are considered to be indicative data rather than "true" data. The SPE method gave good recoveries for

TCEP, though. At some places this method was employed in parallel to the LLE procedure, which gave similar results after correction for recovery rates. Full quality data of the method obtained from three replica extractions at eight different concentrations (2, 10, 20, 100, 200, 1000, 2000 and 10000 ng/L) is given in Table 2.2.

Table 2.2 Quality assurance data for the determination of organophosphates from water for the respective compounds; RSD: relative standard deviation; LOQ: limit of quantification

Compound	Retention time [min]	Analytical Ion [amu]	Verifier Ion [amu]	Recovery Rate [%]	RSD [%]	LOQ [ng/L]
T*i* BP	10.56	155	211	107	12	6.3
T*n* BP	12.17	155	211	98	19	10
TCEP (LLE)	13.50	249	251	31	33	20
TCEP (SPE)	dto	dto	dto	67	15	12
TCPP	13.85	277	279	101	14	4.9
TDCP	18.92	381	379	95	3	14
TPP	19.61	325	326	93	27	10
TBEP	19.57	199	125	89	19	6.4

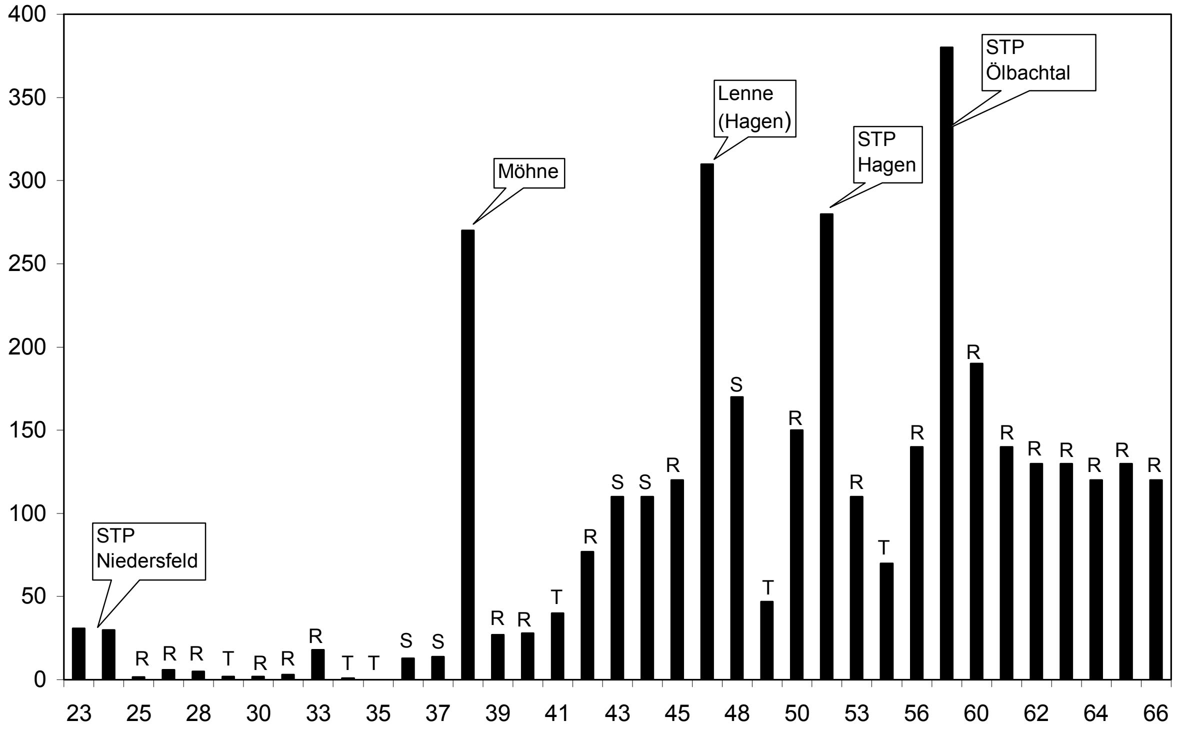
2.3 *Results and Discussion to surface waters*

2.3.1 Organophosphorus flame retardants

In Figure 2.2 the distribution of TCPP concentrations in the river Ruhr, its main tributaries as well as in several STP effluents is shown. The concentrations of TCPP in the river Ruhr varied between 20 and 200 ng/L. All STPs, which were sampled, contribute considerably to the load of TCPP in the river as typical concentrations of 50-400 ng/L were analysed in the effluents. It is no surprise that samples from upstream of STP Niedersfeld (no. 25, 26) were very low in concentration, as no inflow whatsoever is known between that place and the spring of the river, which is at that place a small creek. It is slightly surprising that high concentrations were measured in the tributary Möhne (300 ng/L), which is generally supposed to be little affected by STP effluents as only few towns with little population and no significant industry are located at this river. Typically the concentrations of personal care compounds, which can be taken as some indicator for wastewater introduction are very low (Bester[51], 2005). On the one hand tributary Lenne (46/47) often holds contamination patterns that are connected to STP effluents. The STPs Hagen as well as Bochum Ölbachtal introduced high concentrations of TCPP into the Ruhr. On the other hand tributary Volme (no. 55) showed rather low ones. Interestingly enough, the high concentrations of 100 ng/L were reached at station no. 42 (upstream of Fröndenberg) before the Ruhr enters the densely populated and industrialised Ruhr area. These concentrations were constant at about 100-150 ng/L until the river passes Essen and Mülheim and a few kilometres before it reaches its mouth at the river Rhine in Duisburg. On this way it passes several lakes (such as Lake Kemmnaden 61-63). The lakes did not seem to change the concentrations though they are generally supposed to have a "cleaning effect".

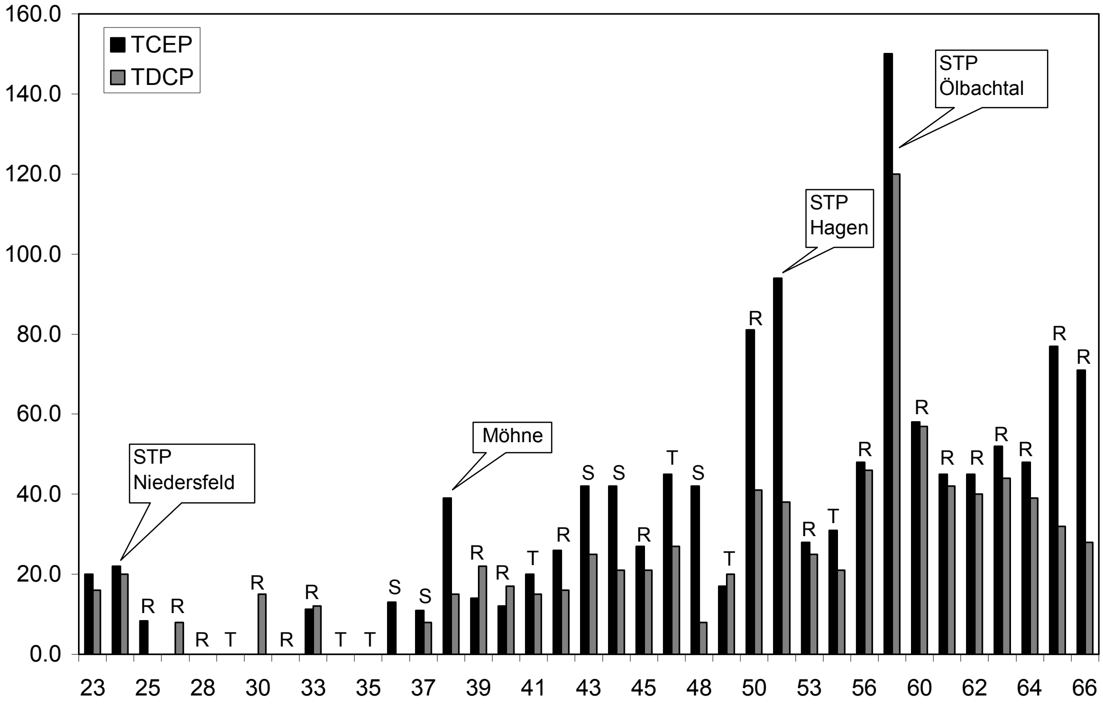
It is interesting to note that the main STPs, which were sampled, gave quite different emissions of TCPP per capita: STP Niedersfeld: 11µg/d per capita; STP Menden: 34 µg/d per capita; STP Hagen-Fley: 31 µg/d per capita and STP Bochum-Ölbachtal: 223 µg/d per capita.

Figure 2.2 Concentrations [ng/L] of TCPP in river Ruhr water (R) as well as some tributaries (T) such as rivers Möhne and Lenne and some sewage treatment plants effluents (S) such as STP Niedersfeld, Hagen and Bochum-Ölbachtal. Samples 57-59 are displayed as average as well as 52-54 and 46/47.



Data on TCEP (indicative) and TDCP basically show a similar distribution, with again high values in tributary Möhne, especially for TDCP. All concentrations are lower than TCPP, though. The Final concentrations near the mouth of the river Ruhr for TCEP and TDCP were about 50 ng/L. The concentrations in STP effluents ranged from 5-130 ng/L TCEP and 20-120 ng/L TDCP (Figure 2.3).

Figure 2.3 Concentrations [ng/L] of TCEP and TDCP in river Ruhr water (R) as well as some tributaries (T) such as rivers Möhne and Lenne and some sewage treatment plants effluents (S) such as STP Niedersfeld, Hagen and Bochum-Ölbachtal. Samples 57-59 are displayed as average as well as 52-54 and 46/47.

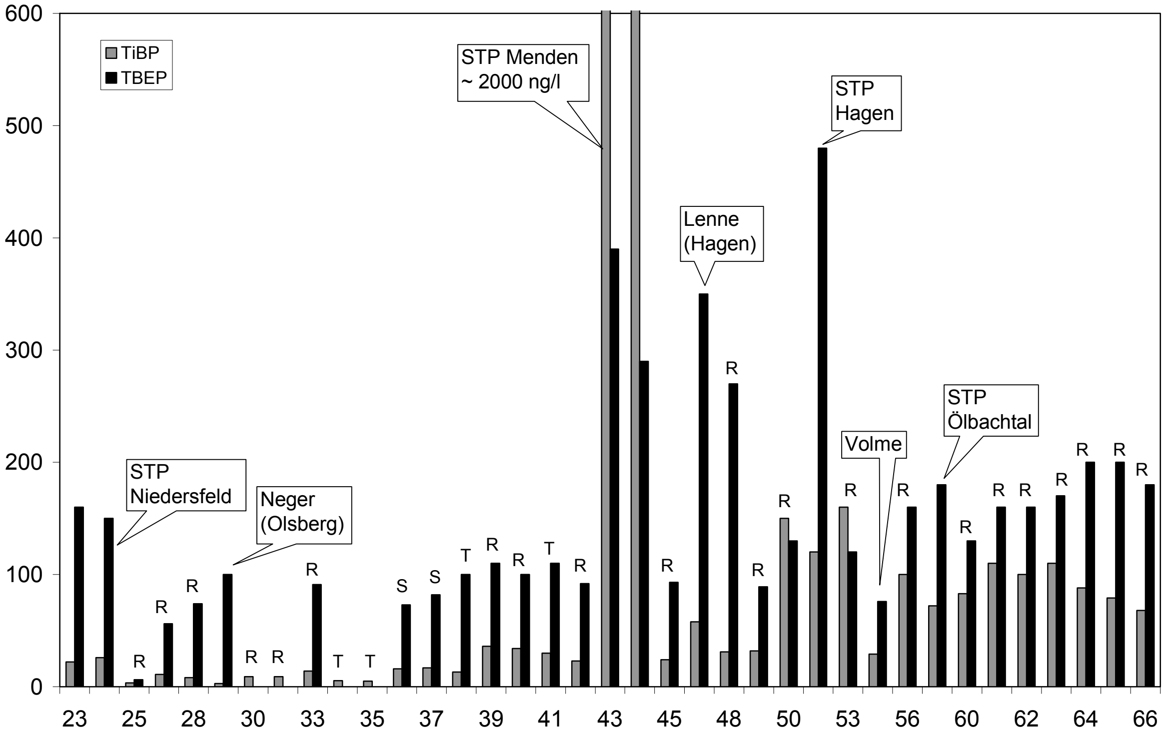


The concentrations especially of TCPP were much too high to be caused by electronic equipment like in the experiment of Carlsson *et al.* (2000). Thus other applications which consume higher amounts such as polyurethane foam plates or liquid polyurethane foam spray are probably more relevant. No data on other sources can be obtained from the literature. On the one hand there were some discussions on emissions of textile industries (Prösch *et al.*[52], 2000) but on the other hand the producers of these compounds state that up to their knowledge TCPP is not utilised in textiles (CEFIC, 2002).

2.3.2 Organophosphorus plasticisers

The concentrations of T*i*BP and TBEP were similar to TCPP (10-200 ng/L) but in selected samples the concentrations were considerably higher (compare Figure 2.4). The concentrations of TBEP ranged up to nearly 500 ng/L in several STP effluents. T*i*BP reached even 2,000 ng/L in the effluent of STP Menden near Fröndenberg. For these compounds only the direct STP discharges and the tributary Lenne were relevant, other tributaries such as the river Möhne, which is a major source for the chlorinated compounds, were not dominant for the plasticisers. Interestingly enough, high concentrations (~ 100 ng/L) for TBEP appeared from sample no. 33 (dam/lock in the river Ruhr with several small STPs between 32 and 33) and are then stable for some time at this concentration. Again tributary Volme (no. 55) was rather uncontaminated. During the passage of the densely populated Ruhr area the concentrations of TBEP rose until they reached a stable level of about 200 ng/L near its mouth. STP Bochum-Ölbachtal did not contribute to the contamination of the river with TBEP.

Figure 2.4 Concentrations [ng/L] of TBEP and T*i*BP in river Ruhr water (R) as well as some tributaries (T), e.g., the river Lenne and some sewage treatment plants effluents (S) such as STP Niedersfeld, Hagen and Bochum-Ölbachtal. Samples 57-59 are displayed as average as well as 52-54 and 46/47.

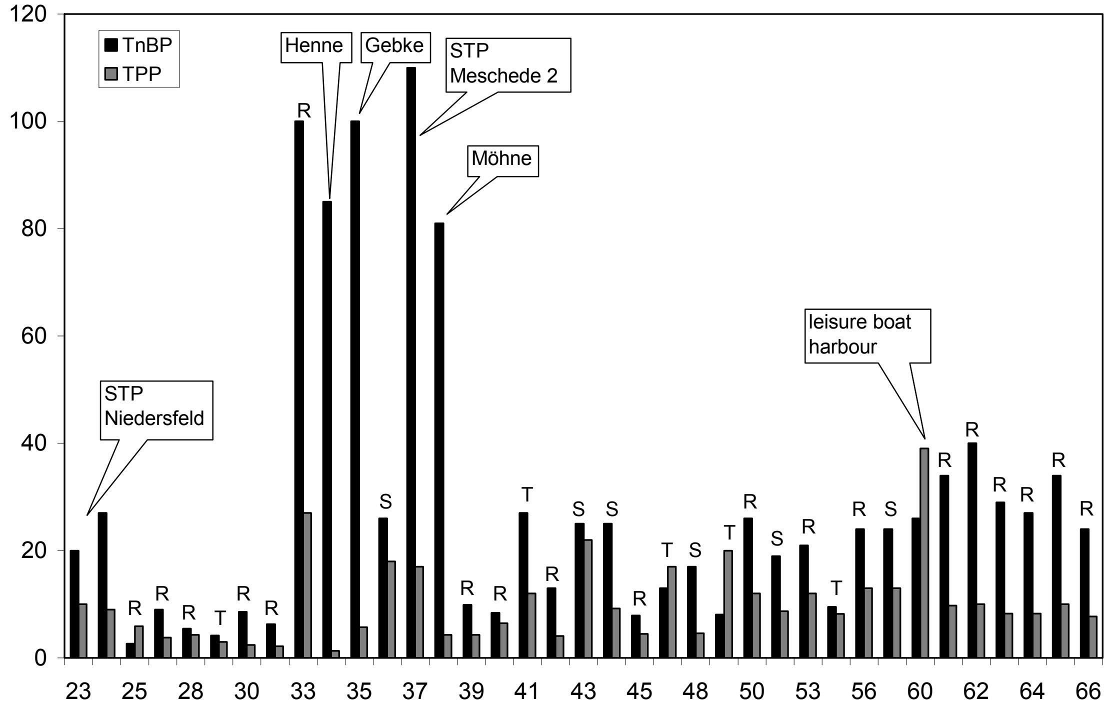


T*i*BP on the other hand exhibited low concentrations <LOQ-25 ng/L on all samples from the upper reaches of the river including STP effluents. The concentrations increased at Arnsberg (no. 37) and huge concentrations were introduced from STP Menden (no. 43, 44) thus leading to elevated concentrations (150 ng/L) in the Ruhr near Schwerte (no. 50), where the raw water for purification for the drinking water supply of the city of Dortmund is abstracted from the river. Neither the tributary Lenne nor the tributary Volme exhibited higher concentrations of T*i*BP than the river Ruhr itself. In the effluent of STP Ölbachtal no elevated levels were determined. The concentrations of T*i*BP were stable from Schwerte to the mouth of the river at around 100 ng/L.

For T*n*BP and TPP lower concentrations were determined in the whole experiment (compare Figure 2.5). T*n*BP reached its highest concentrations of 110 ng/L upstream between Olsberg and Meschede (no. 33-35; 37) mainly in the tributaries Henne and Gebke as well as in the tributary Möhne. Otherwise the concentrations were 30-40 ng/L with the highest concentrations downstream near the mouth.

The highest concentration (40 ng/L) of TPP was detected in a harbour for leisure boats in Lake Kemnaden (no. 60), while some STP effluents had concentrations of 10-30 ng/L. Thus generally the concentrations of TPP are low in comparison to the other organophosphates.

Figure 2.5 Concentrations [ng/L] of TPP and T*n*BP in river Ruhr water (R) as well as some tributaries (T) such as the river Möhne and some sewage treatment plants effluents (S) such as STP Niedersfeld, Hagen and Bochum-Ölbachtal. Samples 57-59 are displayed as average as well as 52-54 and 46/47.



2.3.3 Temporal variability

A temporal comparison was performed by comparing the results from the samples from September to samples from July. These data are shown in Table 2.3. Since the hydrodynamic is not exactly the same for these two periods the results show some differences. The concentrations for T*i*BP and also of TCPP are very similar in both sets. Higher variance is exhibited for T*n*BP. TCEP was determined with a high standard deviation. This may be the main reason, why these values show some variance. TDCP, TBEP and TPP are near the detection limits especially in the first sampling series. Basically all variations are in the order as naturally experienced in such rivers. Thus no variations due to anthropogenic activity are determined. This can be hold for short time periods, e.g., months only. Long term studies obtained from the Institute of Water Research, Schwerte, in which concentrations of TCEP and TBP have been determined over a period of about 7 years revealed a significant variance on the amounts of the selected compounds as documented in Figure 2.6 (Andresen *et al.*, 2005)

Figure 2.6 Occurence of tributylphosphate (TBP) and tris-(2-chloroethyl)phosphate in the River Ruhr, location Hengsen (data: Wasserwerke Westfalen GmbH; Monitoring: Westfälische Wasser- und Umweltanalytik GmbH)

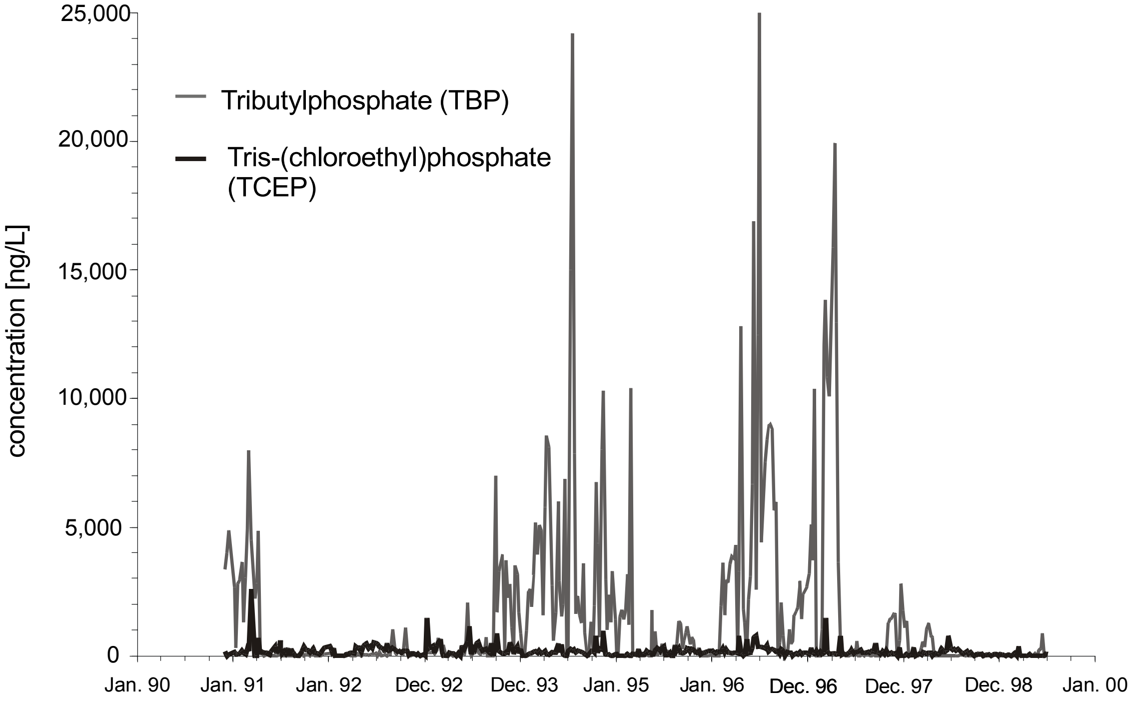


Table 2.3 Comparison of two sampling campaigns in July and September 2002, concentrations given in ng/L

Sample Location	Compound						
	T*i*BP	T*n*BP	TCEP	TCPP	TDCP	TBEP	TPP
46 (July)	70	70	180	100	< LOQ	870	60
46 (September)	58	13	45	310	27	350	17
50 (July)	50	60	190	130	< LOQ	< LOQ	< LOQ
50 (September)	150	26	81	150	41	130	12
57 (July)	70	70	300	280	< LOQ	290	60
57 (September)	100	24	48	140	46	160	13
60 (July)	80	60	250	290	< LOQ	230	80
60 (September)	83	26	58	190	57	130	39
61 (July)	160	130	< 20	230	< LOQ	< 100	< 10
61 (September)	110	34	45	140	42	160	10

2.3.4 Comparison to other rivers

In comparison to the samples from the river Ruhr five samples of river Rhine and a duplicate sample of river Lippe were analysed. Both other rivers are supposed to be less protected than the Ruhr. The results for flame retardants were TCPP 80-

100 ng/L (Rhine) and 100 ng/L (Lippe); TDCP 13-36 ng/L (Rhine) and 17 ng/L (Lippe). The following concentrations were measured for the plasticisers: T*i*BP 30-50 ng/L (Rhine) and 100 ng/L (Lippe); T*n*BP 30-120 ng/L (Rhine) and 30 ng/L (Lippe), TBEP 80-140 ng/L (Rhine) and 130 ng/L (Lippe). It seems that the high standard of protection, which is often claimed for the river Ruhr, is not very effective in concern of the organophosphates. Tentative samples from the river Mulde (an Elbe tributary) exhibited similar concentrations, though the pattern (TCPP vs. TCEP and TDCP etc.) is diverse as in those samples TCEP was detected with higher concentrations than TCPP. These concentrations were in the same range as stated by Aston *et al.*[53] for Japanese (17-350 ng/L), Canadian (~10 ng/L) as well as US rivers (570 ng/L) (all TCEP data). In Spain 10-900 ng/L T*i*BP and about 350 ng/L TCEP were detected by Barcelo *et al.*[54] (1990). Prösch *et al.*[52,55] (2000 and 2002) detected TCEP and TCPP concentrations in STP effluents varying from 14 ng/L to 1,660 ng/L and 18 ng/L to 26,000 ng/L and in surface water and private wells. This group discussed a connection to textile production and textile washing as well as industrial point sources in the sewer system.

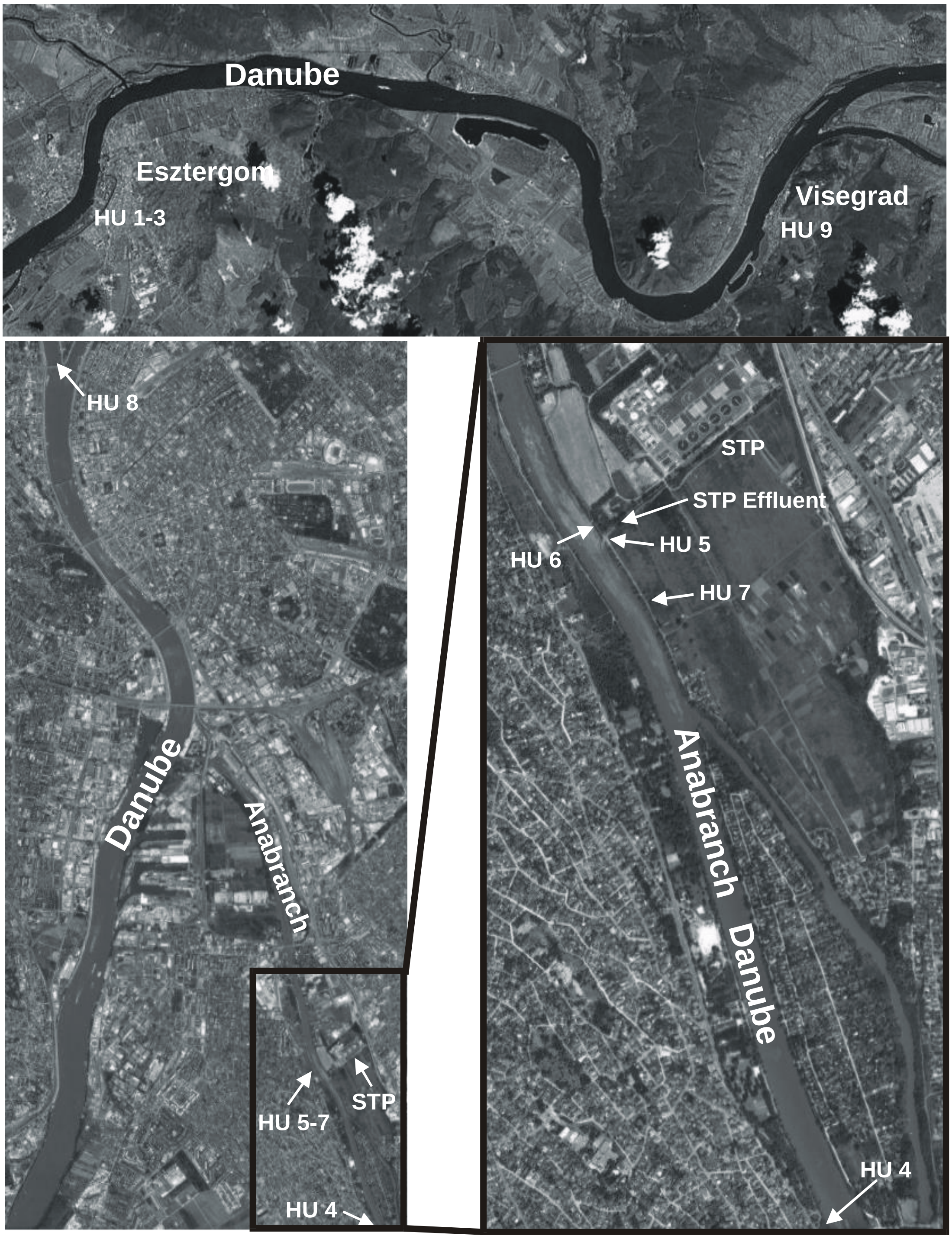
From the data presented in this study it seems that STPs do in some cases emit specific patterns of organophosphates, i.e. not only the absolute, but also the relative concentrations (TCPP vs. TCEP, T*i*BP and TBEP) vary.

2.3.5 Organophosphate ester flame retardants and plasticisers in the river Danube

In October 2004 samples were taken from the river Danube in Hungary. The samples were extracted with the same method described for the sampling of the river Ruhr. Additionally to T*n*BP d_{27} TPP d15 was added as internal standard. For the determination of the selected organophosphates the samples were analysed on a gas chromatography system with mass spectrometric detection (DSQ Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. The PTV (4 µl injection volume) was operated with the following temperature program: 115 °C [0.05 min, 20 mL min^{-1} He] $\rightarrow$ 12 °C s^{-1} (splitless) $\rightarrow$ 280 °C [1.2 min] $\rightarrow$ 1 °C min^{-1} $\rightarrow$ 300 °C [7 min] (cleaning phase).

The GC separation was performed using a DB5-MS column (J&W Scientific, Folsom, CA, USA); length: 15 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 100 °C [2 min] → 30 °C min^{-1} → 130 °C → 8 °C min^{-1} → 220 °C → 30 °C min^{-1} → 280 °C [7 min] using He (5.0) as carrier gas with a flow of 1.5 mL min^{-1}. The mass spectrometer was used with electron impact ionization with 70 eV ionization energy. The MS was operated in selected ion monitoring (SIM) mode. Figure 2.7 displays the different sample locations. Samples HU 1-3 and HU 9 were gathered in Esztergom and Visegrad north-west of Budapest.

Figure 2.7 Sample locations of samples taken of the river Danube and some of its anabranches



Sample 1 (HU 1) was taken from a small brook that flows into an anabranch of the Danube. A small STP uses this brook as receiving water. Sampling points HU 2 and HU 3 are located downstream of sampling point HU 1 at the Danube. Sampling point HU 3 is supposed to be downstream of the effluent of the second STP in Esztergom. Sample HU 9 was gathered in Visegrad. HU 8 is located in the City of Budapest 1km downstream of a STP at the Danube. Sample points HU 4-7 are located in an anabranch that is used as receiving water of another STP downstream of HU 8. HU 6 is located upstream HU 5 directly at the effluent. HU 7 and HU 4 are located 120 m and approximately 2 km downstream of the STP. The results are given in Table 2.4.

Table 2.4 Concentrations of the selected organophosphate esters in ng/L at the different sampling points at the Danube (n.d.: not detected)

Sample	T*i*BP [ng/L]	T*n*BP [ng/L]	TCEP [ng/L]	TCPP [ng/L]	TDCP [ng/L]	TPP [ng/L]	TBEP [ng/L]	EHDPP [ng/L]
HU 1	61	13	51	100	13	11	760	5.9
HU 2	9	12	24	30	7.0	1.1	100	1.0
HU 3	11	13	14	30	7.1	1.1	110	1.0
HU 9	9.5	15	13	29	7.3	1.2	100	1.1
HU 8	15	14	13	27	7.3	1.0	68	n.d.
HU 6	26	24	18	28	7.5	1.3	43	3.7
HU 5	150	260	170	610	96	30	1300	180
HU 7	53	90	58	190	32	10	360	42
HU 4	21	37	23	68	15	4.2	90	13

The concentrations of the selected organophosphate esters measured from samples of the Danube were in the same order of magnitude as for the rivers Rhine and Ruhr although except from TBEP they tended towards somewhat lower amounts. For samples directly influenced by STP effluents (HU 1 and HU 5) significantly higher concentrations were measured. At sampling point HU 3 no increase was observed although it was supposed that an influence by the STP effluent would occur. As the effluent of the STP near this sampling point could not be detected on the one hand it might be that the STP discharges downstream of HU 3 on the other hand it is supposed that the sampling point is not influenced by the effluent as sometimes the treated wastewater is discharged through channels in some distance to the bank. The results for samples HU 4-7 display that the selected organophosphates are emitted by the discharge of treated wastewater. Due to dilution effects the increased amounts measured at STP effluents decrease with the distance.

2.4 *Conclusions to surface waters*

As the Ruhr is among Europe's most important rivers used for drinking water supply, which is kept as clean as possible with low sewage discharges in comparison to other rivers, it was surprising to find these compounds at all. Among the flame-retardants TCPP is the most prominent one which corresponds well with the current sales figures, as industries has phased out TCEP and TDCP. Industry states that in 1998 about 7,500 t TCPP, 750 t TDCP and about 100 t TCEP were sold (IAL, 1999). The sales are supposed to have shifted further to TCPP meanwhile.

TCPP is used to more than 95 % in construction. Thus it is probable that most of its residues found in surface waters stem from current construction activities, either by the handling of rigid foam plates or by usage of liquid spray foam. It seems that the concentrations pattern determined in the Ruhr is to some part a universal background, as TCPP reaches the Ruhr from a multitude of sources. On the other hand some sources are exceptionally high leading to the assumption, that log K_{OW} or point sources (possibly large scale construction sites) are relevant as well. An estimate of transports can be obtained from the concentrations determined in this study and the average water flow in the river. On this basis it can be assumed that about 300 kg TCPP, about 100 kg TDCP and TCEP each are transported from the river Ruhr to the river Rhine annually. This would correspond to 0.005 % of the annual consumption in Germany or ~0.1 % of product assumedly consumed in the Ruhr megalopolis.

The situation of the plasticisers is somewhat similar. TBEP and T*i*BP are the most relevant compounds in the Ruhr system. Though these compounds are omnipresent, there are some relevant point sources as well. In this case the point sources are diverse and not the same emission patterns are determined as for the chlorinated compounds, which were analysed. An estimate of transport leads to the assumption that about 300 kg TBEP and 200 kg T*i*BP are transported into the Rhine annually.

Generally it should be considered that similar concentrations will be detected in surface waters all over Europe as these compounds were found in several rivers of different regions in Germany, e.g., Rhine, Lippe and Elbe. Similar concentrations (20-

200 ng/L TCEP; 200-700 ng/L TBEP) have been published by Fries and Püttmann. (2001)

At the moment this does not necessarily mean harm to the population of the Ruhr area, as most of these compounds are probably effectively eliminated by the water purification plants if an appropriate technology is applied. The authors did detect lower concentrations in drinking than in surface water in a few preliminary samples. In Canada similar compounds (0.6-12 ng/L TBP, 0.3-9.2 ng/L TCEP, 0.2-1.2 ng/L TDCP, 0.9-75 ng/L TBEP, 0.3-2.6 ng/L TPP) were detected in drinking water, though (LeBel *et al.* 1981). On the other hand the consumer has to pay for the installation and maintenance of the considerable efforts, which the water suppliers have to use to eliminate xenobiotics from the raw water from a river like the Ruhr or the Rhine.

The applications that are dominant at the moment should be checked for their potential emissions of the respective compounds. It might be possible that simple changes in installations or applications of either rigid polyurethane foam plates or liquid spray foam can reduce the concentrations in relevant rivers considerably. This could reduce costs for the consumers of water and might improve the evaluation of major rivers considering the water framework directive of the EU (2000)[56]. As TCPP could not be degraded in batch experiments (Kawagoshi *et al.*, 2002, own experiments see chapter 1.6) or in sewage treatment plants (Bester, 2005, Meyer et al. 2004) improving the degradation or elimination powers of sewage treatment plants will probably be a hard and costly way to reduce concentrations of TCPP and other organophosphates in surface waters.

3 Elimination of Organophosphate ester flame retardants and plasticisers in drinking water purification

3.1 *Introduction to drinking water purification*

Recent studies have shown that organophosphate ester flame retardants and plasticisers are emitted from sewage treatment plants and thus they are detected in surface water which is often used for drinking water purification. For this study three waterworks that purify surface water from the river Ruhr were chosen because this river supplies several million people of the Ruhr basin with drinking water. In fact this river is protected since the third decade of the 19th century by sewage treatment plants and additionally it is preferred to introduce waste water not into the Ruhr itself but into other rivers such as the river Emscher wherever possible. However previous studies have shown that it is still affected by STP effluents as treated wastewater of about two million inhabitants is discharged into this river (Andresen *et al.*, 2004). During summer months the Ruhr contains up to 30 % wastewater.

LeBel *et al.*[57] (1981) detected some of the organophosphate esters, e.g., 0.3-9.2 ng/L TCEP and 0.5-11.8 ng/L T*n*BP, in drinking water samples from six Eastern Ontario water treatment plants. The elimination during drinking water purification was not observed though.

A study about persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking- water- treatment plant in the USA showed that the applied treatment processes were not effective in removing TBP, TBEP, TCEP and TDCP (Stackelberg *et al.*[58], 2004). Heberer *et al.*[59] (2002) described the production of drinking water from highly contaminated surface waters applying mobile membrane filtrations units. In this study elimination rates observed for TCEP and TCPP were > 97.2 % and > 98.9 % respectively. The objective of the work presented here was to study the efficiency of different treatment steps in removing organophosphate esters from surface water for drinking water purification. Therefore, the elimination of these substances was studied in three different waterworks with different treatment processes in the Ruhr area.

3.2 *Selected waterworks*

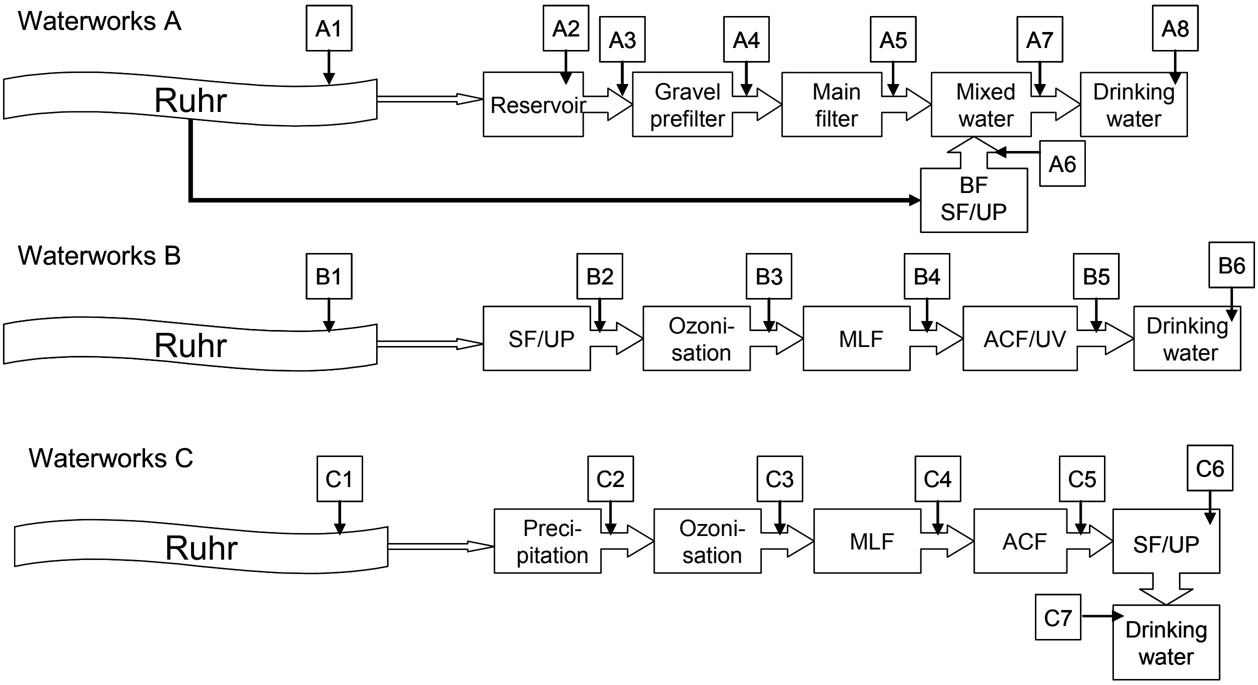
In the Ruhr megalopolis the combination of different treatment processes depends on the quality of the raw water which is used for drinking water purification. This means that purification plants that are located downstream of the highly populated and industrialised area of the Ruhr megalopolis have to use additional treatment processes to obtain drinking water quality. In this study the elimination efficiency of three waterworks was compared. Waterworks A (see Figure 3.1) is located in a more or less rural area upstream of the highly industrialised area. This water treatment facility (A) is subdivided into two waterworks. After the water purification the treated water of both waterworks is fed to the public water supply. One of the two waterworks is equipped with gravel prefilters and main filters (biological active slow sand filtration and underground passage) whereas the other one uses bank filtration and slow sand filtration combined with underground passage.

Waterworks B is located near the mouth of the river Ruhr. In this water treatment facility biological active slow sand filtration with underground passage is combined with secondary treatment processes like ozonisation, multilayer and activated carbon filtration as well as UV irradiation for disinfection purposes (for details see Figure 3.1).

For drinking water purification in waterworks C the same treatment processes are used as in waterworks B. However they are applied in a different order. Additionally the raw water is treated with alumina salts for precipitation and flocculation (see Figure 3.1).

Except from samples of the Ruhr and from the reservoir at waterworks A all samples were taken at sampling points used for routine monitoring at the respective water treatment facilities. In each case the sample volume was more than 2 L that were divided into two 1 L samples for two replica extractions. The Ruhr and the reservoir of waterworks A were sampled near the inflow of the waterworks and the prefilter respectively. The samples were taken at the same time but not according to the supposed residence time. Thus waterworks A was sampled over a period of five days to study the continuity of the elimination efficiency as the contact time for the slow process sand filtration was 12 to 15 days. From each sampling point one grab sample was collected per day.

Figure 3.1 Sampling points at waterworks A, B and C; BF: bank filtration; SF: slow sand filtration; UP: underground passage; MLF: multilayer filtration; ACF: activated carbon filtration; UV: UV-irradiation; Pre/Floc: precipitation and flocculation



3.3 *Analytical Method to drinking water purification*

All samples were collected in glass bottles and stored at 4° C when it was not possible to extract them immediately. The storage time was not longer than 48 h. The results were obtained from two replica extractions of each sample by means of liquid liquid extraction (LLE). 1 L of the samples was extracted with 10 mL toluene after adding an aliquot (100 µL) of internal standard solution containing TnBP d_{27} (1.8 ng/µL) and TPP D15 (1.01 ng/µL). The extraction (30 min) was performed by vigorous stirring with a teflonised magnetic stirrer. After a sedimentation phase of 20 min the organic phase was separated from the aqueous one and the residual water was removed from the organic phase by freezing the samples overnight at -20 °C. The samples were concentrated with a concentration unit (Büchi Syncore, Büchi, Essen, Germany) at 60 °C and 60 mbar to 1 mL. For blank studies water (HPLC grade, Baker Griesheim, Germany) was treated under the same conditions as water samples. None of the selected organophosphates was detected in blank samples except from TPP. The blank value has been traced back to one batch ethyl acetate p.a. that was used for the cleaning of the glass bottles. Afterwards ethyl acetate (suprasolv) was applied for cleaning purposes. For each set of samples instrumental and procedural blanks were analysed.

The samples were analysed on a gas chromatography system with mass spectrometric detection (DSQ, Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. The PTV was operated in large volume injection (LVI) mode (40 µL injection volume) with a sintered glass liner (SGE) with the following temperature program: 115 °C [0.4 min, 130 mL min^{-1} He] → 12 °C s^{-1} (splitless) → 280 °C [1.2 min] → 1 °C min^{-1} → 300 °C [7 min] (cleaning phase)

The GC separation was performed using a DB5-MS column (J&W Scientific, Folsom, CA, USA); length: 15 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 100 °C [1 min] → 30 °C min^{-1} → 130 °C → 8 °C min^{-1} → 220 °C → 30 °C min^{-1} → 280 °C [7 min] using He (5.0) as carrier gas with a flow of 1.5 mL min^{-1}. The mass spectrometer was used with electron impact ionization with 70 eV ionization energy. The MS was operated in selected ion monitoring (SIM) mode. Mass fragments that were used for quantification are given in Table 3.1.

The different organophosphate esters were detected by means of their mass spectral data and retention time. For quantitative measurements the method was validated. Recovery rates range from 28 % to 128 % with 7 % to 19 % RSD for the LLE. Full quality data for the method were obtained from three replica extractions of spiked HPLC water at 9 different concentrations in the range of 1 ng/L to 10,000 ng/L for the LLE. The whole set of parameters is given in Table 3.1. As TCEP was not recovered well by LLE a solid phase extraction (SPE) method was developed for the determination of this substance from surface water. A comparison of both methods gave same results from samples taken from the Ruhr in 2002 (for details compare Andresen *et al.*, 2004).

Table 3.1 Quality assurance data for the applied method

Compound	Analytical Ion [amu]	Verifier Ion [amu]	Recovery Rate [%]	RSD [%]	LOQ [ng/L]	Internal Standard
T*i*BP	211	155	128	13	3	T*n*BP-D27
T*n*BP	211	155	100	11	1	T*n*BP-D27
TCEP	249	251	28	12	0.3	T*n*BP-D27
TCPP	277	279	92	10	1.0	T*n*BP-D27
TDCP	379	381	108	13	1.0	TPP-D15
TBEP	199	299	103	7	3	TPP-D15
EHDPP	251	362	94	11	0.1	TPP-D15
TPP	325	326	101	14	0.3	TPP-D15

3.4 *Results to drinking water purification*

3.4.1 Chlorinated Organophosphates

Table 3.2 gives an overview of the concentrations of TCEP, TCPP and TDCP in waterworks A at the respective sampling points. As samples were taken over a period of 5 days the concentrations are additionally given as mean values. The amounts of TCPP were reduced from 54 ng/L in the river Ruhr to 2.9 ng/L in the finished water (95 % elimination), those of TDCP from 13 ng/L to 2.0 ng/L (85 % elimination) and those of TCEP from 41 ng/L to 2.0 ng/L (95 % elimination) in the complete treatment process. Due to the fact that the respective concentrations for the chlorinated organophosphates in the influent of the prefilter and the influent of the main filter were constant in this experiment the prefilter did not contribute to the elimination of these substances. Moreover Table 3.2 shows that the concentrations for TCEP in the Ruhr, the reservoir, and the influents of the prefilter and of the main filter exhibit a significant variability whereas they were almost stable for TCPP and TDCP. The concentrations of TCEP in the Ruhr ranged from 13 ng/L up to 130 ng/L. This variance is also reflected in the values measured in the reservoir and the inflows of the prefilter and the main filter respectively.

Table 3.2 demonstrates that the concentrations of the chlorinated organophosphates showed a significant day to day variance in the effluent of the main filter whereas they were almost stable in the effluents of the bank filtration and slow sand filtration/underground passage. The elimination rates for TCPP ranged from 73 % to 93 %, from 71 % to 91 % for TDCP and from 80 % to 99 % for TCEP for the main filter. In the effluent of the bank filtration and slow sand filtration/underground passage concentrations for TCPP were below LOQ (1 ng/L) for the whole sampling period whereas the respective elimination rates ranged from 85 % to 94 % for TDCP and from 95 % to 100 % for TCEP.

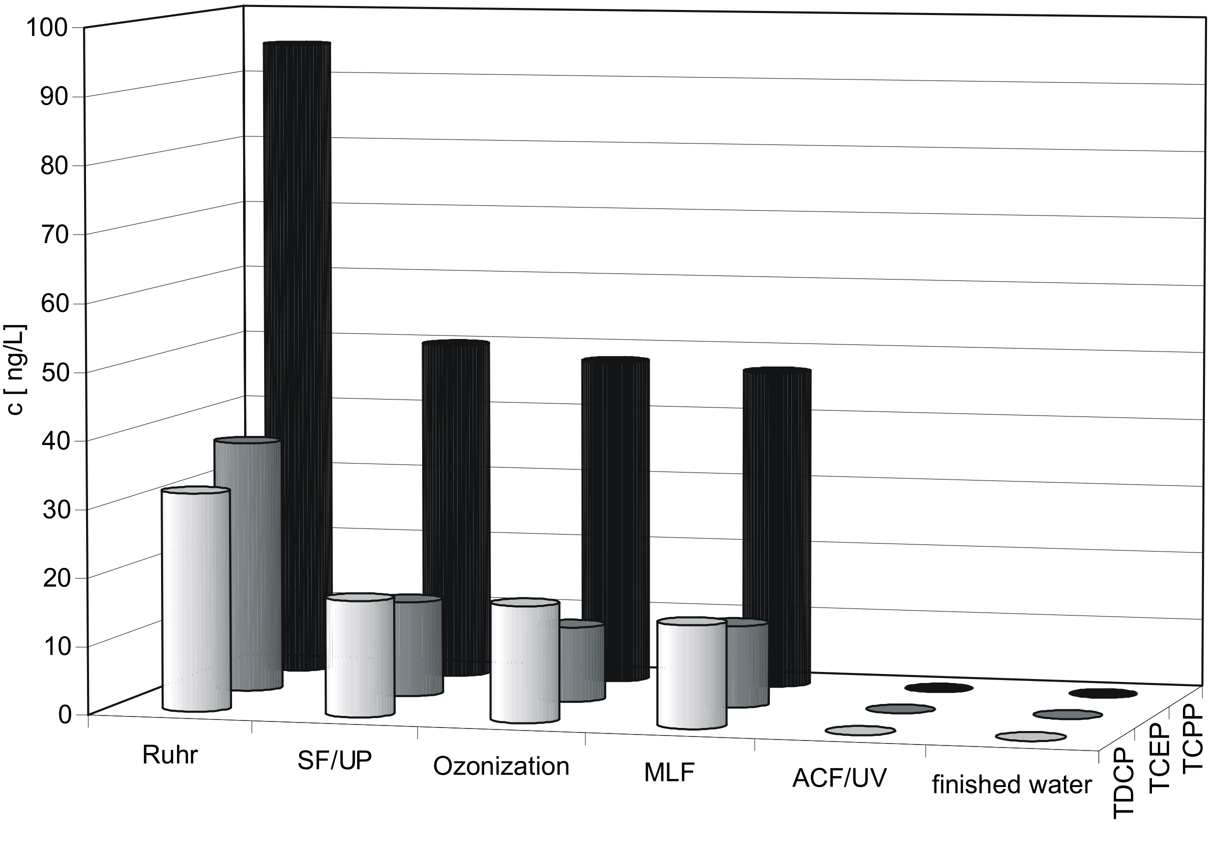
Table 3.2 Concentrations of the selected chlorinated organophosphates at different treatment steps at waterworks A (PF: prefilter; MF: main filter; UP: underground passage; MW: Mixed water; FW: finished water)

Analyte	Ruhr [ng/L] A1	Reservoir [ng/L] A2	PF inflow [ng/L] A3	MF inflow [ng/L] A4	MF effluent [ng/L] A5	UP effluent [ng/L] A6	MW [ng/L] A7	FW [ng/L] A8	day
TCPP	47	49	45	41	< 1	< 1	< 1	< 1	1
	55	50	57	46	< 1	< 1	2.5	1.2	2
	47	52	45	44	12	< 1	2.9	3.4	3
	57	59	52	48	3.5	< 1	6.9	4.1	4
	65	59	57	51		< 1	10		5
Mean	**54**	**54**	**51**	**46**	**7.8**	**< 1**	**5.6**	**2.9**	
TDCP	10	12	11	11	3.2	1.4	1.3	1.2	1
	15	12	13	15	1.3	1.4	1.3	1.9	2
	8.6	10	10	11	6.5	1.3	2.9	2.4	3
	11	12	10	9.8	2.4	1.1	3.4	2.4	4
	18	14	14	14		1.1	4.0		5
Mean	**13**	**12**	**12**	**12**	**3.4**	**1.3**	**2.6**	**2.0**	
TCEP	12	14	13	12	0.61	0.65	1.3	1.2	1
	130	26	23	47	0.56	0.64	1.3	1.9	2
	13	15	13	14	2.8	0.70	2.9	2.4	3
	20	51	21	18	1.4	0.56	3.4	2.4	4
	32	22	23	23		0.51	4.0		5
Mean	**41**	**26**	**19**	**23**	**1.3**	**0.61**	**2.6**	**2.0**	

Figure 3.2 shows the concentrations of the chlorinated organophosphates at waterworks B. In comparison to waterworks A the elimination efficiency of the chlorinated substances by the slow sand filtration and underground passage was lower in this drinking water purification plant. Concentrations were reduced from 95 ng/L to 50 ng/L (53 % elimination) for TCPP, from 37 ng/L to 14 ng/L (38% elimination) for TCEP and from 32 ng/L to 17 ng/L (52 % elimination) for TDCP. The following ozonisation (0.5 g/m^3 ozone, contact time 0.5 h) did not contribute to the elimination neither did the multilayer filter consisting of layers of gravel and sand with different grain sizes. After the activated carbon filtration/UV irradiation the concentrations of TCPP, TCEP and TDCP were below LOQ. To examine whether the chlorinated flame retardants were removed by activated carbon filtration or by UV-

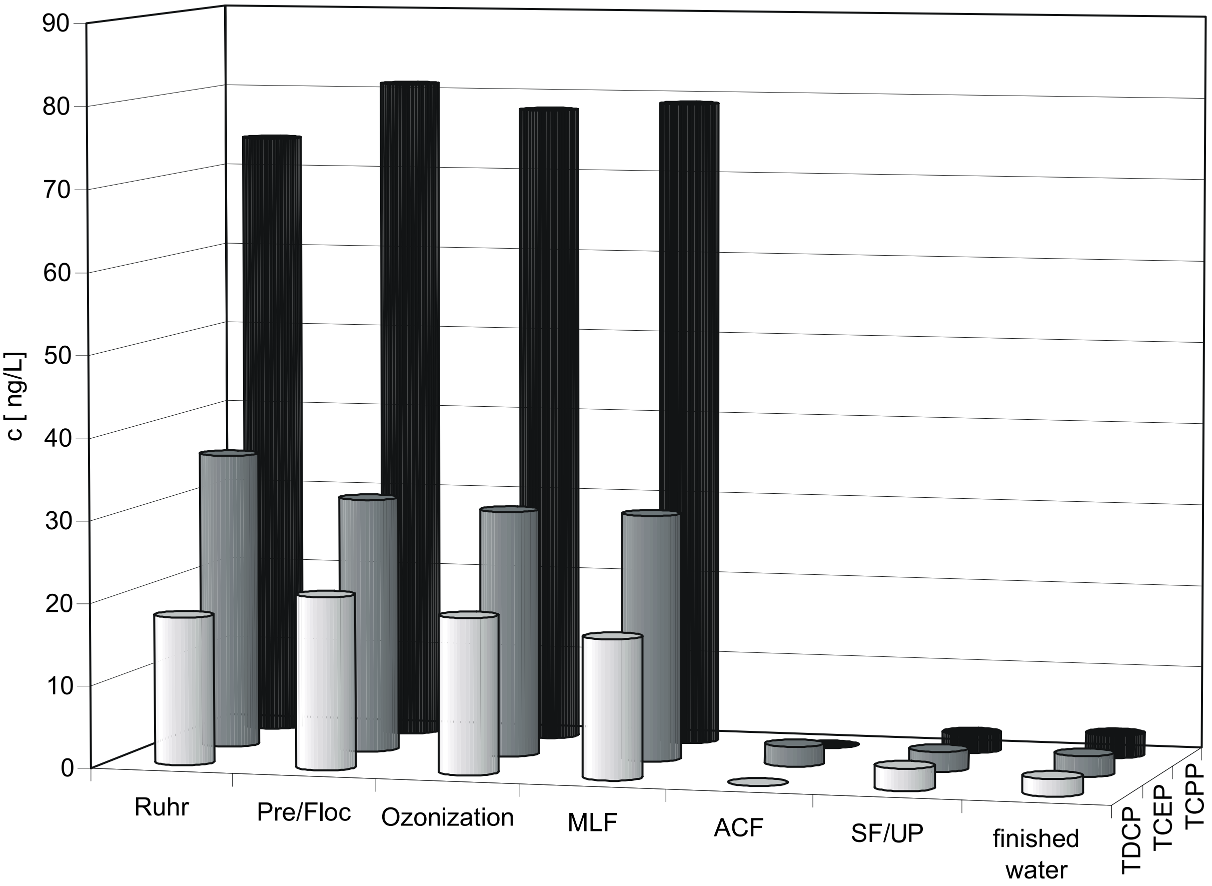
irradiation additionally samples before and after UV-treatment have been taken at the same waterworks during a second sampling campaign. The measurements have shown that after activated carbon filtration the concentrations of TCEP, TCPP and TDCP were below LOQ Thus filtration on activated carbon is the most effective treatment step in this waterworks.

Figure 3.2 Concentrations of the selected chlorinated organophosphorus flame retardants at different treatment steps at waterworks B (SF/UP: sand filtration/underground passage; MLF: multilayer filtration; ACF: activated carbon filtration; UV: UV-irradiation)



The measurements of samples from waterworks C confirm the results that ozonisation and multilayer filtration did not contribute to the elimination of the chlorinated organophosphates. Moreover TCEP, TDCP and TCPP were not eliminated by precipitation with aluminium salts and following flocculation as the concentrations were stable in the raw water and the effluent of the precipitation. The results for the chlorinated organophosphates are given in Figure 3.3.

Figure 3.3 Concentrations of the selected chlorinated organophosphorus flame retardants at different treatment steps at waterworks C (Pre/Floc: precipitation/flocculation; MLF: multilayer filtration; ACF: activated carbon filtration; SF/UP: sand filtration/underground passage)



3.4.2 Non- chlorinated organophosphates

Table 3.3 gives an overview of the concentrations of T*i*BP, T*n*BP, TBEP, EHDPP and TPP of samples taken at waterworks A. Except from TPP the results were obtained from a five days sampling period. Data presented for TPP stem from an earlier one day experiment at the same waterworks. Based on the mean values of the five days sampling period for all substances the concentrations measured at the inflow of the gravel prefilter were similar to those in the inflow of the main filter. This means that the prefilter did not contribute to the elimination of organophosphate esters in this waterworks. Only for TBEP a slight reduction of the concentrations was observed. In the effluent of the main filter and bank filtration slow sand filtration/underground passage the measured values of the non- chlorinated alkylphosphates were below the respective limit of quantification (LOQ). This means that the biological active slow sand filtration combined with underground passage and underground passage without additional treatment were effective for the elimination of non- chlorinated organophosphate esters. Moreover it seems that the elimination efficiency of the main filter concerning the non-chlorinated organophosphates was slightly higher than for the chlorinated substances. In Table 3.3 it is noticeable that the concentrations for T*n*BP in samples from the Ruhr, the reservoir and the inflow of the prefilter varied significantly during the five days sampling. No day to day variance of the concentrations was observed for T*i*BP, TBEP and EHDPP.

Table 3.3 Concentrations of the selected non-chlorinated organophosphates in ng/L at different treatment steps at waterworks A (PF: prefilter; MF: main filter; UP: underground passage; MW: Mixed water; FW: finished water)

Analyte	Ruhr [ng/L] A1	Reser-voir [ng/L] A2	PF inflow [ng/L] A3	MF inflow [ng/L] A4	MF effluent [ng/L] A5	UP effluent [ng/L] A6	MW [ng/L] A7	FW [ng/L] A8	day
T*n*BP	6.5	10	8.4	6.4	6.3	1.9	< 1	< 1	1
	20	9.1	13	8.8	< 1	< 1	< 1	< 1	2
	42	55	34	25	< 1	< 1	< 1	< 1	3
	35	28	21	17	< 1	< 1	3.0	< 1	4
	28	35	35	29		< 1	1.6		5
Mean	**26**	**27**	**22**	**17**	**1.9**	**1.0**	**1.5**	**< 1**	
T*i*BP	36	28	37	40	< 3	< 3	< 3	< 3	1
	36	33	34	30	< 3	< 3	< 3	< 3	2
	39	32	36	32	< 3	< 3	< 3	< 3	3
	43	38	37	34	< 3	< 3	< 3	< 3	4
	24	27	26	23		< 3	< 3		5
Mean	**36**	**32**	**34**	**32**	**< 3**	**< 3**	**< 3**	**< 3**	
TBEP	170	180	170	130	< 3	< 3	< 3	< 3	1
	150	150	150	120	< 3	< 3	< 3	< 3	2
	150	160	160	120	3.3	< 3	< 3	< 3	3
	150	150	140	100	< 3	< 3	< 3	< 3	4
	140	140	140	99		< 3	3.3		5
Mean	**150**	**160**	**150**	**110**	**< 3**	**< 3**	**< 3**	**< 3**	
EHDPP	0.90	1.0	1.0	0.63	0.17	0.12	0.18	0.15	1
	0.75	0.74	0.74	0.55	0.15	0.17	< 0.1	0.14	2
	0.55	0.91	0.65	0.56	< 0.1	< 0.1	< 0.1	< 0.1	3
	0.74	0.66	0.55	0.44	< 0.1	< 0.1	< 0.1	< 0.1	4
	0.64	0.64	0.67	0.46		< 0.1	< 0.1		5
Mean	**0.72**	**0.79**	**0.72**	**0.53**	**0.16**	**< 0.1**	**< 0.1**	**0.15**	
TPP		**7.2**	**4.4**	**3.1**	**0.30**	**< 0.3**	**< 0.3**	**< 0.3**	

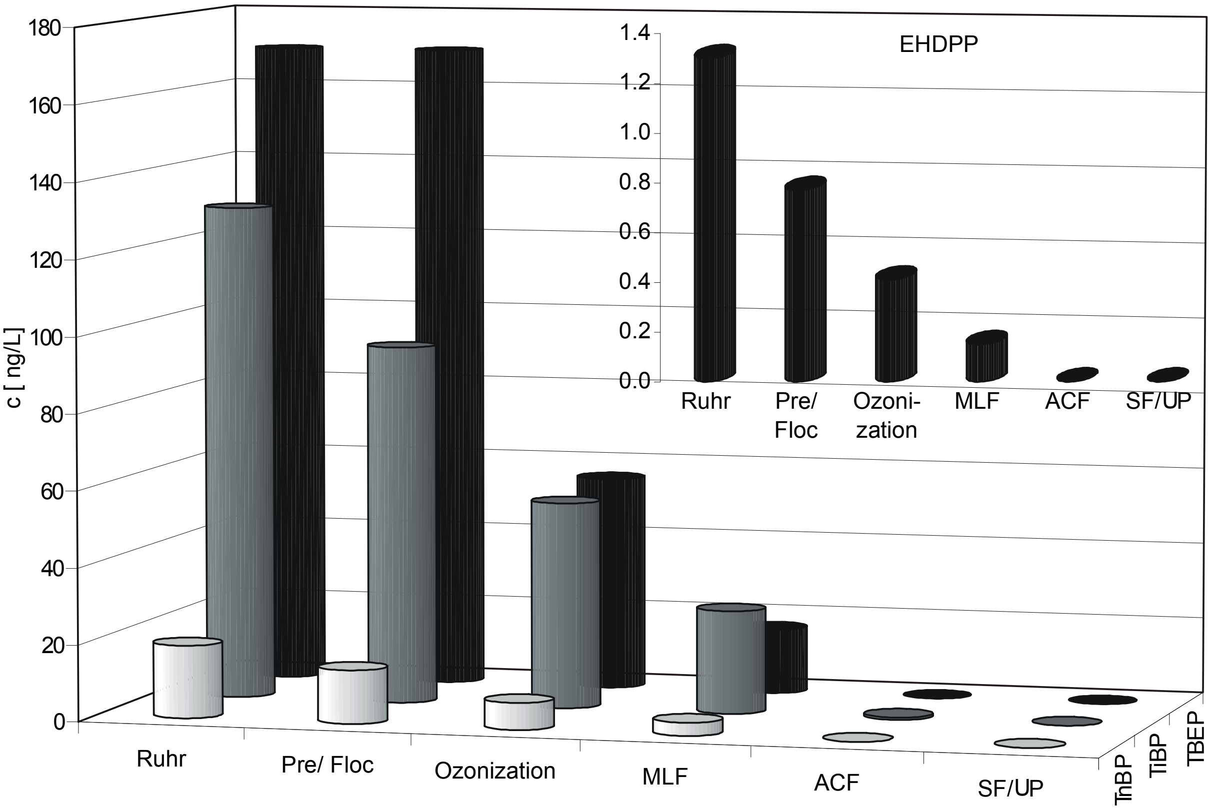
At waterworks B the concentrations in the raw surface water from the Ruhr (B1) for the non- chlorinated organophosphates were in the same order of magnitude as in the raw water from waterworks A. After the water has passed the biological active slow sand filter and underground passage (B2) the concentrations for the observed organophosphates T*i*BP, T*n*BP, TBEP, EHDPP and TPP were below the LOQ. Table 3.4 gives an overview of the results for the non- chlorinated organophosphates in waterworks B.

Table 3.4 Concentrations of selected non-chlorinated organophosphates at different sampling points in waterworks B (SF/UP: slow sand filtration/underground passage; MLF: multilayer filtration; ACF: activated carbon filtration; UV: UV-irradiation)

	T*i* BP [ng/L]	T*n* BP [ng/L]	TBEP [ng/L]	TPP [ng/L]	EHDPP [ng/L]
Ruhr	66	33	140	6.0	1.3
SF/UP	< 3	< 1	< 3	< 0.3	< 0.1
Ozonisation	< 3	< 1	< 3	< 0.3	< 0.1
MLF	< 3	< 1	< 3	< 0.3	< 0.1
ACF/UV	< 3	< 1	< 3	< 0.3	< 0.1
finished water	< 3	< 1	< 3	< 0.3	< 0.1

Figure 3.4 shows the results for TBEP, EHDPP and the tributylphosphates in waterworks C. Due to blank values no data were received for TPP. In contrast to the chlorinated organophosphates the concentrations of the non-chlorinated derivates T*i*BP, T*n*BP and EHDPP were reduced by precipitation/flocculation: The elimination was 130 ng/L to 94 ng/L (elimination rate 28 %) for T*i*BP, 19 ng/L to 14 ng/L (elimination rate 26 %) for T*n*BP and 1.3 ng/L to 0.77 ng/L (elimination rate 41 %) for EHDPP. No effect was observed for TBEP at this treatment step. Moreover Figure 3.4 shows that the non-chlorinated organophosphates were eliminated by ozonisation (elimination rates between 40 % and 67 %) and multilayer filtration with elimination rates from 50 % to 70 % based on the respective preceding treatment. Although the concentrations were reduced by these processing steps activated carbon filtration was needed for an effective elimination which was comparable to the elimination achieved by slow sand filtration combined with underground passage in waterworks A.

Figure 3.4 Concentrations of selected non-chlorinated organophosphates in ng/L at different sampling points in waterworks C (Pre/Floc: precipitation/flocculation; MLF: multi layer filtration; ACF: activated carbon filtration; SF/UP: sand filtration/underground passage)



3.5 *Discussion to drinking water purification*

Opposite to the studies of Stackelberg *et al.* (2004) the selected organophosphates were efficiently removed during drinking water purification. The main differences between the water treatment plant studied by Stackelberg *et al.*, 2004 and the waterworks in the Ruhr catchment area are the applied purification techniques. Whereas in the US facility drinking water was purified by adding powdered activated carbon, flocculation and filtration through tanks that contained sand and either bituminous granular activated carbon (GAC), lignite GAC or anthracite GAC, in the Ruhr catchment area drinking water is mainly produced by natural processes or processes close to nature like bank filtration or groundwater recharge via slow sand filtration with surface water. The natural filter effect of bank zones, soil and underground is supported by biological active slow-process sand filters and other additional preliminary and secondary treatment processes like precipitation with iron or alumina salts, ozonisation or activated carbon filtration. In all three waterworks the selected non- chlorinated organophosphates were effectively eliminated by slow sand filtration combined with underground passage or bank filtration and slow sand filtration/underground passage. The daily variance of the elimination rates for the complete treatment process at waterworks A was low (95 ± 3 % for TCPP, 85 ± 8 % for TDCP and 95 ± 5 % for TCEP). For the non-chlorinated Organophosphates the concentrations were below the respective LOQ in the finished water. Obviously a very good overview on the elimination efficiency of the selected organophosphates was obtained from this study concerning natural drinking water purification processes at waterworks A although samples were taken as grab samples. Moreover the results were not influenced by the daily variance of the concentrations that was observed for T*n*BP and TCEP respectively. Apparently the elimination of the chlorinated substances by means of slow sand filtration combined with underground passage depends on the respective conditions and thus secondary treatment processes like activated carbon filtration is needed for drinking water purification in some cases. In waterworks A higher elimination rates for TCPP, TCEP and TDCP (85-95 %) were observed for this treatment step compared to waterworks B (38-52 %). The difference of the elimination efficiency in the respective treatment facilities possibly occurs due to different residence times in the described filters as well as soil characteristics. The hydraulic residence time in waterworks A (slow sand filtration combined with underground passage) is 10 to 15 days whereas the contact time in waterworks B is only 2 to 5 days. Although the assumed biologically most active area of a slow sand filter is supposed to be only the first 3 to 4 cm and then the biological activity decreases within the filter bed it seems that the additional filter effect of the soil is needed for a sufficient elimination of chlorinated organophosphates. The differences between the main filter and the bank filtration combined with slow sand filtration and underground passage concerning the elimination of TCPP and TDCP might be a hint for differences in the biological activity of both treatment processes. The fact that the multilayer filters did not eliminate the selected chlorinated organophosphates can also be traced back to shorter contact times (about 40 min, filter velocity 8 m/h at waterworks B) in comparison to slow sand filtration. Additionally differences in the biological activity have to be taken into account. Moreover the non-chlorinated organophosphates were partly eliminated by multilayer filtration at waterworks C although the elimination efficiency was lower than for slow sand filtration/underground passage at waterworks A and B for the same reason. The fact that the multilayer filter in waterworks B did not contribute to the elimination of the chlorinated organophosphates confirms earlier studies in STPs in which similar filters were used for the treatment of treated wastewater before it was discharged to the receiving water (Meyer and Bester, 2004). In this case the multilayer filter did not contribute to the elimination of these organophosphates, too. Opposite to the investigations of the previous studies of Stackelberg *et al.* (2004) activated carbon filtration was very effective for the removal of the selected alkylphosphates. The main differences between the respective filters were on the one hand different contact times and on the other hand differences in the biological activity. Whereas the activated carbon filters in the US facility were biologically inactive and the residence time was only 1.5-3 min in the waterworks B and C contact times were significantly longer (1 h) and the filters were biologically active. Further studies in a waterworks with the same treatment steps for drinking water purification as waterworks C revealed that the elimination efficiency of the activated carbon filter decreases with the time of usage. In this waterworks no elimination was observed for the chlorinated organophosphates at the end of the serviceable life of the filter bed. For the non-chlorinated substances the elimination efficiency was significantly lower. Due to the final sand filtration/underground passage the drinking water quality concerning these substances was not significantly affected. The elimination efficiency was in the same range as observed for waterworks A. The activated carbon was changed shortly after the sampling and the concentrations of the phosphororganic flame retardants and plasticisers were determined again. These measurements showed that after exchange of the filter bed the amounts of all substances were below LOQ. Table 3.5 displays the results for the different treatment steps before and after the exchange of the activated carbon for the chlorinated flame retardants. Similar results were obtained for the non-chlorinated organophosphate esters.

Table 3.5 Comparison of the concentrations [ng/L] of the chlorinated flame retardants before and after the exchange of the activated carbon at the effluents of the respective treatment steps

Substance	TCEP		TCPP		TDCP	
	bevor exchange	after exchange	bevor exchange	after exchange	bevor exchange	after exchange
Ruhr	76	97	200	220	35	34
Pre/Floc	70	74	200	190	33	29
Ozonization	78	64	200	190	32	24
MLF	65	51	180	170	27	18
ACF	72	< LOQ	220	< LOQ	16	< LOQ
SF/UP	2.0	< LOQ	13	2.2	2.5	1.9
finished water	2.8	< LOQ	14	8.1	2.5	2.5

As alternative to conventional drinking water purification as described in this work, Heberer *et al.* (2002) demonstrated the production of drinking water by applying mobile membrane filter units. These studies revealed elimination rates for TCEP and TCPP (> 97.2 % and > 98.9 % respectively). Although this is a powerful technique, the described units produce comparable small amounts of 1.6 m³ h^{-1} drinking water compared to 3000 m³ h^{-1} of the waterworks in this study.

3.6 *Conclusions to drinking water purification*

Organophosphate ester flame retardants and plasticisers may be a problem for drinking water production. However the selected compounds have effectively been eliminated in the studied waterworks by slow sand filtration, underground passage and activated carbon filtration. However the elimination efficiency of the natural purification processes depends on parameters like residence time and soil characteristics.

The study demonstrated that the chlorinated organophosphates TCPP, TCEP and TDCP were not eliminated by secondary treatment processes like ozonisation or the use of multilayer filters. As it is discussed to use these techniques for the treatment of treated wastewater to optimise wastewater treatment processes, no effect is expected for chlorinated organophosphates if similar conditions are chosen as in the studied waterworks. The non-chlorinated derivatives were eliminated by multilayer filtration or ozonisation but the efficiency was lower than for slow sand filtration combined with underground passage.

Although organophosphates are detected in surface water that is used for drinking water purification, the drinking water quality is not affected by these compounds at the three waterworks in this study. However it can currently not be excluded that the purified drinking water contains degradation products of the parent compounds. It is planned to further investigate into this issue.

4 Occurrence of organophosphorus flame retardants and plasticisers in pristine waterbodies such as the German Bight and Lake Ontario

4.1 *Introduction to occurrence in pristine waterbodies*

Former studies have shown that organophosphorus flame retardants and plasticisers are important contaminants in German surface waters, e.g., the river Ruhr or the river Rhine. Sewage treatment plants have been identified as point sources of these substances. As large rivers as the rivers Rhine and Elbe flow into the German Bight it is thus likely that these compounds might be detected in this waterbody as well.

For this study samples from the German Bight were taken during an expedition with the German research vessel Gauss from Mai 25. 2005 – July 06. 2005.

TCPP has already been identified in water in several parts of the North Sea (Weigel *et al.*[60], 2004) but measured concentrations were only indicative.

In the current study the chlorinated organophosphorus flame retardants TCPP, TCEP and TDCP and the non-chlorinated alkylphosphates TBEP, T*n*BP and TPP were quantified in the German Bight for the first time. In comparison to samples from the German Bight some samples from the Lake Ontario (Hamilton Harbour) have been analysed for chlorinated and non-chlorinated alkylphosphates. The concentrations and the behaviour of the selected alkylphosphates in samples from Lake Ontario were compared to those obtained from the German Bight.

4.2 *Materials and Methods to occurrence in pristine waterbodies*

The samples were taken from board of the research vessel with 10 L glass-sphere-samplers. The respective sampling depth was 5 m below the water surface. For the analysis of the organophosphate ester flame retardants and plasticisers 2 L of each sample were decanted into 2 L glass bottles. All samples were stored at 4 °C until they were extracted with toluene.

1 L of the samples was extracted with 10 mL toluene after adding an aliquot of internal standard solution containing T*n*BP d_{27} and TPPd_{15}. The extraction (30 min) was performed by vigorous stirring with a teflonised magnetic stirrer. After sedimentation phase of 20 min the organic phase was separated from the aqueous one and the residual water was removed from the organic phase by freezing the

samples overnight at -20 °C. The samples were concentrated with a concentration unit (Büchi Syncore, Büchi, Essen, Germany) at 60 °C and 60 mbar to 1 mL.

It was not possible to remove residual water from the organic phase by freezing in some of the extracts. In this case the respective samples were dried over sodium sulphate.

The gas chromatographic separation and quantification was performed with the same gas chromatography mass spectrometry system under the same conditions as described in chapter 3.3.

Sampling positions and sampling characteristics are given in Table 4.1.

Table 4.1 Sampling position and water salinity of the respective samples in the German Bight

Sample	Position		Salinity [‰]
	Latitude	Longitude	
1	53°37.2' N	09°32.5' E	n.a.
2	53°52.5' N	08°43.8' E	25.00 (estimated)
3	54°00.0' N	08°06.1' E	32.35
4	54°13.5' N	08°23.0' E	28.56
5	54°40.0' N	07°50.0' E	31.42
6	55°00.0' N	08°15.0' E	29.48
7	55°00.0' N	07°30.0' E	32.85
8	54°10.7' N	07°26.0' E	33.56
9	54°20.0' N	06°47.0' E	33.71
10	54°41.0' N	06°47.3' E	34.01
11	54°40.0' N	06°14.9' E	34.10
12	54°40.0' N	05°30.0' E	34.50
13	54°20.0' N	05°40.0' E	34.00
14	53°40.5' N	06°25.0' E	32.19

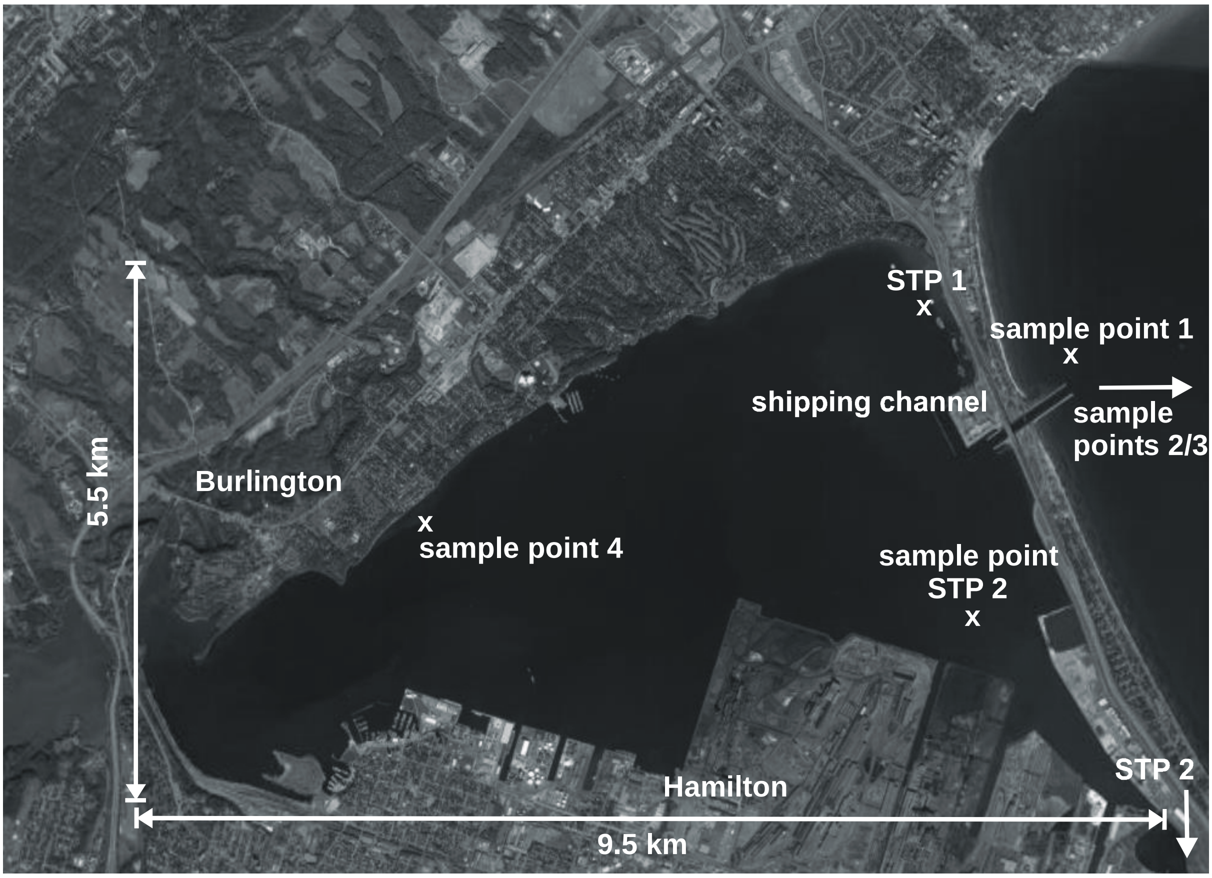
Samples from Lake Ontario were taken from board of a research vessel. The respective sampling depth was 1 m. Samples were taken on Oct. 18th 2004 (Lake Ontario, samples 1-3) and on Oct. 27th 2004 (samples STP 1 and 2, sample 4). They were transported to the laboratory by air cargo and extracted on Nov. 24th 2004 immediately after arrival by liquid- liquid extraction with toluene (for details compare 3.2).

Table 4.2 Characterisation of the respective sampling points at Lake Ontario

Sample	Position		Sample characteristics
	Latitude	Longitude	
1	43°18.2' N	79°47.5' W	Lake Ontario, slightly north east of shipping channel
2	43°18.3' N	79°45.4' W	Lake Ontario, approx. 3 km east of shipping channel
3	43°18.6' N	79°40.0' W	Lake Ontario, approx. 10 km east of shipping channel
4	43°17.3' N	79°51.6' W	Lake Ontario, mid-point at west end of bay
STP 1	43°18.5' N	79°48.4' W	Burlington STP outflow
STP 2	43°17.1' N	79°48.8' W	north of Dofasco (Thyssen-Krupp), influenced by outflow of STP Hamilton

Sample characteristics of each sample point are given in Table 4.3. Figure 4.4 gives an overview on the sampling area at Hamilton harbour.

Figure 4.1 Overview on the sampling area at Hamilton harbour



For the measurements the same gas chromatography mass spectrometry system was used as for the determination of organophosphate esters in marine water samples (see 3.2).

4.3 *Results and Discussion to occurrence in pristine waterbodies*

4.3.1 Chlorinated organophosphorus flame retardants in the German Bight

Figure 4.1 shows the distribution of the chlorinated organophosphate esters TCPP, TDCP and TCEP in the German Bight. The highest amounts were determined at sample station 1 (river Elbe estuary near the City of Stade) with TCPP as dominant substance. The measured concentrations were 90 ng/L for TCPP, 22 ng/L TCEP and 15 ng/L TDCP in this sample respectively. This corresponds with earlier measurements from 2003 (own data). The determined amounts at that time were 160 ng/L TCPP, 140 ng/L TCEP and 10 ng/L TDCP. Comparable results were obtained for TCPP in 1996 at the same sampling point (ARGE Elbe[61], 2000). Concentrations ranged from 70 ng/L to 300 ng/L. In the region of the mouth of the river (sample point 2) concentrations were noticeable lower (28 ng/L TCPP, 5.9 ng/L TCEP and 3.5 ng/L TDCP). Sample points 2 to 7 are located in the plume of the river Elbe. Along the coast in northern direction the amounts of the chlorinated organophosphates decreased with increasing salinity. Thus in samples taken in a shorter distance to the coast the concentrations were higher then offshore. In the Elbe plume amounts detected were approximately 10 ng/L for TCPP and 1 ng/L TDCP and TCPP.

Sample points 8 to 13 were influenced by the inflow of water from the central North Sea that consists mainly of North Atlantic water. Further offshore in western direction the concentrations of the selected organophosphates decrease with increasing salinity indicating a supposable dilution with North Sea water. Concentrations were significantly lower than in the river Elbe plume and ranged from 7.2 – 4.7 ng/L TCPP and 1 - 0.5 ng/L TDCP and TCEP respectively. Higher amounts of the chlorinated organophosphates were detected at sample point 14. The measured concentrations were 13 ng/L TCPP, 2.8 ng/L TCEP and 1.5 ng/L TDCP. According to Weigel *et al.* this sample point is influenced by the plume of the river Rhine. The contributing concentrations of the river Rhine attain 50 – 150 ng/L (Andresen *et al.*[62], 2004 and ARW[63], 2001).

Figure 4.2 Distribution of the chlorinated organophosphate ester in the German Bight, concentrations given in ng/L

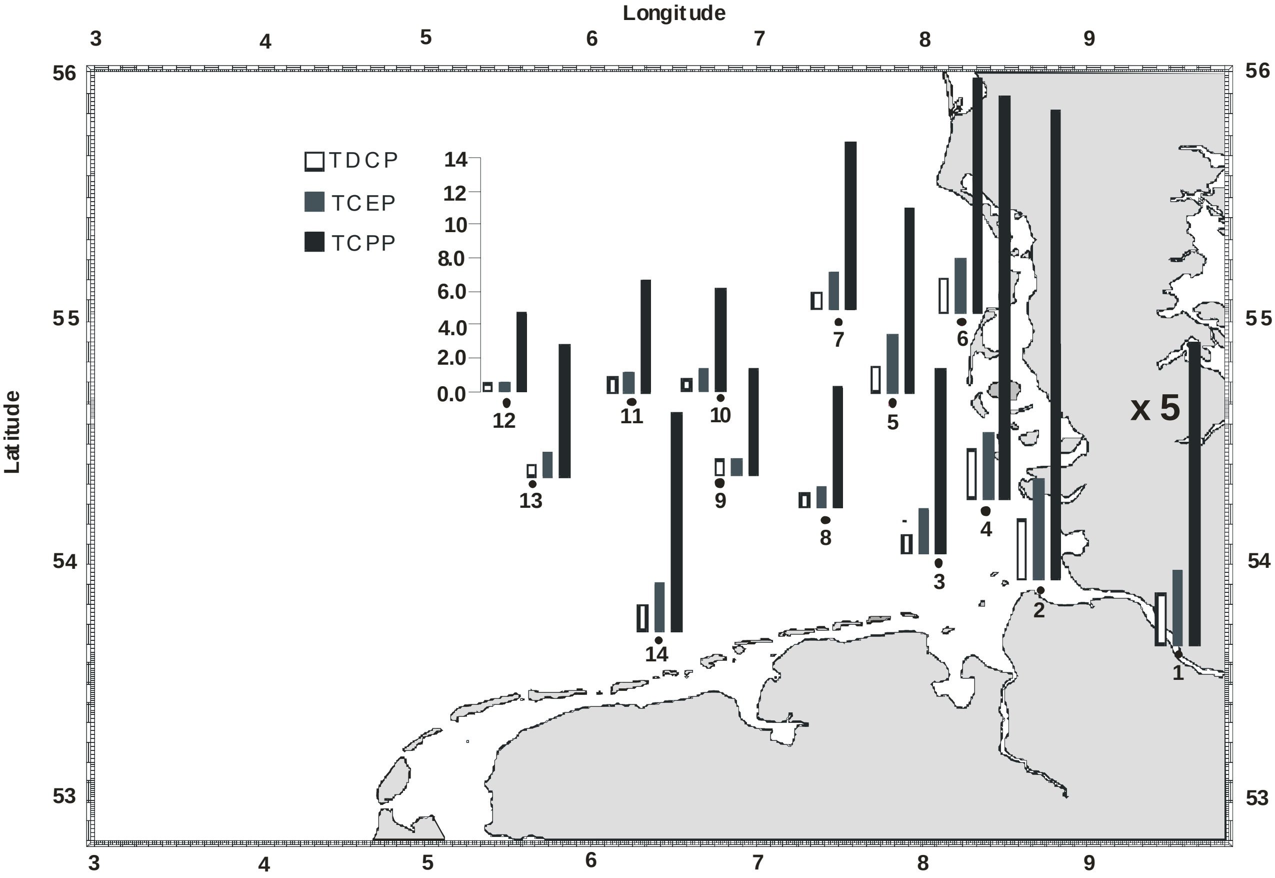
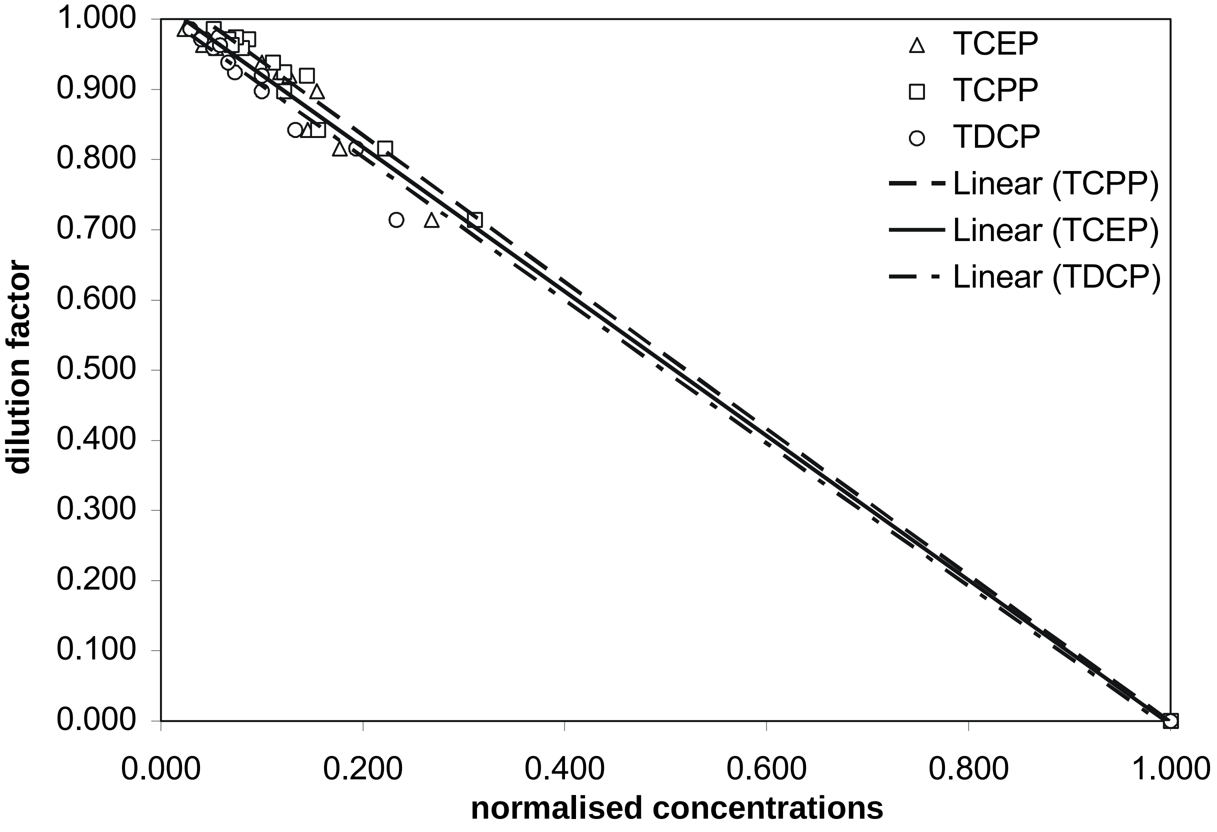


Figure 4.2 displays the dilution factor (quotient of salinity of Atlantic water and salinity at the respective sampling point) at each sampling point in comparison to the normalised concentrations of TCPP, TDCP and TCEP under the assumption of an average salinity of 35 ‰ for Atlantic water. For sample point 2 the salinity was estimated from data achieved from the BSH for the German Bight 2003 (BSH[64], 2003). For the chlorinated organophosphates a linear relationship was observed. This signifies that the decrease of the concentrations is just attributed to dilution. Moreover these substances showed a widespread distribution in the German Bight.

$$\text{dilution factor} = \frac{\text{salinity at sampling point}}{\text{salinity of Atlantic water}} \tag{3}$$

$$\text{normalised concentration} = \frac{\text{concentration at respective sampling point}}{\text{concentration at sampling point 1}} \qquad (4)$$

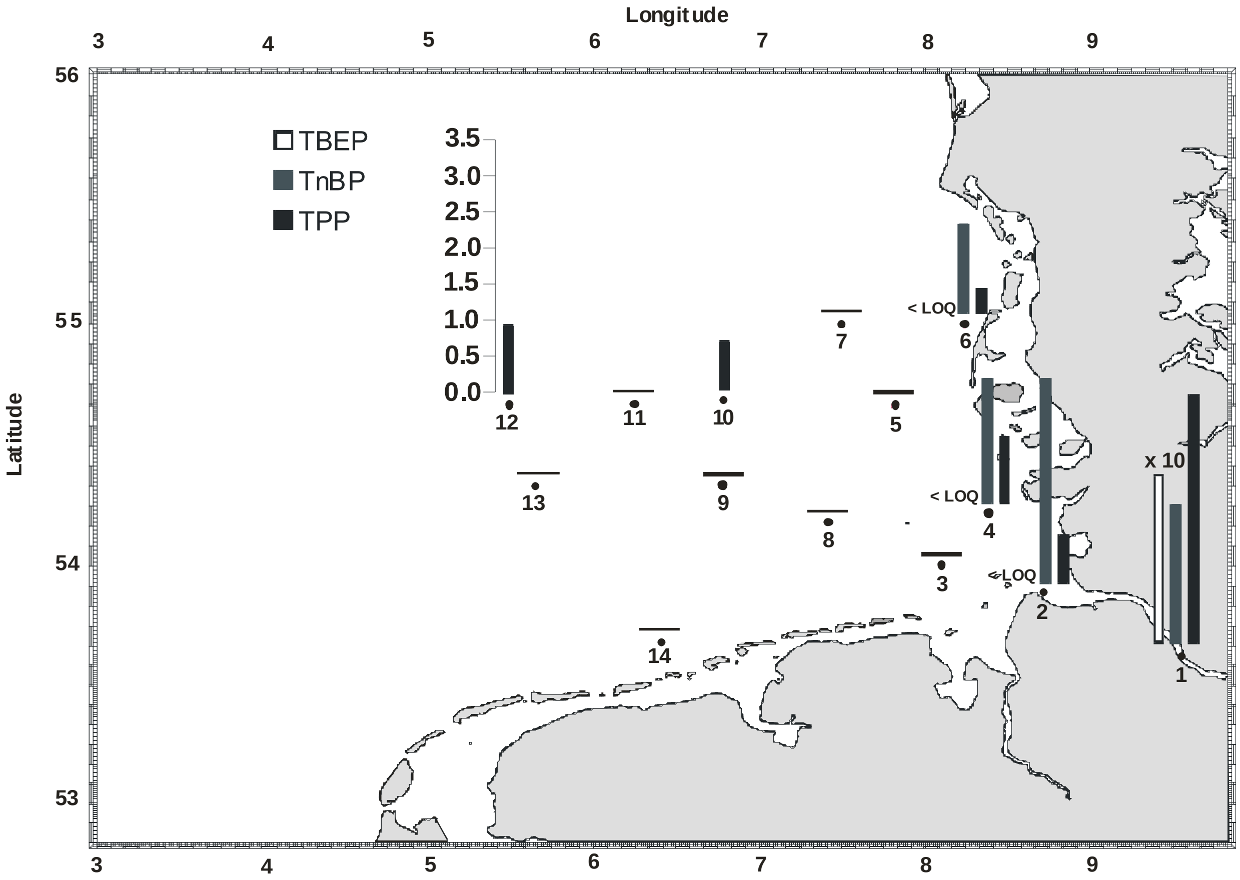
Figure 4.3 Correlation of dilution factor and normalised concentrations fort he selected organophosphorus flame retardants



4.3.2 Non-chlorinated organophosphorus plasticisers and flame retardants in the German Bight

Similar to the chlorinated organophosphates the highest amounts of the selected non-chlorinated organophosphates were detected at sample point 1 in the river Elbe. The respective concentrations were 23 ng/L TBEP, 19 ng/L T*n*BP and 3.1 ng/L TPP. Whereas EHDPP was below LOQ in all samples it was not possible to determine T*i*BP due to blank values. The measured amounts correspond with results from samples analysed in May 2003 (TBEP 24 ng/L, T*n*BP 38 ng/L and TPP 6.0 ng/L) near Stade (sample point 1, own data). Figure 4.3 displays the distribution of T*n*BP, TBEP and TPP in the German Bight.

Figure 4.4 Distribution of selected non-chlorinated organophosphate esters in the German Bight; concentrations given in ng/L



In the estuarine region (sample point 2) the concentrations of the selected organophosphates were noticeable lower for T*n*BP and TPP whereas the amount for TBEP was below LOQ. In contrast to the chlorinated organophosphates the concentrations for T*n*BP and TPP in the river Elbe plume were above LOQ only in samples near the coast (sample points 4 and 6). Values for TBEP were below LOQ in all samples, though. Apart from two offshore samples (sample points 10 and 12) in which TPP was detected, the concentrations for all selected non-chlorinated organophosphates were below the respective LOQ. The detection of TPP in the respective samples might stem from the research vessel as TPP is used, e.g., in hydraulic fluids or can be attributed to contaminations during the sampling procedure. Due to the fact that similar starting concentrations of T*n*BP and TBEP in comparison to the chlorinated organophosphates were detected a faster reduction for the non-chlorinated compounds was observed. Thus the conclusion can be drawn that other parameters influence the decrease of the non-chlorinated organophosphate ester besides the dilution with Atlantic water.

4.3.3 Comparison to other contaminants in the German Bight

In the 1990ies diverse organic pollutants such as polycyclic musk fragrances or diverse herbicides and by-products of pesticide production have been identified and quantified in the German Bight. Compared to these studies the chlorinated organophosphates exhibit very high concentrations in the North Sea. Table 4.2 gives an overview of the concentrations measured at sampling point 4 in the current study and comparable sampling points of former studies.

Table 4.3 Comparison of divers organic pollutants at sample point 4 of this study and a comparable sampling point of former studies

Compound	Concentration [ng/L]	Literature
Chlorinated organophosphates	2.9-24	This study
Polycyclic musk fragrances	0.2-0.6	Bester *et al.* 1998[65]
Musk xylene	0.08	Gatermann *et al.* 1995[66]
α- HCH	0.5	Theobald *et al.* 1996[67]
Atrazine	42	Bester/Hühnerfuss 1993 a/b[68,69]
Thiophosphates	1-8	Gatermann *et al.* 1996[70]
MTB	0.6-1.1	Bester *et al.* 1997[71]
Nonylphenol	2.5	Bester *et al.* 2001[72]
BPA	n.d.-4.8	Heemken *et al.* 2001[73]

MTB: Methylthiobenzothiazol; BPA: Bisphenol-A; HCH: Hexachlorocyclohexane; n.d: not detected

Table 4.2 shows that the concentrations of the chlorinated organophosphate esters are 1-2 orders of magnitude higher than polycyclic musk fragrances or α- HCH. Similar amounts were detected for herbicides (atrazine), by-products of pesticide production (thiophosphates) or endocrine disruptors such as nonylphenol or BPA.

4.4 *Comparison with Lake Ontario*

Table 4.4 gives an overview on the results of the chlorinated and non-chlorinated organophosphate esters. The highest concentrations were found in samples which were influenced by the STP outflows (samples STP 1 and STP 2) with highest amounts for TBEP (230-290 ng/L) and TCPP (69-78 ng/L). For the other selected organophosphate esters the respective concentrations ranged from 25 ng/L for TPP to 49 ng/L T*n*BP for the non-chlorinated substances. For the chlorinated flame retardants TDCP and TCEP they were in the same range (26-35 ng/L TDCP and 35-46 ng/L TCEP). At sample point 4 the amounts of all measured organophosphate esters were slightly lower.

Table 4.4 Overview on the respective concentrations of the chlorinated and non-chlorinated alkylphosphates at the different sampling points

Sample	Analyt c [ng/L]					
	T*n* BP	TPP	TBEP	TCPP	TCEP	TDCP
1	4.6	2.0	18	7.1	5.7	3.7
2	1.6	0.40	5.4	3.5	3.5	2.3
3	1.2	0.34	3.2	3.4	3.5	2.1
4	35	24	170	49	25	19
STP 1	49	25	290	78	46	35
STP 2	49	26	230	69	35	26

Slightly north of the shipping channel (sample point 1) the concentrations for all selected organophosphates were an order of magnitude lower than in the bay itself (sample point 4). This shows that Hamilton harbour is a more or less isolated bay with little water exchange with fresh water from Lake Ontario. At a distance of 3 km to the shipping channel (sample point 2) a decrease of the amounts of the plasticisers and flame retardants was observed. They ranged from 0.40 ng/L TPP to 5.4 ng/L TBEP for the non-chlorinated substances whereas they were approximately 3 ng/L for the chlorinated ones. The reduction of the concentrations was most likely a dilution effect within the lake. At a distance of 10 km from the shipping channel (sample point 3) the determined concentrations did not change in comparison to those observed at sample point 2. Thus no additional dilution was observed.

Moreover this indicates that the different organophosphate esters are stable under the conditions found in Lake Ontario.

4.5 *Conclusions to occurrence in pristine waterbodies*

The chlorinated organophosphate esters TCEP, TCPP and TDCP are persistent organic pollutants that are not only detected in surface waters like rivers but also in marine water samples. The current study has shown that a decrease of these substances in the German Bight is only attributed to dilution. On the one hand the determined concentrations for the respective chlorinated organophosphates were only in the lower ng /L-range and the bioaccumulation potential is expected to be low due to the log KOW-value, but on the other hand almost nothing is known on the toxicity of these substances especially in combination with other synthetic chemicals although the determined concentrations are lower than effect levels found in laboratory studies. Thus the widespread distribution of these compounds in the German Bight in addition to the demonstrated persistence in environmental samples has to be regarded as a reason for concern. Apparently these results are contrary to the Esbjerg Declaration from 1995[74]. The objective of this declaration was to ensure a sustainable, sound and healthy North Sea ecosystem. For that purpose the discharges, emissions and losses of hazardous substances should be reduced. The guideline principle therefore is the precautionary principle considering zero emissions of synthetic substances into the North Sea. Moreover this study demonstrated that chlorinated organophosphates exhibit very high concentrations compared to other organic pollutants.

The behaviour of the selected non-chlorinated organophosphate esters differed to some degree. Whereas the amounts of the chlorinated organophosphates were only reduced by dilution other parameters might influence the reduction of the T*n*BP, TBEP and TPP as these substances were detected only in samples from the river Elbe plume near the coast although “starting” concentrations for these substances were in the same range as for the chlorinated alkylphosphates.

The results obtained from the measurements of samples from Lake Ontario confirm the results achieved for the German Bight as a reduction of the concentrations for the selected substances is attributed to dilution as well.

5 Organophosphorus flame retardants and plasticisers in fish samples

5.1 *Introduction to fish samples*

Organophosphorus flame retardants and plasticisers are important contaminants in German surface waters. Especially the chlorinated flame retardants are very persistent as they have recently been detected and quantified even in marine water samples from the German Bight (Weigel *et al.*, own studies (chapter 4)). As almost nothing is known on subchronical effects of the selected organophosphates a guideline value of 0.1 µg/L was proposed for TCPP in surface waters. This value is often exceeded in German surface waters as concentrations of 100 ng/L-200 ng/L were observed for the rivers Rhine, Ruhr and Lippe. The observed LC_{50}-values were several orders of magnitude higher than the guideline value. For e.g., rainbow trout the 96 h-LC_{50}-values ranged from 0.36 mg/L to 250 mg/L for the selected alkylphosphates. NOEC-values were in the same range if determined. An overview is given in Table 5.1.

Table 5.1 Overview on bioconcentration, log K_{OW}-value and toxicity of selected organophosphates

Substance	BCR	log k_{ow}	96 h-LC_{50} [mg/L]	NOEC [mg/L]	Literature
TnBP	11-49 killifish; 6-11 goldfish	4.0	4.2-11.8	-	Sasaki et al.[80], EHC 112[17]
TPP	250-480 killifish; 110-150 goldfish	4.61-4.76	0.36-290	-	Sasaki et al.[80], EHC 111[20]
TBEP	-	3.65	16-24	10	EHC 218[19]
TCPP	-	2.59	51-180	9.8 estimated	EHC 209[18]
TDCP	47-107 killifish; 3-5 goldfish	3.8	1.1-5.1	0.56	Sasaki et al.[80], EHC 209[18]
TCEP	~ 1 (goldfish/killifish)	1.7	90-250	50	Sasaki et al.[80], EHC 209[18]

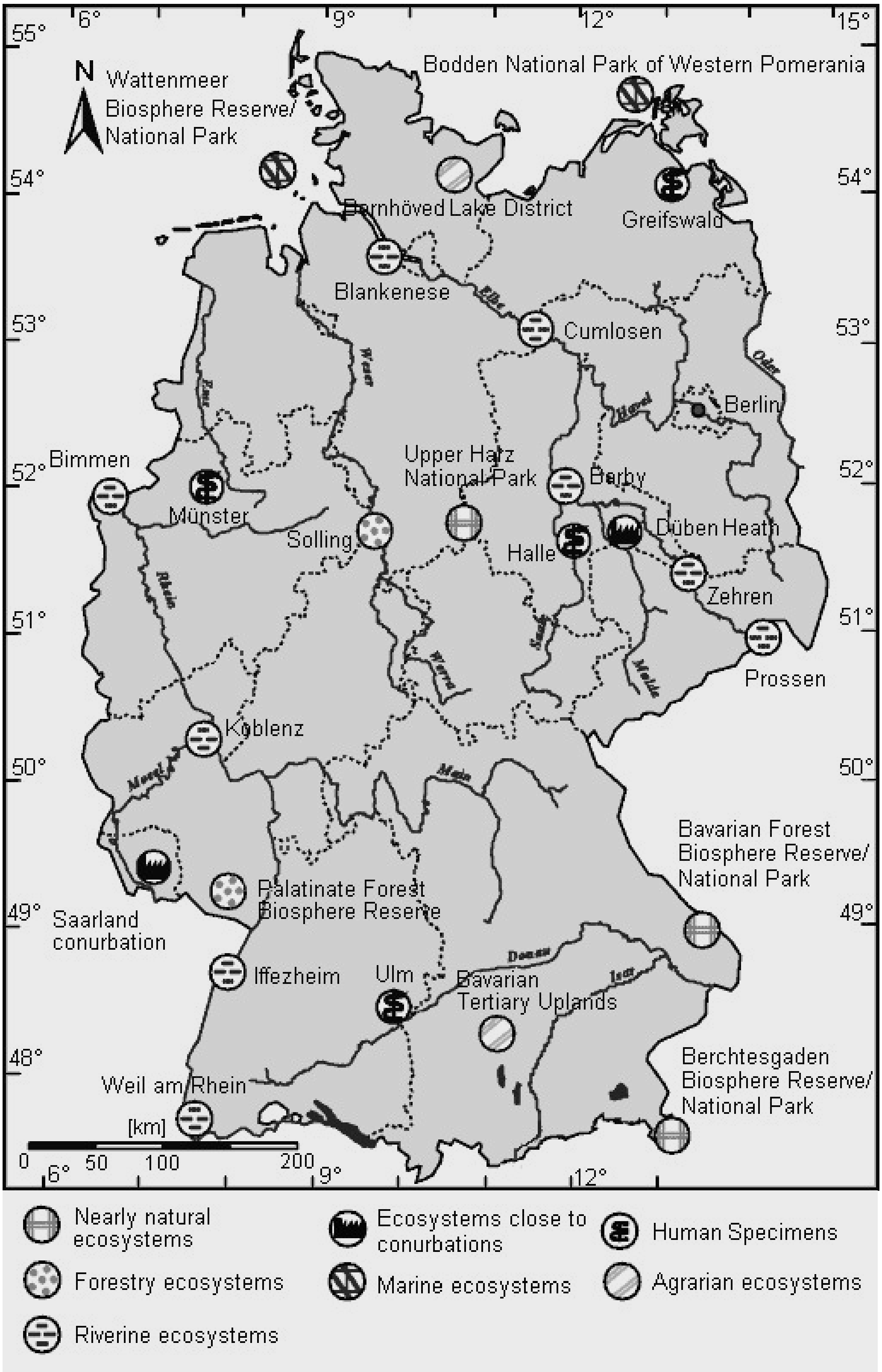
Only few data is available on the concentrations of the selected alkylphosphates in fish. Amounts of 1-30 ng/g for TBP (EHC 112, 1991), 100-600 ng/g for TPP (EHC 111, 1991) and 0.005-0.14 mg/kg for TCEP (EHC 209, 1998) were reported. Most of these data were obtained from samples taken in Japan und US rivers such as the Mississippi and the Missouri. No data is available for TCPP and TDCP. Most of these studies were performed about 30 to 20 years ago. In this long period of time the usage and production of the different substances has changed as, e.g., TCEP was substituted by TCPP. Thus it is crucial to get information on current concentrations in these organisms. The bioaccumulation potential is expected to be low due to the log KOW-values. In studies from Sasaki *et al.* (1981, 1982)[79,80] the bioconcentration ratios (BCR) for TBP, TPP, TCEP and TDCP were determined in laboratory experiments with killifish and goldfish. Muir *et al.*[75,76] studied the uptake and bioaccumulation of triphenylphosphate and 2-ethylhexyldiphenylphosphate by rainbow trout.

A very good example on the changes of organophosphate concentrations in the river Ruhr has been documented by Andresen *et al.* [77] (compare Figur 2.6).

5.2 *Materials and methods to fish samples*

In this study the concentrations of the selected flame retardants and plasticisers were determined in bream muscle (abramis brama) from different locations in Germany. The samples were obtained from the German Environmental Specimen Bank. Bream was chosen because of the widespread presence, the adaptability to changings in the environment and the resulting substantial biomass availability. The sampling is confined to bream aged eight to twelve years and takes place in the late summer after the spawning season. The samples were stored under liquid nitrogen. For the determination of the organophosphate esters the bream muscle was freeze dried and cryo grinded. Samples were analysed from six different places located at the rivers Rhine (Weil am Rhein), Elbe (Blankenese, Barby) and Saar (Rehlingen, Güdingen). An overview on the sampling locations of the German Environmental Specimen Bank is given in Figure 5.2. The sample points Rehlingen and Güdingen are located in the Saarland conurbation whereas sampling stations Barby, Weil and Blankenese represent riverine ecosystems. To observe a possible temporal development in changes of the concentrations samples were taken from different years.

Figure 5.1 Overview on the sample location of the Environmental Specimen Bank in Germany[78]



5.2.1 Sample extraction

5 g of each sample were mixed with 15 g diatomeous earth and filled in a 33 mL ASE extraction cell that was sealed with a circular cellulose filter at the bottom. The extraction was performed with ethyl acetate with following conditions: preheat: 0 min; static: 10 min; flush: 50 %; purge: 120 sec; cycles: 1; pressure: 150 bar; temperature: 90 °C. After the extraction 100 µl of internal standard solution were added and the samples were concentrated with a concentration unit (Büchi Syncore, Büchi, Essen, Germany) at 60 °C and 60 mbar to 1 mL.

5.2.2 Clean up

The sample extract contains components with high molecular masses such as lipids and proteins. Before these substances were removed by size exclusion chromatography (SEC) a clean up with dried silica gel was carried out. 1 g of dried silica gel (105°C, 24h) was put into an 8 mL glass column between two PTFE frits. After conditioning with *n*-hexane, 1 mL of the sample extract was applied to the column. The analytes were then eluted with 12 mL ethyl acetate. After concentrating the extract to a volume of 1 mL, 1 mL of cyclohexane was added and the complete sample was injected onto the SEC column (SX-3, biorad). A mixture of cyclohexane/ethyl acetate (50:50 v/v) was used as eluent at a flow rate of 5 mL/min. The first fraction from 0 to 19.5 min contains the higher molecular weight compounds, the selected organophosphates are eluted in the second fraction from 19.5-30 min which was collected in a 100 mL amber flask. The SEC-column was rinsed with the eluent for another 20 min before the next sample was injected. The second fraction was concentrated to 1 mL and the solvent was changed to toluene. Before the samples were measured a second clean up using dried silica gel was performed. For this purpose 1 g of dried silica gel (105°C, 24h) was put into an 8 mL glass column between two PTFE frits. After conditioning with *n*-hexane, 1 mL of the sample extract was applied to the column. After a cleaning step with 8 mL *n*-hexane/MTBE (95:5 v/v) the organophosphates were eluted with 12 mL ethyl acetate. The samples were concentrated to 1 mL and the solvent was changed to toluene.

5.2.3 Instrumental determination

The samples were analysed on a gas chromatography system with mass spectrometric detection (DSQ Thermo Finnigan, Dreieich, Germany) equipped with a PTV injector. To increase the sensitivity of the method, the PTV was operated in large volume injection mode (10 µl injection volume) with a sintered glass liner (SGE) with the following temperature program: 115 °C [0.4 min, 130 mL min^{-1} He] → 12 °C s^{-1} (splitless) → 280 °C [1.5 min] → 1 °C min^{-1} → 300 °C [7 min] (cleaning phase).

The GC separation was performed using a DB5-MS column (J&W Scientific, Folsom, CA, USA); length: 15 m, ID: 0.25 mm, film: 0.25 µm and the following temperature programme: 100 °C [2 min] → 30 °C min^{-1} → 130 °C → 8 °C min^{-1} → 220 °C → 30 °C min^{-1} → 280 °C [7 min] using He (5.0) as carrier gas with a flow of 1.5 mL min^{-1}. The mass spectrometer was used with electron impact ionization with 70 eV ionisation energy. The MS was operated in selected ion monitoring (SIM) mode. The different organophosphate esters were detected by means of their mass spectral data and retention time. Two internal standards, i.e., deuterated T*n*BP (T*n*BP d_{27}) and deuterated TPP (TPP d_{15}) were utilized for the more and less volatile compounds respectively. For quantitative measurements the method was validated. Full quality data for the method were obtained from three replica extractions of a spiked mixture of solids (soil/manure) as this method was developed for the determination of organophosphate esters in sewage sludge. A transfer of this method was obtained by standard addition analysis of fish samples prior to this study. For that purpose fresh bream muscle was freeze dried and spiked with 5 ng/g of each selected organophosphate ester. These experiments resulted in the same recovery rates and standard deviations as for soil/manure, though. The full quality data of the method is given in Table 5.2. To prove the reproducibility of the method samples from Weil, Blankenese and Güdingen were analyzed with four replica extractions. Examples for the reproducibility are given in figures 5.3 and 5.4. They demonstrate that for replica extractions even in the range of the LOQ the same concentrations were determined for the selected organophosphate esters. A few exceptions were observed, e.g., for T*i*BP (compare Figure 5.4). The full set of numerical data is given in Table 5.2

Table 5.2 Quality assurance data fort he applied method

Compound	Analytical Ion [amu]	Verifier Ion [amu]	Recovery Rate [%]	RSD [%]	LOQ [ng/g]	Internal Standard
T*i*BP	211	155	76	6	3	T*n*BP-D27
T*n*BP	211	155	87	7	1	T*n*BP-D27
TCEP	249	251	70	11	1	T*n*BP-D27
TCPP	277	201, 279	76	10	2	T*n*BP-D27
TDCP	379	381	77	6	3	TPP-D15
TBEP	199	299	51	15	10	TPP-D15
EHDPP	251	362	117	7	3	TPP-D15
TPP	325	326	96	6	1	TPP-D15

Figure 5.2 reproducibility of the method for concentrations in the range of the LOQ (data for samples from Weil (Rhine 2000)

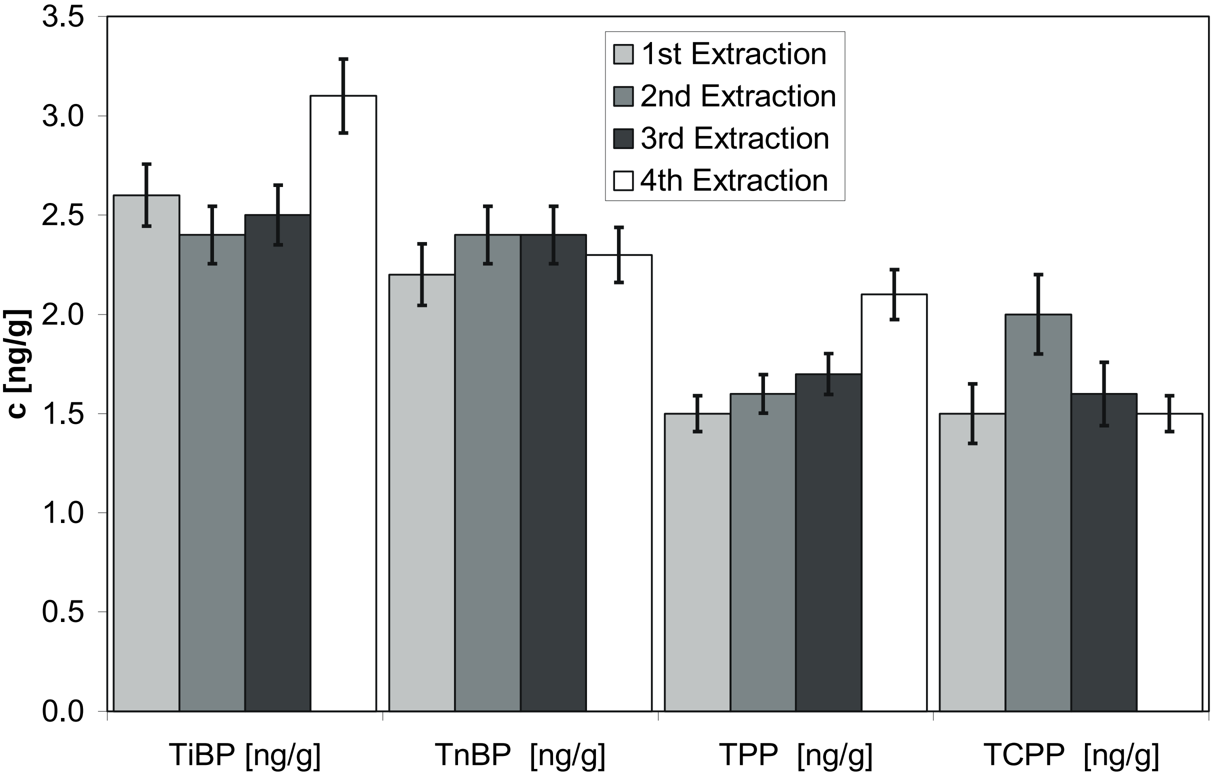
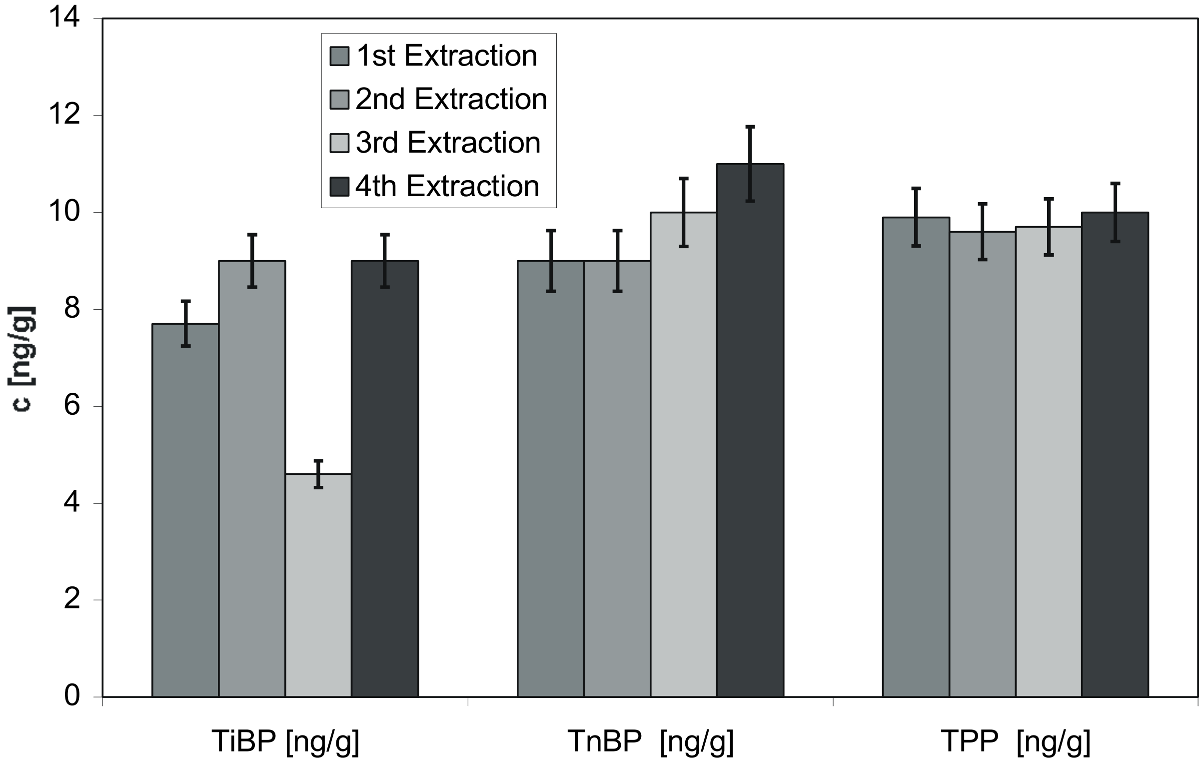


Figure 5.3 Reproducibility of the method for higher concentrations (data for samples from Güdingen (Saar conurbation 1992)



5.3 *Results and Discussion to fish samples*

In all samples the concentrations of organophosphates were in the low ng/g (dry weight) range. This was expected due to the low log K_{OW} of these compounds. Besides of the chlorinated organophosphate TCPP some non-chlorinated organophosphates were determined. However the pattern varied considerably depending on the origin of the samples.

In Table 5.3 the results for bream muscle from the selected sampling locations are shown. For the chlorinated flame retardants TCEP and TDCP and for the non-chlorinated plasticisers TBEP and EHDPP all concentrations were below the limit of detection.

Table 5.3 Concentrations of selected organophosphate esters at different sampling location in Germany given in ng/g dry weight (Concentrations for TCEP, TDCP, TBEP and EHDPP were below the respective limit of detection)

sample	location/year	T*i* BP [ng/g]	T*n* BP [ng/g]	TPP [ng/g]	TCPP [ng/g]
1	Weil a. R. (Rhine) 2000	2.4	3.4	1.7	1.5
2	Weil a. R. (Rhine) 1997	20	5.6	< 1	< 1
3	Blankenese (Elbe) 2002	-	3.8	1.9	1.4
4	Barby (Elbe) 1997	6.7	4.6	< 1	9.5
5	Rehlingen (Saar) 2004	3.6	3.8	5.5	< 1
6	Güdingen (Saar) 1992	8.4	11	10	1.6

For T*i*BP and T*n*BP similar amounts were detected in most samples. The concentrations ranged from approximately 2 ng/g to 20 ng/g T*i*BP and 11 ng/g T*n*BP respectively. Due to matrix interferences it was not possible to determine the concentrations for T*i*BP in sample 3. Lower concentrations were determined for TCPP and TPP. The concentrations for these compounds ranged from < 1 ng/g to 10 ng/g. It is also noticeable that the amounts of the detected organophosphate esters vary at the different sample locations. The highest concentrations for TCPP were determined in bream muscle from Barby of the year 1997 whereas at the other sampling points the amounts showed almost no variance. Similar results were obtained for T*i*BP, T*n*BP and TPP as different distribution patterns were observed at the selected sampling locations for each of the organophosphates. Moreover it seems that the respective sampling location is an important factor concerning the concentrations in fish as e.g., for TPP higher amounts were detected in samples from the Saarland conurbation in comparison to the riverine ecosystems Rhine and Elbe. Although the amounts of the selected alkylphosphates were determined in a limited number of samples a temporal trend was noticeable. In the Saarland conurbation (sample points Rehlingen and Güdingen) a significant decrease of the concentrations for T*i*BP, T*n*BP and TPP was observed from 1992 to 2004. As the samples from the Saarland conurbation area were taken at different sampling location the observed temporal trend is only indicative. Similar results were obtained for T*i*BP at Weil am Rhein (Rhine) between 1997 and 2000. A comparison of the results for T*i*BP in the Saarland conurbation and Weil (Rhine) shows that changes in the concentrations can

be observed in comparable short time periods This is in accordance to the findings of temporal trends in the river Ruhr (compare Figure 2.6)
Sasaki et al[79,80]. (1981, 1982) demonstrated a correlation between the log log K_{OW} and the log BCR. The BCR is defined as the quotient of the concentrations found in the respective species and the concentration in the environment (equation 5[81]).

$$\text{BCR} = \frac{\text{concentration of substance in organism}}{\text{concentration of substance in environment}} \quad (5)$$

Although no BCR was determined for TCPP in the studies of Sasaki *et al.* the correlation between BCR and log K_{OW} might indicate why higher amounts of the non-chlorinated alkylphosphates were detected in bream muscle for non-chlorinated alkylphosphates than for TCPP. In the literature the log K_{OW} for TCPP is quoted to be 2.59 (EHC 209, 1998) whereas it is 4.0 for T*n*BP (EHC 112, 1991) and 4.61-4.76 for TPP respectively (EHC 111, 1991). In the experiments of Sasaki TCEP remained due to the low log K_{OW} of 1.7 almost quantitatively in the water and thus it was not accumulated in killifish and goldfish. Consequently the observed BCR was very low (0.7-2.2). These findings were confirmed by the current study as TCEP was not detected in any sample. The log K_{OW} for TBEP is quoted to be 3.65 (EHC 218, 2000) and concentrations in the environment were reported to be in the same range as for TCPP. However TBEP was not detected in the analysed bream muscle. On the one hand the current method is less sensitive for this substance than for the other selected compounds, on the other hand it might be that TBEP is rapidly metabolised in fish and thus not accumulated. Similar results were obtained for TDCP. Although the log K_{OW} is 3.8 and thus higher than the one for TCPP, TDCP was not found in bream muscle at the selected sampling sites.

5.4 *Conclusions to fish samples*

Although the number of sample was limited in the current study it has been shown that T*i*BP, T*n*BP, TPP and TCPP were bioaccumulated in fish as these substances have been detected in bream muscle from different sampling sites in Germany. The concentrations of the determined organophosphate esters in fish were in the low ng/g-range, though. Moreover a temporal trend in the concentrations was observed as the detected amounts were lower in samples from the years 2004 (Rehlingen, Saar) and 2000 (Weil am Rhein, Rhine) in comparison to the years 1992 (Güdingen, Saar) and 1997 (Weil am Rhein, Rhine). The sampling location seems to be an important factor that influences the detected levels of these substances in fish muscle as in the conurbation area higher amounts were detected than in riverine ecosystems. From these samples first trends were obtained concerning the bioaccumulation of these substances. It will be interesting to confirm these results with further studies on different locations and time periods. As especially the chlorinated organophosphate esters are very persistent and have been recently detected and quantified in the marine ecosystem of the Germen Bight it would be of special interest to get information if these compounds are found in marine organisms as well. Although the bioaccumulation of these substances is low in comparison e.g., to brominated flame retardants as PBDEs almost nothing is known on toxicological issues especially in combination with other substances.

6 Overall Discussion and Conclusions

The studies have shown that chlorinated and non-chlorinated phosphate esters are emitted from a multitude of sources. In the indoor and outdoor environment they are emitted under normal conditions of use and thus they were detected in wastewater. Whereas the non-chlorinated alkylphosphates were partly eliminated in wastewater treatment plants the amounts of the chlorinated flame retardants were hardly reduced. The elimination efficiency of wastewater treatment depends on the one hand on the dimension of the respective STP and on the other hand on the technique that is used. The elimination rates for the large STPs A to C were significantly higher than for the smaller STPs D and E. A comparison of the elimination in activated sludge plants and trickling filters showed that the trickling filters were less effective than activated sludge. Moreover the wastewater volume influences the elimination as a decrease of the elimination rates was observed during rainfall. To assure a permanent elimination especially of the non-chlorinated alkylphosphates a constant wastewater flow is necessary. During rainfall this could be reached by building more stormwater overflow tanks near wastewater treatment plants. In degradation experiments with activated sludge in batch reactors bis-(2-chloroethyl) phosphate (BCEP) was identified as metabolite of tris-(2-chloroethyl) phosphate (TCEP).

As almost nothing is known on the subchronic toxicology of the organophosphate ester flame retardants and plasticisers a guidance value of 0.1 µg/L was proposed for TCPP in surface waters by the German Federal Environmental Agency although EC values for diverse species are almost three orders of magnitude higher. In the Ruhr Basin treated wastewater is rather not drained into the river Ruhr but into the river Emscher. This guideline value is exceeded near the mouth, though. Similar results were obtained for other rivers in Germany. A reason of concern is that the chlorinated flame retardants were found to be very persistent as they have been detected and quantified in the German Bight or other large waterbodies as Lake Ontario. A reduction of these substances in marine water samples was traced back to dilution effects. The bioaccumulation for the selected organophosphates in bream is low, though.

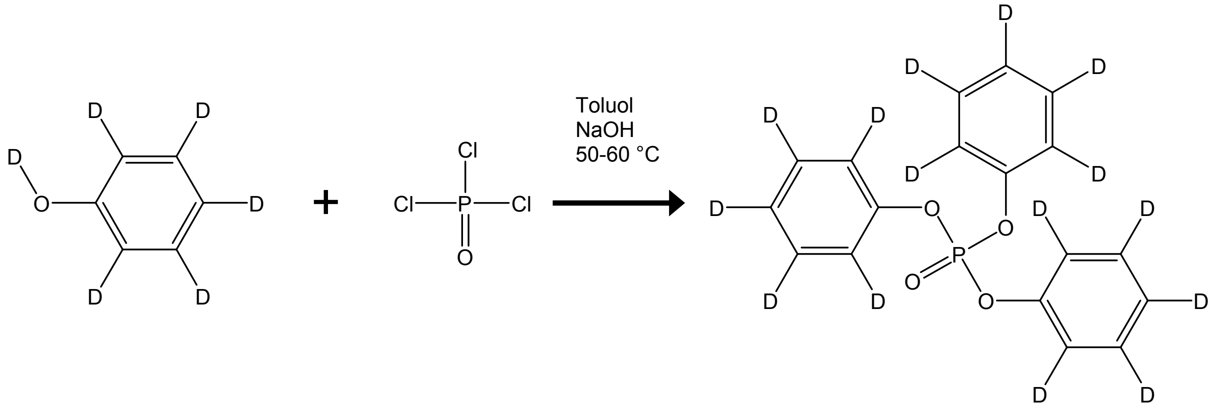
An ADI-value of 0.04 mg/kg day and guidelines values for indoor air of 0.05 and 0.005 mg/kg were proposed for TCEP. Former studies have shown that no health risks were expected due to inhalative intake of selected organophosphate esters. As the drinking water supply often depends on artificial groundwater recharge the elimination efficiency of drinking water purification plants in the Ruhr Basin was observed. At all studied plants the concentrations of the respective organophosphates were below LOQ. This means that no additional health risk is expected from drinking water. It has been demonstrated that the elimination especially of the chlorinated organophosphates by means of natural drinking water purification techniques such as bank filtration, underground passage and slow sand filtration depends on a multitude of parameters. To guarantee a constant drinking water quality concerning the selected alkylphosphates additional treatment techniques such as multilayer filtration, flocculation/precipitation, ozonisation and activated carbon filtration are needed.

As expected from the respective log K_{OW} values of the selected organophosphate esters the bioaccumulation of these substances in fish is low. The concentrations of T*n*BP, T*i*BP, TPP and TCPP in bream muscle from different sampling locations in Germany were in the lower ng/g range (dry weight). TCEP, TDCP, TBEP and EHDPP were not detected in any sample. Moreover a temporal trend in the concentrations was observed. The sampling location seems to be an important factor that influences the detected levels of these substances in fish muscle as in the conurbation area higher amounts were detected than in riverine ecosystems.

The current work has demonstrated the emission, fate and behaviour of phosphororganic flame retardants and plasticisers in the aquatic environment and it has been shown that these substances are important contaminants.

7 Synthesis of the internal standard triphenylphosphat D_{15} (TPP D_{15})

7.1 *Reaction*



7.2 *Chemicals and Materials*

3 mmol phosphorus oxytrichloride (0.46 g)
10 mmol phenol D_6 (1.00 g)
sodium hydroxide solution 20 % (w/w)
toluene suprasolv
sodium carbonate solution saturated
dried silica (105 °C, 24h)
n-hexane

methyl *tert*. butyl ether (MTBE)

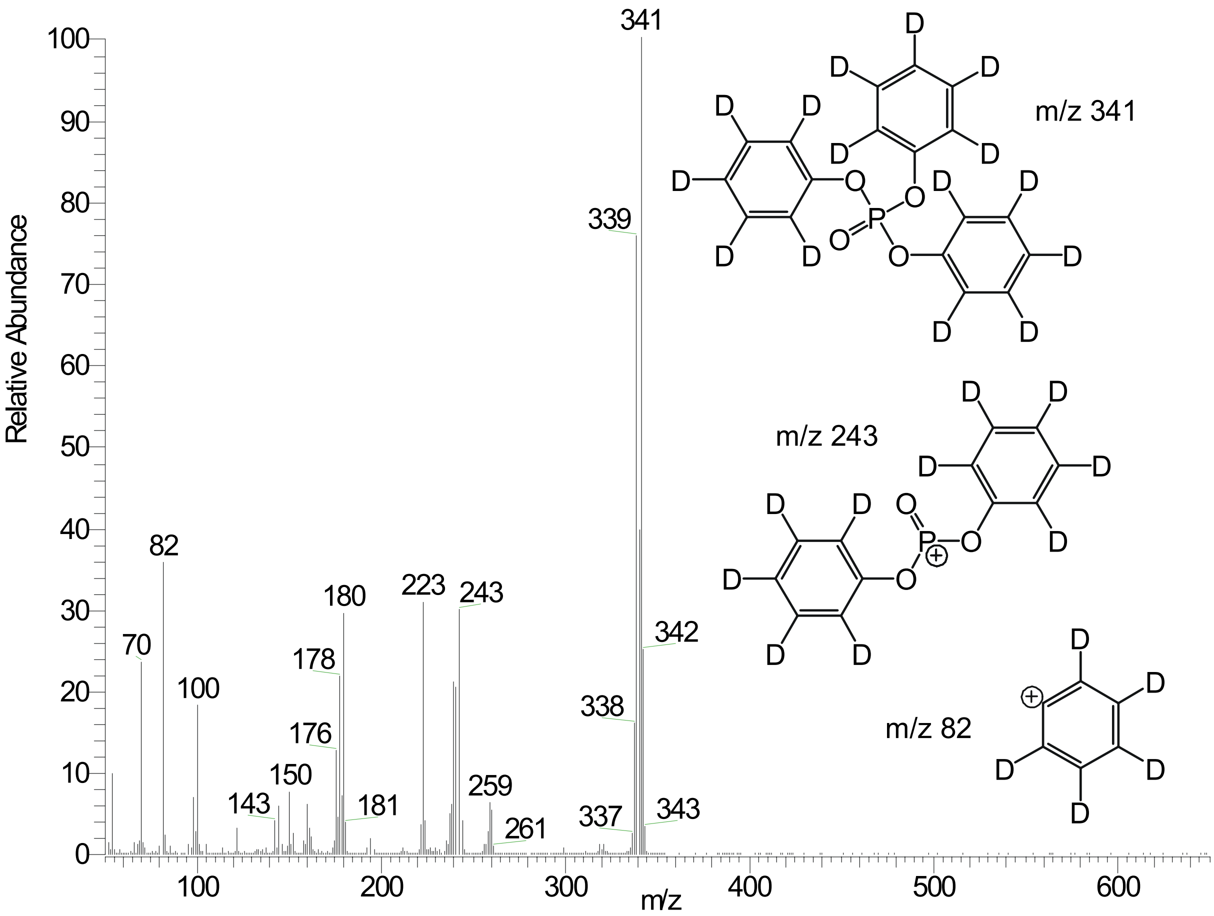
rotary evaporator
magnetic stirrer
30 mL amber bottle

Phosphorus oxytrichloride (Aldrich, Seeze, Germany) and phenol d_6 (Aldrich, Seeze, Germany) are dissolved in 15 mL toluene in a 30 mL amber bottle. After adding 4 mL sodium hydroxide solution 20 % (w/w) the reaction mixture is stirred for 30 min at room temperature. Subsequently the reaction mixture is heated to 50-60 °C and stirred for another 48 h. The toluene phase is separated from the aqueous one and extracted twice with saturated sodium carbonate solution. The toluene phase is concentrated to dryness (rotary evaporator, 60 °C, 60 mbar). The raw product remains as white crystalline substance.

As the raw product contains about 16-20 % diphenylphosphate d_{10} and other contaminations the product was cleaned up with silica gel.

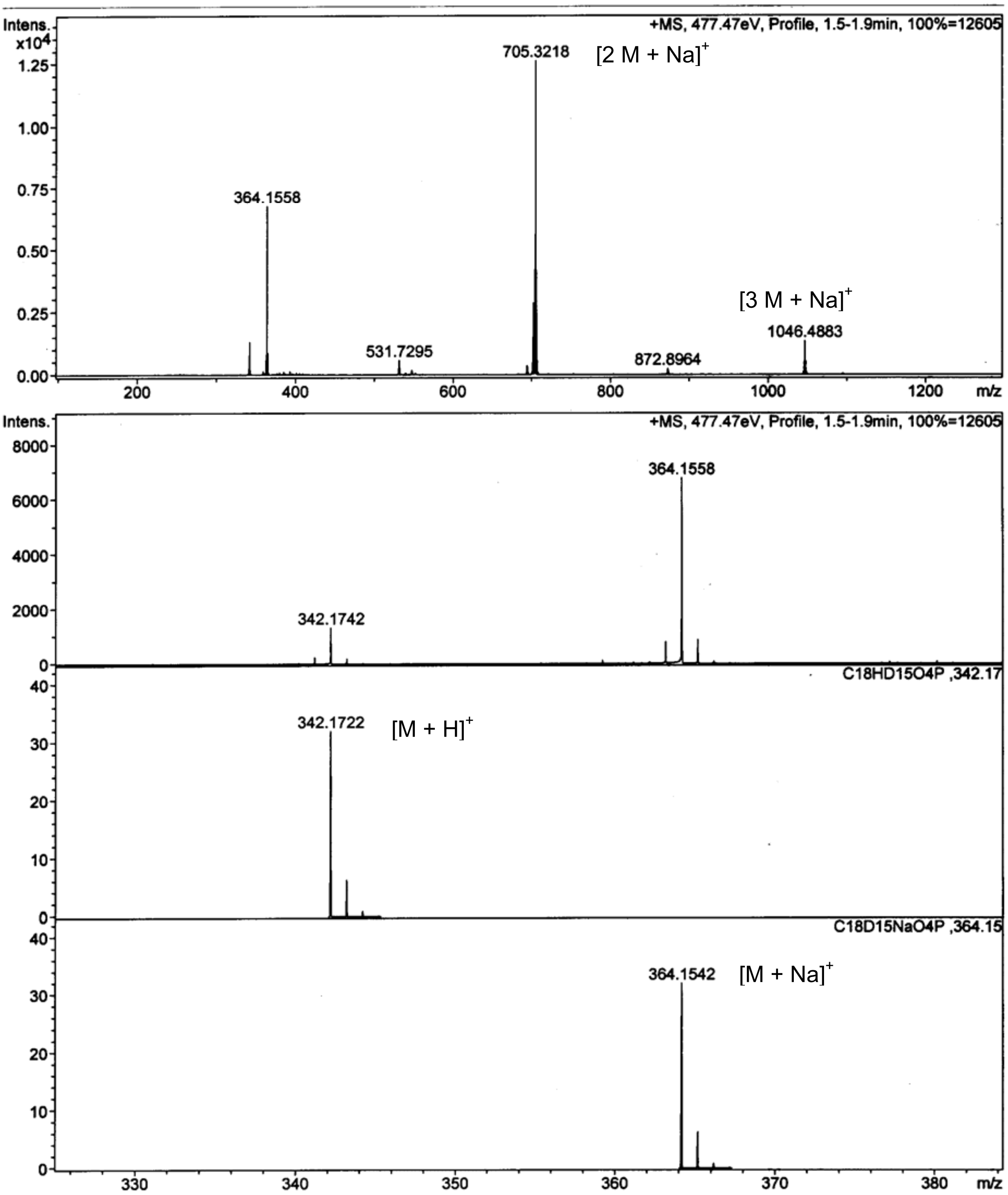
1 g of dried silica gel is put into an 8 mL glass column between to PTFE frits. After conditioning of the silica gel with 8 mL *n*-hexane the raw product dissolved in 1 mL *n*-hexane was applied to the column. Triphenylphosphate d_{15} is eluted with 30 mL toluene. Subsequently the column is eluted with 10 mL MTBE and 10 mL ethyl acetate. The MTBE phase contains besides diphenylphosphate d_{10} a small amount of TPP d_{15}. The purity was proved by GC-MS and electrospray ionization high resolution time of flight mass spectrometry (ESI-HR-TOF-MS). The respective mass spectra of TPP d_{15} are given in Figure 7.1. and Figure 7.2. The proposed fragmentation pathway is given in Figure 7.1 according the one proposed for TPP by Rodil *et al.*[82] (2005).

Figure 7.1 Electron impact mass spectrum of D15 TPP with proposals for the fragmentation



m/z	341 amu	[M]
	339 amu	$[M - D]^+$
	243 amu	$[M - C_6D_6O]^+$
	223 amu	$[M - C_6D_6O - D_2O]^+$
	82 amu	$[C_6D_5]^+$

Figure 7.2 ESI-HR-TOF mass spectrum of TPP d_{15} with suggested elemental composition for selected ions



The suggesed elemental composition of selected ions from the ESI-HR-TOF mass spectrum was compared with the theoretical mass for the respective ion. The differences of the theoretical mass of the and mass obtained from the spectrum were below 10 ppm each. Thus the empiric formulae were confirmed by the theoretical data. Furthermore this indicates that the purity of the synthesised TPP d_{15} is high as the detected sodium adducts of the di- and trimer is most probably formed in the ion source. For details compare table 7.1.

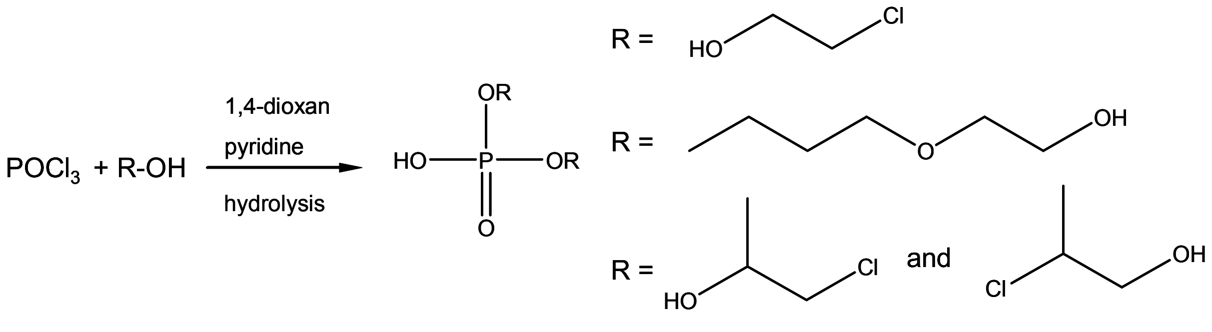
Table 7.1 Measured mass of selected ions, suggested and theoretical mass for each selected ion, as well as the mass differences

Measured mass [amu]	Suggested elemental composition	Theorethical mass of elemental composition [amu]	Difference [ppm]
342.1722	$[C_{18}D_{15}O_4P + H]^+$	342.1728	1.8
364.1542	$[C_{18}D_{15}O_4P + Na]^+$	364.1547	1.4
705.3210	$[C_{36}D_{30}O_8P_2 + Na]^+$	705.3197	1.8
1046.4883	$[C_{54}D_{45}O_{12}P_3 + Na]^+$	1046.4846	3.5

8 Synthesis of dialkylphosphates

As it is supposed that dialkylphosphates are the main degradation products of trialkylphosphates, bis-(chloroethyl) phosphate (BCEP), bis-(chloro*iso*propyl) phosphate (BCPP) and bis-(butoxyethyl) phosphate (BBEP) were synthesized as reference for the identification of these metabolites. Diphenylphosphate and dibutylphosphate were purchased from Sigma-Aldrich, Steinheim, Germany.

8.1 *Reaction*



8.2 *Chemicals and Materials*

50 mmol phosphorus oxytrichloride
100 mmol chloropropanol, butoxyethanol
    or chloroethanol
pyridine
TMSH
water (HPLC grade)
paper filter
rotary evaporator
magnetic stirrer
100 mL amber bottle
1,4-dioxan

50 mmol phosphorus oxytrichloride were dissolved in 70 mL 1,4-dioxan in an amber bottle. To this solution a mixture of 100 mmol of the respective alcohol and 50 mmol pyridine in 20 mL 1,4-dioxan was added dropwise under temperature control by cooling with ice. The reaction mixture was stirred for 24 h at room temperature. For the removal of pyridiniumchloride the mixture was filtrated. The product of this reaction is the respective dialkylated phosphorus chloride. The dialkylated phosphate was obtained by the hydrolysis of the product with water and pyridine. For this purpose 100 mmol pyridine and water were added to the filtrate and the mixture was stirred for another 24 h. Again pyridiniumchloride was removed. The filtrate was concentrated with a rotary evaporator for the removal of 1,4-dioxan, pyridine and water. The respective raw product was obtained as yellowish liquid. For the control of the reaction the raw product was treated with TMSH. The respective methyldialkylphosphate ester was analysed by GC-MS in scan mode (for details compare 1.5.3). For further identification the GC-MS measurements were repeated using positive chemical ionisation (PCI). The gas chromatographic conditions for the PCI-measurements were the same as for the respective EI ones. The MS was operated in scan mode (scan range 90-650 amu, scan rate 1000 amu/s). Methane was used as regent gas with a flow of 1 mL/min. The ion source temperature was set to 180 °C. The ionisation energy was set to 70 eV. The raw products contained the respective methylated dialkyl and trialkyl phosphates. The methyldialkyl phosphate esters were identified by the respective mass spectral data.

8.2.1 Identification of bis-(chloroethyl) phosphate (BCEP)

Figure 8.1 EI and PCI spectrum of BCEP

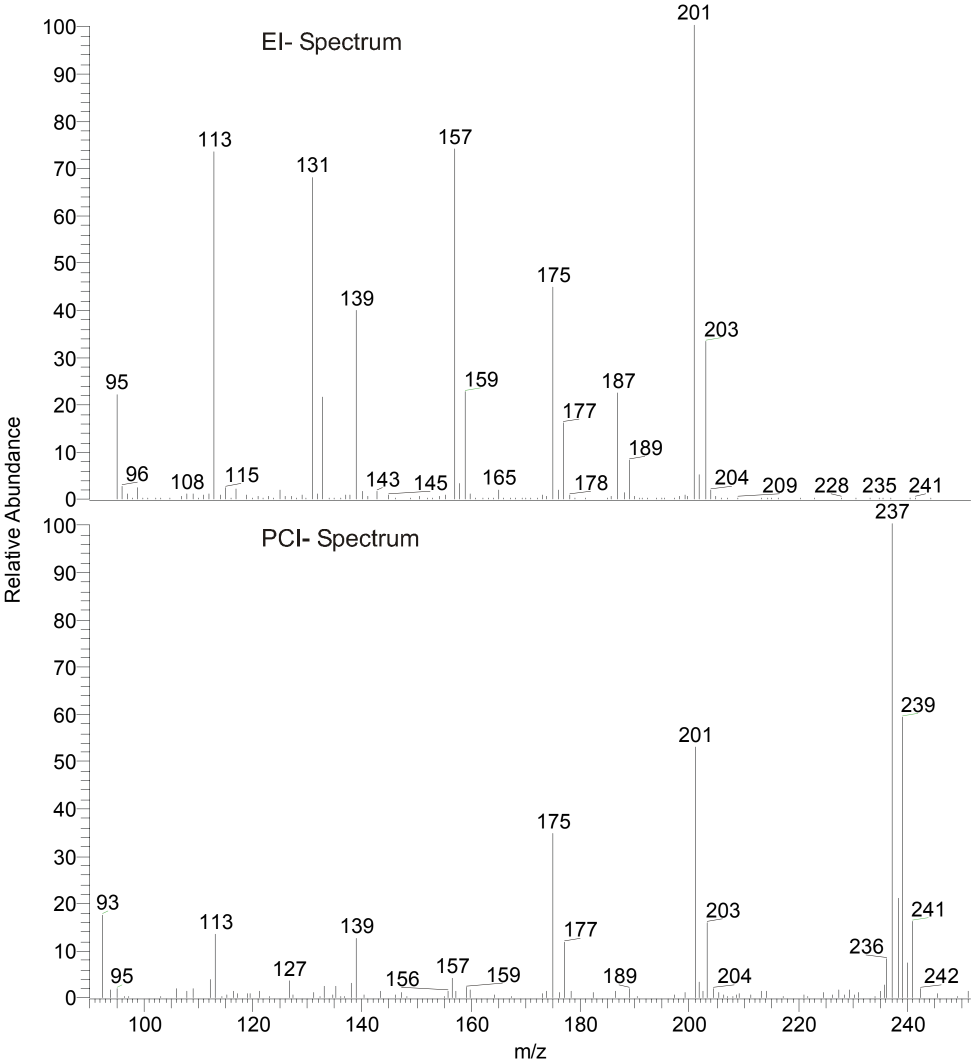


Table 8.1 Proposals for the fragmentation of BCEP with EI and PCI

EI			PCI		
m/z	201 amu	$[M - Cl]^+$	m/z	237 amu	$[M + H]^+$
	187 amu	$[M - CH_2Cl]^+$		201 amu	$[M - Cl]^+$
	175 amu	$[M - C_2H_2Cl]^+$		175 amu	$[M - C_2H_2Cl]^+$
	157 amu	$[M - C_2H_2Cl - H_2O]^{+\bullet}$		139 amu	$[M - C_2H_4Cl_2]^+$
	113 amu	$[M - C_4H_6Cl_2]^+$		113 amu	$[M - C_4H_6Cl_2]^+$

8.2.2 Identification of bis-(chloro*iso*propyl) phosphate (BCPP)

Figure 8.2 EI and PCI spectrum of BCPP

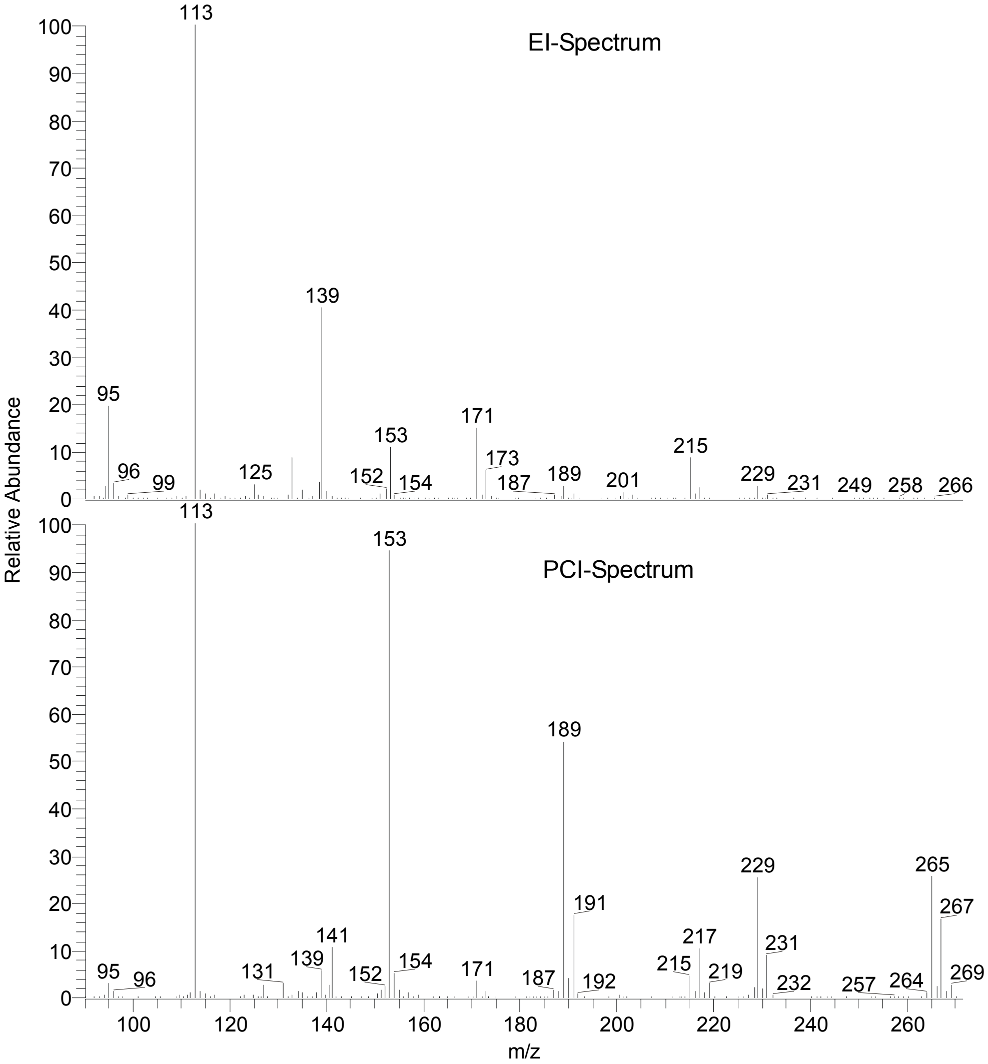


Table 8.2 Proposals fort he fragmentation of BCPP with EI and PCI

EI			PCI		
m/z	215 amu	[M - CH_2Cl]$^+$	m/z	265 amu	[M + H]$^+$
	171 amu	[M - C_3H_5Cl - H_2O]$^+$		229 amu	[M - Cl]$^+$
	153 amu	[M - $C_3H_5Cl_2$]$^+$		189 amu	[M - C_3H_5Cl]$^+$
	139 amu	[M - $C_4H_7Cl_2$]$^+$		153 amu	[M - $C_3H_5Cl_2$]$^+$
	113 amu	[M - $C_6H_{11}Cl_2$]$^+$		113 amu	[M - $C_6H_{11}Cl_2$]$^+$

8.2.3 Identification of bis-(butoxyethyl) phosphate (BBEP)

Figure .8.3 EI and PCI spectrum of BBEP

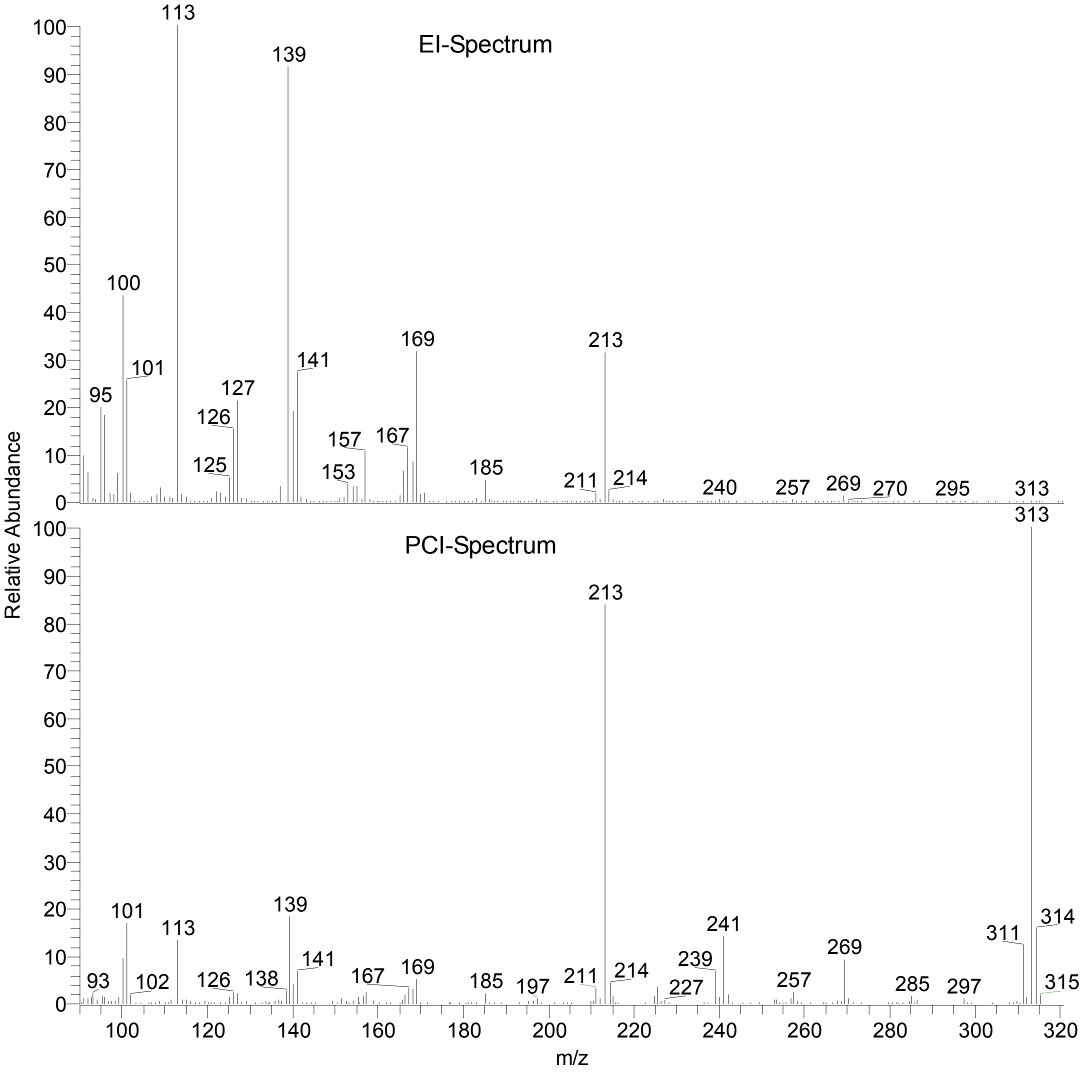


Figure 8.4 Proposals fort he fragmentation of BBEP with EI and PCI

EI			PCI		
m/z	213 amu	[M - CH_2Cl]$^+$	m/z	313 amu	[M + H]$^+$
	169 amu	[M - $C_9H_{19}O$ - H_2O]$^+$		213 amu	[M - $C_6H_{11}O$]$^+$
	139 amu	[M - $C_{10}H_{21}O$]$^+$		139 amu	[M - $C_{10}H_{21}O$]$^+$
	113 amu	[M - $C_{12}H_{23}O_2$]$^+$		113 amu	[M - $C_{12}H_{23}O_2$]$^+$

9 Used equipment and analytical standards

9.1 *Equipment*

9.1.1 Gas chromatography mass spectrometry systems

Thermo-Finnigan Trace (Thermo-Finnigan, Dreieich, Germany) equipped with a PTV-injector
Thermo-Finnigan DSQ (Thermo-Finnigan, Dreieich, Germany) equipped with a PTV-injector
Bio TOF III with ESI multispray ion source (Bruker, Bremen, Germany)

9.1.2 Autosampler

Both gas chromatography mass spectrometry systems were equipped with an AS 2000 autosampler (Thermo-Finnigan, Dreieich, Germany)

9.1.3 Size exclusion chromatography

BASIX (LC Tech GmbH, Dorfen, Germany)
SEC column: 2.5 x 30 cm, Biorad SX-3 (Bio-Rad Laboratories, Inc., Hercules, CA, USA)

9.1.4 Extraction Unit

ASE© 200 (Dionex, Idstein, Germany)

9.1.5 Evaporators

Rotary evaporator: Laborota 4001 with Rotavac Control (Heidolph, Kehlheim, Germany
Evaporation Unit: Büchi Syncore© Analyst 12 port (Büchi, Essen, Germany)

9.1.6 Columns

DB-5MS; length: 30 m, ID: 0.25 mm, film: 0.25µm (J&W Scientific, Folsom, CA, USA)
DB-5MS; length: 15 m, ID: 0.25 mm, film: 0.25µm (J&W Scientific, Folsom, CA, USA)

9.1.7 Software

Xcalibur ^{TM} Vers. 1.2 (Thermo Electron Corporation, West Palm Beach, FL, USA)
Xcalibur ^{TM} Vers. 1.3 (Thermo Electron Corporation, West Palm Beach, FL, USA)
Xcalibur ^{TM} Vers. 1.4 (Thermo Electron Corporation, West Palm Beach, FL, USA)

9.2 *Analytical Standards*

Tris-(chloro*iso*propyl) phosphate, technical mixture, Akzo Nobel (Amersfoort, The Netherlands
Tris-(dichloro*iso*propyl) phosphate, technical product, Akzo Nobel (Amersfoort, The Netherlands)
Tri-*n*-butylphopshate, Sigma-Aldrich, Steinheim, Germany
Tri-*n*-butylphopshate d_{27}, Ehrenstorfer, Augsburg, Germany
Tri-*iso*-butylphopshate, Sigma-Aldrich, Steinheim, Germany
Tris-(chloroethyl) phosphate, Sigma-Aldrich, Steinheim, Germany
Tris-(butoxyethyl) phosphate, Sigma-Aldrich, Steinheim, Germany
Triphenylphosphate, Sigma-Aldrich, Steinheim, Germany
Dibutylphosphate, Sigma-Aldrich, Steinheim, Germany
Diphenylphosphate, Sigma-Aldrich, Steinheim, Germany
Ethylhexyldiphenylphosphate, technical product, Bayer AG, Deutschland
Parathion-ethyl d_{10}, Ehrenstorfer, Augsburg, Germany

9.3 *Chemicals and Solvents*

Toluene (suprasolv), methanol (suprasolv), 1,4-dioxan (analytical grade, p.a.), acetone (analytical grade, p.a.), ethyl acetate (analytical grade/p.a. and suprasolv), *tert.* butylmethyl ether (suprasolv), *n*-hexane (suprasolv), chlorpropanol (isomeric mixture of 1-chloro-2-propanol, 2-chloro-1-propanol, purity > 97), pyridine (analytical grade/p.a.), silica gel 60 were purchased from Merck, Darmstadt, Germany.

2-chloroethanol (purity > 99%), phenol d_6 (purity > 99%) and phosphorus oxytrichloride (purity > 99%) were bought from Aldrich, Seelze, Germany.

2-butoxyethanol was purchased from kmf-laborchemie, Lohmar, Germany.

DVB-hydrophobic Speedisk cartridges and water (HPLC grade) were obtained from Mallinckrodt Baker, Griesheim, Germany.

Trimethylsulphoniumhydroxide solution (TMSH) was bought from Macherey-Nagel, Düren, Germany.

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