Joint Danube Survey 3

International Commission for the Protection of the Danube River
Internationale Kommission zum Schutz der Donau

Chapter (full report) on: Organophosphorous Compounds (OPCs) in surface waters of the Danube and selected tributaries

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1 Introduction

In this study we report on the occurrence of chlorinated and non-chlorinated organophosphorus compounds (OPCs) in selected water samples obtained from third Joint Danube survey and (JDS3, summer 2013) from Germany to the Black Sea.

Flame retardants (FRs) are used in a variety of products, such as electronic equipment, plastics products, rubbers, textiles and building materials (EFRA, 2007).

Since the application of brominated flame retardant (BFRs) class of polybrominated diphenyl ethers (PBDEs, i.e. Penta- and OctaBDE mixtures) was regulated in 2009 by the Stockholm Convention, an increase in the usage of chlorinated and non-chlorinated OPCs, as a substitute for PBDEs is observed.

Due to their widespread usage, OPCs have already been detected in several environmental matrices (Van der Veen and de Boer, 2012).

The persistence of OCPs' together with their toxic properties suggests adverse health effects on man. Some OPCs such as triphenyl phosphate (TPhP), tri-n-butyl phosphate (TnBP) and tritolyl phosphate (o-, m-, p-Tris (methylphenyl) phosphate TMPP) are supposed to be neurotoxic, and chlorinated OPCs such as (TCEP) and tris(2-butoxyethyl) phosphate (TBEP) act carcinogenic (Van Veen and De Boer, 2012, World Health Organization (WHO) 1990, World Health Organization (WHO) 1991a, World Health Organization (WHO) 1991b, World Health Organization (WHO) 1998 and World Health Organization (WHO) 2000). Meeker and Stapleton (2010) report associations between levels of TPhP and Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) in house dust and reduced semen quality in men, suggesting endocrine disruption.

Although the focus on OPCs is mainly on human exposure in indoor environments (Marklund et al. 2003, Saito et al. 2007), their presence and fate in aquatic environments and their foodwebs have gained scientific attention.

OPCs have been found ubiquitarily distributed in effluents from sewage treatment plants (STPs)in concentrations ranging from ng/L up to several µg/L. Especially the chlorinated OPCs tend to pass through the STPs without being removed, while alkyl-OCPs, are more successfully retained (Marklund et al. 2005). Consequently OPCs are observed in freshwaters (Sundkvist et al. 2010, Yan et al. 2012, Cristale et al. 2013), to some extent in groundwater (Fries and Püttmann, 2003) and in marine environments (Sundkvist et al. 2010). Investigations on the removal of OPCs within a waterworks facility revealed the presence of chlorinated OPCs such as Tris (1-chloro-2-propyl) phosphate (TCPP) and Tris(2-chloroethyl) phosphate (TCEP) also in the state of the art treated drinking water (Stackelberg et al. 2004, Cristale et al. 2012).

Apart from the major input into aquatic systems via municipal and industrial waste water discharge as suggested by Fries and Püttmann (2003), the findings from Bacaloni et al. (2008), who detected OPCs in volcanic lakes without direct urban impacts, suggest also long range atmospheric transport. This is supported by Moeller et al. (2011), who detected OPCs in the in oceanic and arctic air masses, with highest concentrations observed in continental air masses.

Some OPCs are bio accumulative and can be found in freshwater and marine biota (Sundkvist et al., 2010) as well as in breast milk from remote locations (Sundkvist et al. 2010, Kim et al. 2014)

Aquatic toxicity to fish, daphnia and algae mid to low mg/L concentration ranges is reported for OPCs (Verbrueggen et al. 2005). However, compared to the PBDEs they are replacing, acute aquatic toxicities of OPCs range generally between 2-4 orders of magnitude lower (Cristale et al. 2013). So far TCEP, TCPP, and TDCPP are registered in the European Commission priority lists (Reemtsma et al. 2008, Commission Regulation (EC) No 2268/95, Commission Regulation (EC) No 2364/2000).

2 Methods

2.1 Experimental approach

The sampling approach was designed for providing an overview on current spatial distribution and inputs of OPCs through analyses of dissolved phase water samples in the Danube and in selected tributaries.

2.2 Sampling

Sampling was done on board of the Argus using 1L aluminium bottles. The locations and details about the sampling can be obtained the chapter on the survey preparation (JDS3 report, chapter 2).

2.3 OPCs investigated

Please note that in particular the abbreviations used in literature do not allways follow an agreed scheme. Also CAS Numbers are sometimed used erroneously, e.g. when that of the main component is used for the technical mixture or vice versa. In the following Table 1an overview on the investigated compounds, their commonly used abbreviations and their CAS Numbers is given.

Table 1 Investigated compounds

Analyte Abbreviation	Analyte Common Name	CAS nr
T*n*PP	Tri-n-propyl phosphate	513-08-6
T*i*BP	Tris(isobutyl) phosphate	126-71-6
T*n*BP	Tris(butyl) phosphate	126-73-8
TCPP #	Tris(chloropropyl) phosphate	13674-84-5
TEHP	Tris(2-ethylhexyl) phosphate	78-42-2
TCEP	Tris(2-chloroethyl) phosphate	115-96-8
TBEP	Tris(2-butoxyethyl) phosphate	78-51-3
TDCPP$	Tris(1,3-dichloropropyl) phosphate	13674-87-8
	Tris(2,3-dichloropropyl) phosphate	78-43-3
TPhP	Triphenyl phosphate	115-86-6
EHDP	2-ethylhexyl diphenyl phosphate	1241-94-7
TMPP&	Tris(methylphenyl) phosphate, Tritolyl phosphate	1330-78-5
T35DMPP	Tris(3,5-dimethylphenyl) phosphate	25653-16-1
T2*i*PPP	Tris(2-isopropylphenyl) phosphate	64532-95-2

We report on the technical mixture of Tris(1-chloro-2-propyl) phosphate (TCPP, CAS No. 13674-84-5). TCPP is manufactured to a purity of 75 ± 10% of Tris(1-chloro-2-propyl) phosphate. Major impurities are the isomers bis (1-chloro-2-propyl)-2-chloropropyl phosphate (20-30%) and bis (2-chloropropyl)-1-chloro-2-propyl phosphate (3-5%). Both Fyrol PCF and Antiblaze 80 (trade names) have a similar composition/purity. http://www.inchem.org/documents/sids/sids/13674845.pdf

$ We report on the commercial product which consists mainly of 1,3-dichloro-2-propyl groups but can contain trace amounts of tris(2,3-dichloropropyl) phosphate (CAS 78–43–3). In literature TDCPP has been mistakenly referred to as TCPP, which is tris(1-chloro-2-propyl) phosphate (CAS 13674–84–5).

&TMPP concentration was measured as a sum of its orto-, meta- and para-isomers

2.4 Instrumentation

An Agilent 5869N GC system coupled to an Agilent 5973 Mass Selective Detector were used. For technical information see the Table 2 below.

Table 2: Equipment and conditions of the GC-MS system

GC	Agilent 6890 N			
Column:	RXI-17SIL MS			
Nominal length:	60 m			
Nominal Diameter:	250 µm			
Nominal film thickness:	0.25 µm			
Gas Type	Helium			
Mode:	constant flow			
Initial flow:	1.5 mL/min			
Oven:				
Initial Temperature:	80°C			
Initial Time:	1 min			
Ramps:	#	Rate	Final Temp	Final Time
	1	30°C/min	180°C	0 min
	2	10°C/min	300°C	15 min
Run Time	31.33 min			

Front Inlet (CIS4)	
Mode	Splitless
Initial Temperature	250°C
Pressure	186 kPa
Purge Flow	100 mL/min
Purge Time	1 min
Total Flow	104.2 mL/min

Gerstel CIS 4	
Initial Temperature	80°C
Equilibration Time	0.05 min
Initial Time	0.10 min
Rate	10 °C/sec
Final Temp	280 °C
Hold Time	10 min

MS	Agilent 5973 Mass Selective Detector
Mode	EI
MS Quad	150 °C
MS Source	230 °C

2.5 Reagents

Ethyl acetate for trace analysis (Carlo Erba Reactifs-SDS);
Methanol, code 701091.1612, (LC-MS) PAI, Panreac Quimica, Barcelona (Spain);
MilliQ water obtained from a MilliQ water system, Millipore, Bedford, MA (USA);
Hexane for analysis of dioxins, furans and PCB (Sigma-Aldrich, Germany);
OASIS HLB cartridges 6CC (0.2 g), code WAT106202, Waters, Milford, MA, USA;

Acetone, for analysis of dioxins, furans and PCB, Code 34410, lot 7207A, Riedel de Haen (Germany), Triphenyl phosphate-13C18 (50 ng/µL), Wellington Laboratories (used as syringe standard). Following labelled analogues (see the Table 3 below) were used as internal standards:

Table 3: List of labelled analogues used as internal standards.

Standard		C (ng/µL)	Solvent	Producer
T*n*PP-d21	Tri-n-propyl phosphate-d21	100	Isooctane	Chiron AS
T*n*BP-d27	Tris(butyl) phosphate-d27	100	Isooctane	Chiron AS
TPhP-d15	Triphenyl phosphate-d15	100	Isooctane	Chiron AS
M6TBEP	Tris(2-butoxy(13C2)-ethyl) phosphate	50	Toluene	Wellington Laboratories
TDCPP-d15	Tris(1,3-dichloro-2-propyl) phosphate-d15	50	Toluene	Wellington Laboratories
T35DMPP-d9	Tris(3,5-dimethylphenyl) phosphate-d9	solid	N.A.	Hayashy Pure Chemical Ind., Co., Ltd
TCEP-d12	Tris(2-chloroethyl) phosphate-d12	solid	N.A.	Hayashy Pure Chemical Ind., Co., Ltd

Following certified standards (see the Table 4 below) were used for calibration and QC samples preparation:

Table 4: List of certified standards used in method development.

Standard		C (ng/µL)	Solvent	Producer
T*n*PP	Tri-n-propyl phosphate	1000	Isooctane	Chiron AS
T*i*BP	Tris(isobutyl) phosphate	1000	Isooctane	Chiron AS
T*n*BP	Tris(butyl) phosphate	1000	Isooctane	Chiron AS
TCPP	Tris(1-chloro-2-propyl) phosphate	50	Toluene	Accustandard
TCEP	Tris(2-chloroethyl) phosphate	50	Toluene	Accustandard
TBEP	Tris(2-butoxyethyl) phosphate	50	Toluene	Accustandard
TDCPP	Tris(2,3-dichloropropyl) phosphate	1000	Methanol	Chiron AS
TPhP	Triphenyl phosphate	1000	Isooctane	Chiron AS
TMPP	Tritolyl phosphate	1000	Isooctane	Chiron AS
T2*i*PPP	Tris(2-isopropylphenyl) phosphate	50	Toluene	Wellington Laboratories
T35DMPP	Tris(3,5-dimethylphenyl) phosphate	50	Toluene	Wellington Laboratories
EHDP	2-Ethylhexyl diphenyl phosphate	50	Toluene	Wellington Laboratories
TEHP	Tris(2-ethylhexyl)phosphate	50	Toluene	Wellington Laboratories

2.6 Preparation of standard solutions

2.6.1 OPC working standard stock solution (5 ng/µL)

Table 5: Preparation of OPC working solution.

Analyte	C of cert. standard (ng/µL)	solvent in standard	V of cert. standard taken (µL)	Analyte in prepared solution (ng)	C of prepared solution (ng/µL)
TEP	1000	Isooctane	12	12000	5
T*n*PP	1000	Isooctane	12	12000	5
T*i*BP	1000	Isooctane	12	12000	5

T*n*BP	1000	Isooctane	12	12000	5
TCPP	50	Toluene	240	12000	5
TCEP	50	Toluene	240	12000	5
TBEP	50	Toluene	240	12000	5
TDCPP	1000	Methanol	12	12000	5
TPhP	1000	Isooctane	12	12000	5
TMPP	1000	Isooctane	12	12000	5
T2*i*PPP[1]	50	Toluene	60	3000	1.25
T35DMPP[2]	50	Toluene	120	6000	2.5
EHDP	50	Toluene	240	12000	5
TEHP	50	Toluene	240	12000	5

The total volume of 2400 µL was obtained by adding hexane.

2.7 OPC internal standard solution (2 ng/µL)

Table 6: Preparation of OPC IS solution.

Analyte	C of cert. standard (ng/µL)	solvent in standard	V of cert. standard taken (µL)	Analyte in prepared solution (ng)	C of prepared solution (ng/µL)
TMP-d9	100	isooctane	200	20000	2
TEP-d15	100	isooctane	200	20000	2
T*n*PP-d21	100	isooctane	200	20000	2
TnBP-d27	100	isooctane	200	20000	2
M6TBEP	50	toluene	400	20000	2
TDCPP-d15	50	toluene	400	20000	2
TPhP-d15	100	isooctane	200	20000	2
TCEP-d12	100[3]	toluene	200	20000	2
T35DMPP-d9	100[4]	toluene	200	20000	2

The total volume of 10000 µL was obtained by adding hexane.

2.7.1 Preparation of calibration standards and QC samples

1 L glass bottle was filled with 1L MilliQ water and 1 mL of working standard solutions was added according to the following scheme shown in the Table 7 below:

Table 7: Scheme of calibration standards and QC samples for OPCs.

Working solution	OPCs concentration ng/mL			concentration in water ng/L			Sample type
	OPCs (ex T35DMPP and T2IPPP)	T2IPPP	T35DMPP	OPCs (ex T35DMPP and T2IPPP)	T2IPPP	T35DMPP	

---

[1] Due to the lack of standard, the concentration 5 ng/µL was not achieved; it must be taken into account when estimating methods linear range and trueness evaluations for concerned compound(s).

[2] See the previous footnote.

[3] Stock solution with concentration of 100 ng/µL, prepared using the solid standard.

[4] Stock solution with concentration of 100 ng/µL, prepared using the solid standard.

A	500	125	250	500	125	250	Calibration samples
B	100	25	50	100	25	50	„
C	50	12,5	25	50	12,5	25	„
D	25	6,25	12,5	25	6,25	12,5	„
E	10	2,5	5	10	2,5	5	„
Low QC	30	7,5	15	30	7,5	15	QC samples
High QC	300	75	150	300	75	150	„

2.8 Sample preparation

- 50 µL of IS (internal standard) solution of OPCs (2 ng/µL) were added to 1 L water samples, (likewise to the 1 L calibration standards and QC samples).
- Samples were shaken.
- SPE OASIS HLB cartridges were conditioned with 10 mL of ethyl acetate.
- SPE cartridges were conditioned with 10 mL of methanol.
- SPE cartridges were conditioned with 10 mL of water.
- Water samples were loaded at flow 10 mL/min.
- Sorbent was dried under nitrogen flow for 30 min.
- Samples were eluted with 10 mL ethyl acetate at flow 5 mL/min.

Half of received extract (i.e. about 5 mL) was evaporated to dryness and reconstituted in 0.2 mL of reconstituting solution for LC-MS/MS analysis. The remaining aliquot (i.e. about 5 mL) was evaporated to 50-100 µL under nitrogen flow for GC-MS determination.

2.9 Method performance

2.9.1 Selectivity

The analytes were identified in GC-MS SIM (Selected Ion Monitoring) mode, recording the two ions (target ion and one qualifier ion). The quantified analytes were identified through their retention time comparison of the corresponding standards and the isotopic ratio between two ions recorded (±20%).

All the target and qualifier ions of the analytes and their corresponding standards can be found in the following Table 8:

Table 8: GC-MS SIM parameters or analytes and their corresponding standards.

Analyte/IS Abbreviation	M/Z (target) *amu*	M/Z (qualifier) *amu*
T*n*PP-d21	103	151
T*n*PP	99	141
T*i*BP	99	155
T*n*BP-d27	103	167
T*n*BP	99	155
TCPP	277	279
TEHP	99	113
TCEP-d12	263	264
TCEP	249	251
M6TBEP	303	259

TBEP	227	299
TDCPP-d15	394	197
TDCPP	379	381
TPhP-d15	339	341
TPhP	325	326
EHDP	251	362
TMPP	367	368
T35DMPP-d9	420	421
T35DMPP	410	411
T2*i*PPP	335	293

2.9.2 Linearity

Linearity of developed procedure was studied in the following concentration range: 10-500 ng/L[5] on 8 different days. R^2 values were calculated, the results can be seen in the following Table 9.

Table 9: Calculated R^2 values for each analyte

Analyte	R2 values for different calibration								Average
	23/9/13	**24/9/13**	**25/9/13**	**30/9/13**	**16/10/13**	**7/11/13**	**18/11/13**	**3/3/14**	
T*n*PP	0.9980	0.9991	0.9982	0.9996	0.9993	0.9997	0.9994	0.9998	1.00
T*i*BP	0.9953	0.9998	0.9999	1.0000	0.9994	0.9997	0.9995	0.9999	1.00
TNBP	0.9999	0.9997	0.9995	0.9998	0.9991	1.0000	0.9993	1.0000	1.00
TCPP	0.9970	0.9982	0.9970	0.9987	0.9985	0.9992	0.9991	0.9998	1.00
TEHP	0.9751	0.7795	0.9917	0.9966	0.9877	0.9640	0.9948	0.9994	0.96
TBEP	0.9996	0.9999	0.9997	1.0000	0.9997	0.9997	0.9999	0.9888	1.00
TDCPP	0.9999	1.0000	0.9992	0.9996	0.9992	1.0000	0.9998	0.9938	1.00
TCEP	0.9998	0.9998	0.9996	0.9998	0.9996	1.0000	0.9997	1.0000	1.00
TPhP	0.9999	0.9998	0.9996	0.9999	0.9995	1.0000	0.9997	0.9998	1.00
EHDP	0.9664	0.9879	0.9994	0.9914	0.9996	0.8524	0.9988	0.9999	0.97
TMPP	0.9689	0.9355	0.9923	0.9901	0.9971	0.8879	0.9984	0.9646	0.97
T35DMPP	0.9981	0.9996	0.9987	0.9991	0.9996	0.9387	0.9999	0.9663	0.99
T2*i*PPP	0.9986	0.9973	0.9973	0.9973	0.9986	0.9464	0.9999	0.9978	0.99

2.9.3 LOD and LOQ

Limit of detections were visually estimated in the chromatograms of blank samples as the lowest signals which gave a signal to noise ratio about 5/1 for LOD and 10/1 for LOQ. The results are shown in the Table 10 below.

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[5] 2,5-125 ng/L for T2IPPP and 5-250 ng/L for T35DMPP

Table 10: LOD and LOQ values for measured OPCs.

Analyte	LOD	LOQ
	ng/L	ng/L
T*n*PP	0.2098	0.699
T*i*BP	0.1518	0.506
T*n*BP	0.0911	0.3038
TCPP	1.291	4.30
TEHP	0.0351	0.1171
TBEP	1.51	5.03
TDCPP	0.85	2.83
TCEP	0.287	0.96
TPhP	0.156	0.52
EHDP	0.0838	0.279
TMPP	0.237	0.79
T35DMPP	1.032	3.44
T2*i*PPP	12.0	39.9

2.9.4 Trueness/bias

Results of replicate analysis of spiked samples can be used for bias evaluation presented as percentage of theoretical value. The results should not exceed the value of 30%. The results are reported in the Table 11, Table 12: Coefficients of variance (CV) of QC samples on different concentration levels below.

Table 11: Bias estimate

Analyte	Bias (% of theoretical value)	
	Low C	High C
T*n*PP	-17	-6
T*i*BP	-13	-26
T*n*BP	-6	-5
TCPP	-27	-11
TEHP	-96	-93
TBEP	16	14
TDCPP	-3	1
TCEP	8	5
TPhP	-5	-3
EHDP	-60	-73
TMPP	35	3
T35DMPP	-9	6
T2*i*PPP	24	25

2.9.5 Precision

Results of replicate analysis of control samples can be used for precision (reproducibility) evaluation presented as relative standard deviations (RSD) or coefficients of variance (CV). The results should not exceed the value of 30%. The results are reported in the Table 12 below.

Table 12: Coefficients of variance (CV) of QC samples on different concentration levels

Analyte	Coefficient of variance CV	
	Low C	High C
T*n*PP	4%	11%
T*i*BP	3%	15%
T*n*BP	2%	10%
TCPP	2%	21%
TEHP	9%	40%
TBEP	6%	12%
TDCPP	3%	8%
TCEP	6%	10%
TPhP	2%	7%
EHDP	4%	17%
TMPP	3%	16%
T35DMPP	4%	13%
T2*i*PPP	5%	25%

2.9.6 Recovery

Internal standard recovery values were evaluated by the ratio between each surrogate standard and the labelled compound added to sample extract as syringe standard. The recovery was estimated to be in range of 53% to 63% in the higher (300 ng/L) concentration level and 60% to 72% in the lower (30 ng/L) concentration level. However, the recovery rate got no implication on the quantification based on surrogate standards. Therefore, no correction for recovery losses was done.

2.9.7 Note

For analytes TEHP, EHDP the results are not supported by the quality control measurements and the method needs further improvement. For this reason the findings for TEHP are not reported and results for EHDP can only be taken as an indication, bearing in mind that due to the insufficient recovery an underestimation of the concentration of a factor of around 3-4 must be considered.

3 Results

OPCs are a relatively new compound class in the focus of environmental scientists. For this reason we are amending the results with selected physical chemical properties and information on the application for the individual analytes. This includes also the CAS Numbers for an unambiguous identification of the analytes, since the use of nomenclature and especially the abbreviations in literature is manifold.

The results presented for the OPCs refer to the dissolved fraction of surface water. All 68 JDS 3 sites were analysed. The locations of the individual sites are specified in the chapter on the survey preparation (JDS3 report, chapter 2). In addition 3 extra sites were sampled, Upstream River Olt (JDS 51a), River Olt (JDS 51b) and downstream River Siret (JDS 63 a). The concentration data for the individual sites are given in chapter 7 of this report.

Due to the complex survey and shipping logistics (the survey fell into the holiday period), the water samples could not be extracted immediately after arrival at the JRC. Holding times were between between 27 and 106 days; 30 samples were stored for longer than 70 days.

Although sample custody could assure continuous cooling of the samples during transport and storage (shipping and storage at 4°C in aluminum containers), degradation of the OPCs might have occurred. For this reason 3 exemplary water samples taken in parallel were extracted again after an additional storage period. The parallel samples taken from these sites were analyzed again after 173 days from reception. The “118 day variation” between the two analyses from the 3 sites was determined for all compounds > LOQ and is reported and discussed together with the results below.

In the graphs with the downstream concentration profiles, all sites with samples available are labeled with respective JDS site codes. In addition incoming rivers are indicated in the graph. Only for the rivers with a JDS site code samples were available; the results are displayed in blue colour. The other rivers are indicated in the order of their confluence in relation to the sampling sites for a better understanding of the eventual impact of their discharges on the Danube itself.

When looking at the potential influence of the incoming rivers on the concentrations observed in the Danube, the discharge measurements generated during the JDS3 survey reveal, that only few rivers display sufficient discharges which could impact the OPC concentrations in the Danube (Table 13).

Table 13: Discharge contribution from the Danube Tributaries

Tributary	Confluence with the Danube (rkm)	Contribution to the discharge after the confluence	Sample
Lech	2496, between JDS1, -02	40% #	no
Σ RMD canal, Naab, Regen	2411, 2385, 2379, between JDS2, -3	6,0%	no
Isar	2282, between JDS4, -5	18.5%	no
Inn	2225, between JDS5, -6	60%	no
Traun	2125, between JDS6, -7	10% @	
Enns	2111, between JDS8, -9	15%	no
Morava	1880	1.7%	JDS12
Vah	1766	6.5%	JDS18
Drava	1379	20%	JDS29
Tisa	1215	8.4%	JDS35
Sava	1170	12%	JDS37
Velica Morava	1103	1.5%	JDS41
Timok	845	< 1%	JDS48
Iskar,	601	Σ2.7%	JDS51
Olt	637		no
Jantra	537	< 1%	JDS54
Rusenski Lom	498	< 1%*	JDS56
Arges	432	< 1%	JDS58
Siret	154	2.8%	JDS63
Prut	135	2.0%	JDS64

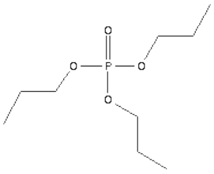
#,@ no data were obtaiuned during JDS3
estimate based on discharge data from 12.07.2014 obtained form the Bavarian Environmental Agency
http://www.nid.bayern.de/abfluss/tabellen/index.php?gknr=1&wert=abfluss&thema=niedrigwasser&days=6, accessed on 18.07.2014
@ estimated on the basis of an annual discharge of typically 70% of that of the River Enns
*www.eea.europa.eu/data-and-maps/data/reference-waterbase-rivers/..

3.1 Tri-n-propyl phosphate (T*n*PP) CAS No 513-08-6

T*n*PP was positive in 68 of 71 samples. The majority of the results were obtained close to the limit of detection. Since we report an average LOD, some data reported and displayed below in Figure 1 result below LOD, since the individual LODs display some variability.

The results we obtained for T*n*PP in the dissolved phase can be considered as robust, since the decrease during our stability experiments (Table 15) was moderate. As indicated by a log Kow of 1.87 (Table 14), the dissolved phase concentrations can be interpreted as total water concentrations.

Table 14: T*n*PP properties and application

Properties and application: Tri-*n*-propyl phosphate (T*n*PP) CAS. No. 513-08-6 -		
log K_{ow} [#]	1.87	
Ws [#]	6.5 g L^{-1}	
Vp [#]	0.58 Pa	
Applications[&, $]	P, F, I	
[#] Bollmann et al (2012) from SRC physProp Database Demo 2010 [&] FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance [$] Excerpt from Van der Veen and De Boer 2012		

The downstream concentration profile (Figure 1) in the Danube displays a concentrations range between 0.075 and 2.1 ngL^{-1}, (JDS 43), with an average concentration of 0.35 ngL^{-1}. The concentrations in the tributaries are similar, ranging from 0.085 to 1.0 ngL^{-1}, with an average of 0.42 ngL^{-1} (Table 16).

Upper middle and lower stretch do not display remarkable differences in concentration of T*n*PP.

Figure 1: T*n*PP – downstream profile dissolved phase

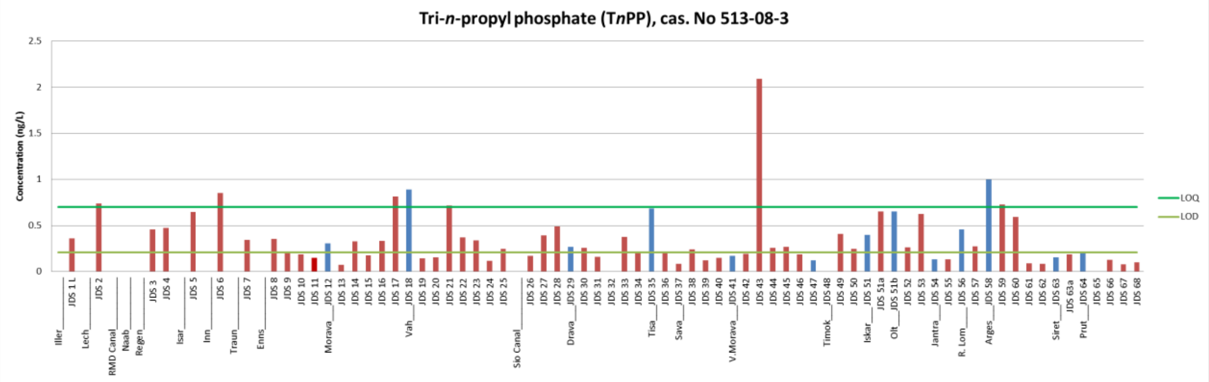


Table 15: T*n*PP – stability during storage

TnPP	**118 days variation in % of the value reported**
JDS 11	46.5
JDS 12	91.9
JDS 16	60.5

Table 16: T*n*PP –summary dissolved phase

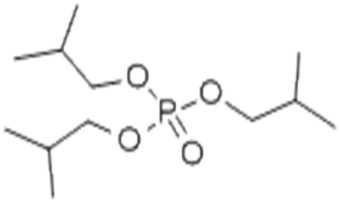
TnPP (ng L-1)-	all samples	Danube	tributaries
$N_{analyzed}$	71	57	14
$N_{positive}$	68	55	13
min	0.075	0.075	0.085
mean	0.359	0.346	0.416
max	2.09	2.094	0.999
C50	0.259	0.256	0.305
C90	0.729	0.722	0.954

3.2 Tris(isobutyl) phosphate (T*i*BP) CAS No. 26-71-6

T*i*BP was quantified in all 71 samples.

The results we obtained for T*i*BP in the dissolved phase can be considered as robust, since the decrease during our stability experiments (Table 18) was moderate (20-40%). Moreover, as indicated by a log Kow of 3.6 (Table 17), the dissolved phase concentrations reported can be interpreted as total water concentrations. For comparison: During JDS 3, where dissolved phase and SPM associated concentrations were analysed separately, Lindane (log Kow of 3.7, SRC Physprop database) was present to > 99% in the dissolved phase.

Table 17: T*i*BP – properties and application

Properties and application: Tris(isobutyl) phosphate (TiBP) CAS No. 26-71-6		
log K_{ow} #	3.6	
Ws #	$1.6*10^{-2}$ g L^{-1}	
Vp #	1.71 Pa	
Applications&, $	L, A, I	

Bollmann et al (2012) from SRC physProp Database Demo 2010
& FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance
$ Bollmann et al (2012) from Marklund et al., 2013

The downstream concentration of T*i*BP in the Danube (Figure 2) displays a concentrations range between 6.8 and 48 ngL^{-1} (JDS2), with an average concentration of 19 ngL^{-1}. The concentrations in the tributaries are similar, ranging from 2.6 to 97 ngL^{-1} (River Arges), with a slightly higher average of 23.4 ngL^{-1} (Table 19).

The rise in concentration between JDS1 and JDS2 suggests higher concentrations of T*i*BP in the River Lech contributing to 60% of the discharge at the site JDS2.

The moderately higher concentration for the Rivers Vah and Arges do not impact the concentrations in the Danube downstream their influence due to their low contributing to the total discharge (6.5% and < 1%).

Similar to T*n*PP the upper middle and lower stretch do not display remarkable differences in concentration of T*i*BP.

Figure 2: T*i*BP – downstream profile dissolved phase

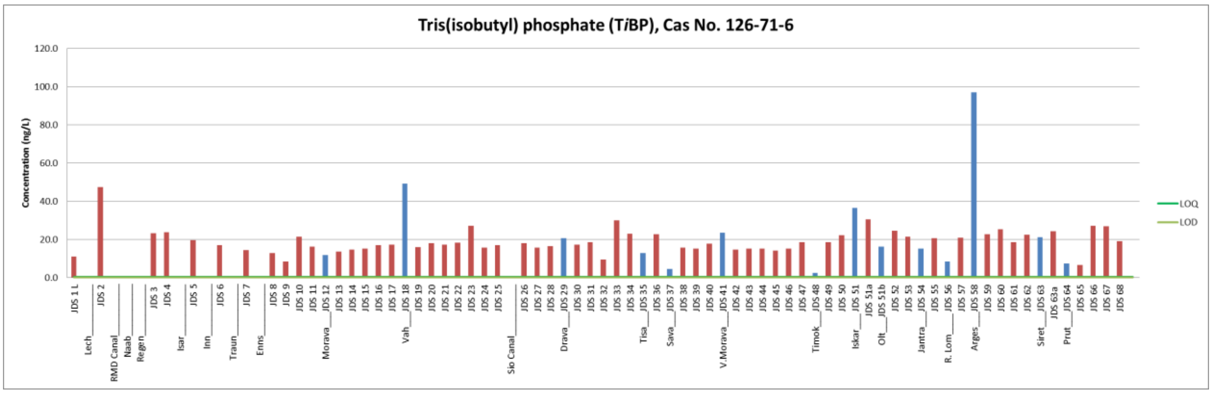


Table 18: T*i*BP – stability during storage

T*i*BP	**118 days variation in % of the value reported**
JDS 11	59.6
JDS 12	79.5
JDS 16	61.2

Table 19: T*i*BP – dissolved phase summary

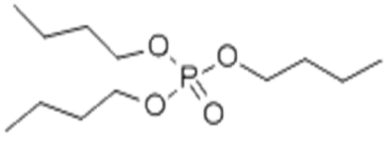
T*i*BP (ng L^{-1})$^{-}$	**all samples**	**Danube**	**tributaries**
$N_{analyzed}$	71	57	14
$N_{positive}$	71	57	14
min	2.54	6.79	2.54
mean	20.0	19.2	23.4
max	97.1	47.6	97.1
C50	17.9	18.0	15.8
C90	27.3	27.0	73.1

3.3 **Tris(butyl) phosphate (T*n*BP) CAS No. 126-73-8**

T*n*BP was quantified in all 71 samples.

The results we obtained for T*n*BP in the dissolved phase can be considered as moderately underestimated, since the decrease during our stability experiments was more than 50 % (Table 21). As suggested by a log Kow of 4.0 (Table 20), the dissolved phase concentrations reported can be interpreted as representative for the total water concentrations. For comparison: During JDS 3, where dissolved phase and SPM associated concentrations were analysed separately, Endrin (higher log Kow of 5.2, SRC Physprop database 2014) was still present to > 80% in the dissolved phase.

Table 20: T*n*BP – properties and application

Properties and application:Tris(butyl) phosphate (T*n*BP) CAS No. 126-73-8		
log K_{ow} $^{\#}$	4.0	
Ws $^{\#}$	0.28 g L^{-1}	
Vp $^{\#}$	0.15 Pa	
Applications$^{\&, \$}$	P, H, F, L, A, I	
# Bollmann et al (2012) from SRC physProp Database Demo 2010 & FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance $ Bollmann et al (2012) from Marklund et al., 2013		

The downstream concentration profile in the Danube (Figure 3) displays a concentrations range between 0.42 and 9.4 ngL^{-1} (JDS20), with an average of 4.3 ngL^{-1}. The concentrations in some of the tributaries are higher, ranging from 0.26 to 69.8 ngL^{-1} (River Vah), with a higher average 10.6 ngL^{-1}, mainly caused by the high concentrations in Rivers Vah and Iskar (Table 22).

The higher concentrations in the River Vah and Iskar do not impact the concentrations in the Danube downstream their influence due to their low contribution to the total discharge 6.5% and <2.7 %).

Figure 3: T*n*BP – downstream profile dissolved phase

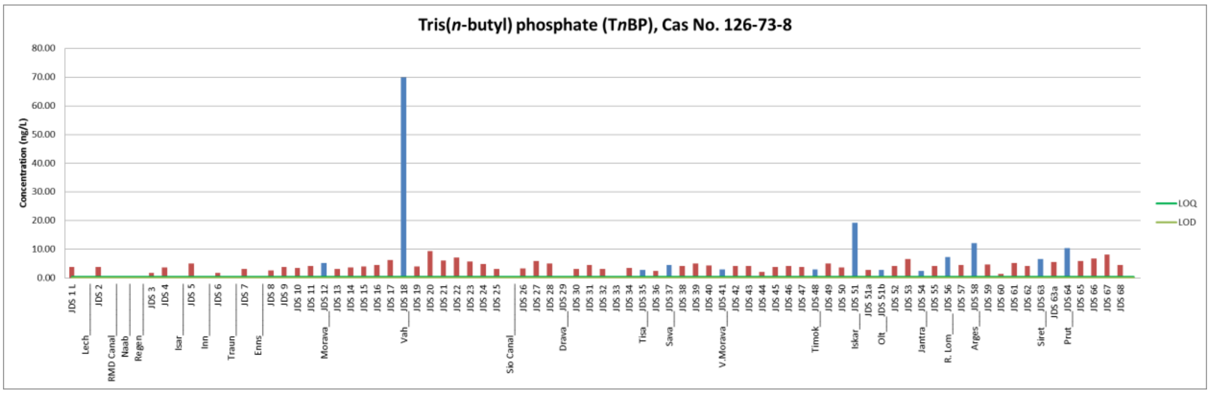


Table 21: T*n*BP– stability during storage

T*n*BP	**118 days variation in % of the value reported**
JDS 11	40.4
JDS 12	43.2
JDS 16	28.6

Table 22: T*n*BP – dissolved phase summary

T*n*BP (ng L^{-1})$^{-}$	**all samples**	**Danube**	**tributaries**
N$_{analyzed}$	71	57	14
N$_{positive}$	71	57	14
min	0.26	0.42	0.26
mean	5.52	4.27	10.6
max	69.8	9.37	69.8
C50	4.13	4.13	4.80
C90	7.24	6.28	44.5

3.4 Tris(monochloropropyl) phosphate (TCPP), CAS No. 13674-84-5

TCPP is with about 22950 t per year production/use volume (year 1995) the most important of the chlorinated OPCs used in Europe (Van der Veen, De Boer 2012).

We report on the technical mixture of TCPP consisting mainly of Tris(1-chloro-2-propyl) phosphate (TCPP, CAS No. 13674-84-5). TCPP is manufactured to a purity of 75 ± 10%. Major impurities are bis (1-chloro-2-propyl)-2-chloropropyl phosphate (20-30%) and bis (2-chloropropyl)-1-chloro-2-propyl phosphate (3-5%). The most frequently used technical formulations *Fyrol PCF* and *Antiblaze80* (trade names) have got a similar composition/purity.

http://www.inchem.org/documents/sids/sids/13674845.pdf

TCPP, the by far highest OPC in concentration, was quantified in all 71 samples.

The results we obtained for TCPP in the dissolved phase can be considered as robust, since the decrease during our stability experiments (Table 24) was moderate. Moreover, as indicated by a log K_{ow} of 2.59 (Table 23), the dissolved phase concentrations reported can be interpreted as total water concentrations.

Table 23: TCPP – properties and application

Properties and application: Tris(1-chloro-2-propyl) phosphate(TCPP) CAS No 13674-84-5		
log K_{ow} #	2.59	
Ws #	1.2 g L^{-1}	
Vp #	2,7*10^{-3}Pa	
Applications&, $	FR, P	
# Bollmann et al (2012) from SRC physProp Database Demo 2010 & FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance $ Bollmann et al (2012) from Marklund et al., 2013		

The downstream concentration in the Danube (Figure 3) displays a uniform profile, with concentrations in a range between 45 and 549 ngL^{-1}, with an average concentration of 103 ngL^{-1}. Some isolated peaks were found along the whole river with an isolated concentration maximum of 549 ngL^{-1} (JDS 32) and exceeding 200 ngL^{-1} at the sites JDS 8 and JDS 65. The concentrations in some of the tributaries are somewhat higher, with a range of 28 - 603 ngL^{-1}, 151 ngL^{-1} at average. 200 ngL^{-1} were exceeded in some tributaries in the lower stretch, Rivers Iskar, Arges and Timok, where overall maximum of 603 ngL^{-1} was detected (Table 25). However, no impact from the tributaries with higher concentrations was observed in the Danube. This is not surprising since the discharges again were at a range of some % of that in the Danube.

The concentration rise between JDS 7 and JDS 8 suggests some impact from the river Enns, contributing 15% to the Danube's discharge after the confluence.

Figure 4: TCPP – downstream profile dissolved phase

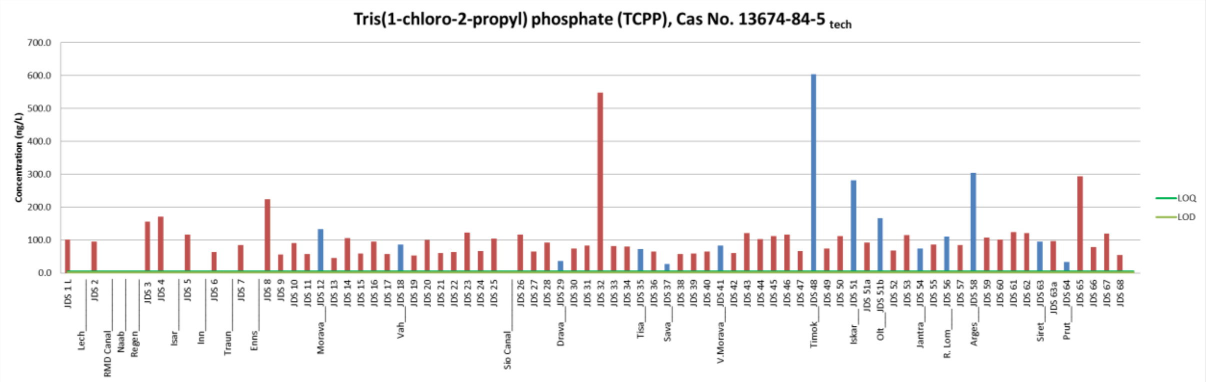


Table 24: TCPP – stability during storage

TCPP	**118 days variation in % of the value reported**
JDS 11	95.9
JDS 12	77.2
JDS 16	80.5

Table 25 TCPP– dissolved phase summary

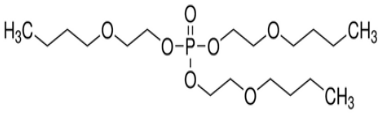
TCPP (ng L^{-1})	all samples	Danube	tributaries
N analyzed	71	57	14
$N_{positive}$	71	57	14
min	28.0	45.4	28.0
mean	112	103	151
max	603	549	603
C50	91.5	91.5	91.1
C90	170	130	454

3.5 Tris(2-butoxyethyl) phosphate (TBEP) CAS No. 78-51-3

TBEP was positive in 66 of 71 samples.

The results we obtained for TBEP in the dissolved phase can be considered as underestimated, since the decrease during our stability experiments was in a range of 43-82% % (Table 27). As suggested by a log K_{ow} of 3.75 (Table 26), the dissolved phase concentrations reported can be interpreted as representative for the total water concentrations. For comparison: During JDS 3, where dissolved phase and SPM associated concentrations were analysed separately, Lindane (log K_{ow} of 3.7, SRC Physprop database, 2014) was present to > 99% in the dissolved phase.

Table 26: TBEP – properties and application

Properties and application: Tris(2-butoxyethyl) phosphate (TBEP) CAS No. 78-51-3		
log K_{ow} #	3.75	
Ws #	1.1 g L^{-1}	
Vp #	3.3*10^{-6} Pa	
Applications&, $	FR, P, F, L, A	

Bollmann et al (2012) from SRC physProp Database Demo 2010
& FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance
$ Bollmann et al (2012) from Marklund et al., 2013

The downstream concentration in the Danube (Figure 5) shows a prevalence of TBEP in the upper stretch with an isolated peak at JDS 43. A concentrations range between 2.0 and 53.6 ngL^{-1} (JDS8), with an average of 14.3 ngL^{-1} is observed. The concentrations in the tributaries are similar, ranging from 1.25 to 93 ngL^{-1} (River Arges), with an average of 15.4 ngL^{-1} (Table 28). Tendencially the tributaries in the upper stretch are lower in concentration compared to the Danube itself, while in the lower stretch the situation is inverted.

The high concentrations in the River Arges does not impact the concentrations in the Danube downstream its influence due to the low contribution to the total discharge (< 1%).

In the upper stretch the Rivers Inn (60% discharge contribution) and Isar (18%) seem to dilute, while Lech (40% discharge contribution) and Enns (15%) seem to impact the Danube River.

Figure 5: TBEP – downstream profile dissolved phase

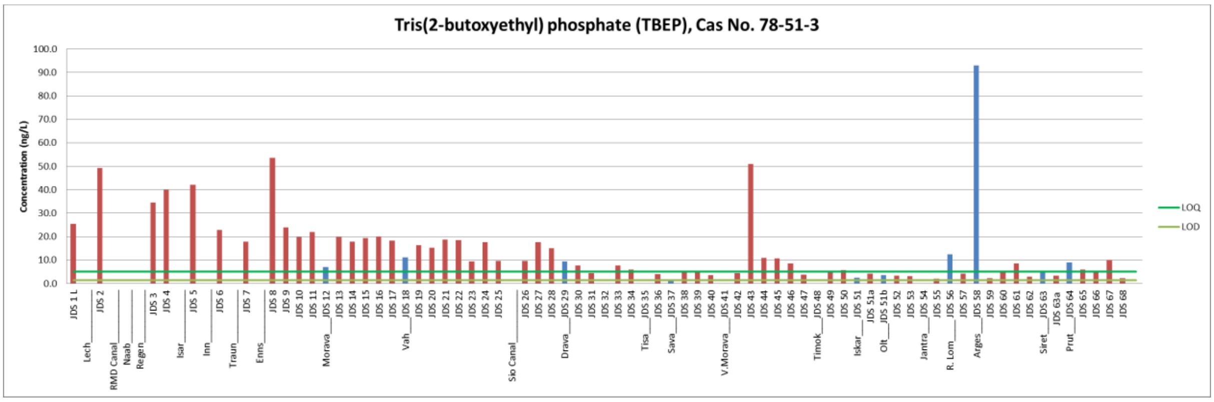


Table 27: TBEP– stability during storage

TBEP	118 days variation in % of the value reported
JDS 11	38.6
JDS 12	66.8
JDS 16	17.4

Table 28: TBEP– dissolved phase summary

TBEP (ng L^{-1})$^{-}$	all samples	Danube	tributaries
N_{analyzed}	71	57	14
N_{positive}	66	56	10
min	1.25	2.00	1.25
mean	14.5	14.3	15.4
max	93.0	53.6	93.0
C50	9.47	9.62	7.96
C90	36.1	36.1	84.9

3.6 Tris (1,3-dichloro(iso)propyl) phosphate and Tris(2,3-dichloropropyl) phosphate (TDCPP) CAS No. 13674-87-8 and 78-43-3

We report on the commercial product containing mainly 1,3-dichloro-2-propyl groups but can contain trace amounts of tris(2,3-dichloropropyl) phosphate (CAS 78–43–3). In literature TDCPP is frequently mistakenly referred to as TCPP, which is tris(1-chloro-2-propyl) phosphate (CAS 13674–84–5).

TDCPP got less than 10000 tons annual production/usage volume (year 2000, referenced in Van der Veen, De Boer, 2012). Main Applications are flame retardant in automotive industry and furniture. In PU foams used for baby products in TDCPP is frequently detected (referenced in Van der Veen, De Boer, 2012). Other applications are fire retardant sprays.

TDCPP was quantified in 70 of 71 samples.

The results we obtained for TDCPP in the dissolved phase can be considered as slightly underestimated, since the decrease during our stability experiments was moderate (21-42%), (Table 31). The log K_{ow} of 3.65 (Table 30) suggests that the dissolved phase concentrations reported can be interpreted as total water concentrations. . For comparison: During JDS 3, where dissolved phase and SPM associated concentrations were analysed separately, Lindane (log K_{ow} of 3.7, SRC Physprop database 2014) was present to > 99% in the dissolved phase.

Table 29: T12DCPP – properties and application

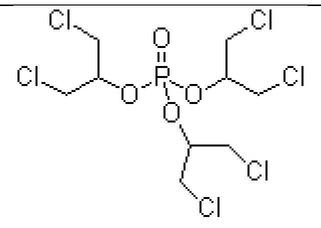
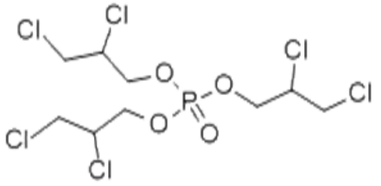
Properties and application: Tris(1,2-dichloropropyl) phosphate (TDCPP) CAS No. 13674-87-8		
log $K_{ow}^{\#}$	3.65	
Ws$^{\#}$	7 mg L^{-1}	
Vp$^{\#}$	0.0000000736 mm Hg	
Applications$^{\&,\$}$	FR, P, L. Fire retardant for PVC, soft or hard foam polyurethane, epoxy resin, unsaturated resin, polyester fiber & rubber conveyer belt. Can improve other performances of product, such as water proof, element resistance, antistatic performance, soft feeling. Dosage is 15-10% for soft or hard foam polyurethane, 10% in pvc, 5% for polyester fiber.	
# SRC physProp Database accessed 23/6/2014 & FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance $http://www.huahaichem.com/product-detail_e/id/26.html		

Table 30: T23DCPP – properties and application

Properties and application: Tris(2,3-dichloropropyl) phosphate (TDCPP) CAS No. 78-43-3		
log $K_{ow}^{\#}$	3.65	
Ws$^{\#}$	1.51 mg L^{-1}	
Vp$^{\#}$	0.000000228 mm Hg	
Applications$^{\&,\$}$	FR, P, L. Fire retardant for PVC, soft or hard foam polyurethane, epoxy resin, unsaturated resin, polyester fiber & rubber conveyer belt. Can improve other performances of product, such as water proof, element resistance, antistatic performance, soft feeling. Dosage is 15-10% for soft or hard foam polyurethane, 10% in pvc, 5% for polyester fiber.	
# SRC physProp Database accessed 6/6/2014 & FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance $http://www.huahaichem.com/product-detail_e/id/26.html		

The downstream concentration in the Danube (Figure 6) displays a uniform disrtibution with slightly higher concentrations in the upper stretch. Concentrations in a range between 5.9 and 22 ngL^{-1}(JDS4), with an average concentration of 11.4 ngL^{-1}. The concentrations in the tributaries are partially slightly higher, (Rivers Morava and Arges) with a range of 2.8 – 28.4 ngL^{-1} (River Arges), and 10.8 ngL^{-1} at average (Table 32). No impact from the tributaries Rivers Morava (1.7% contribution to discharge) and Arges (<1% contribution) was observed at the Danube sites downstream, again due to their low discharges. The river Inn (60% contribution to discharge) seems to dilute.

Figure 6: TDCPP – downstream profile dissolved phase

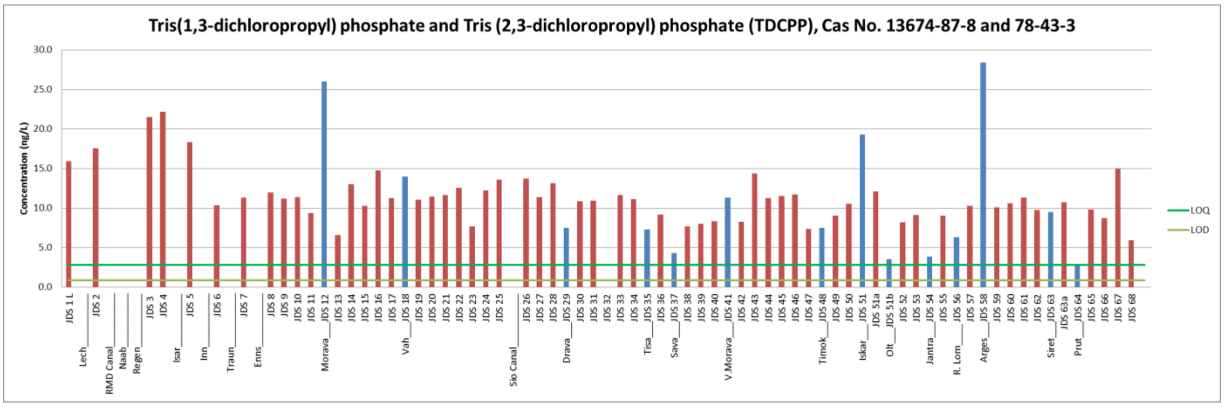


Table 31: TDCPP– stability during storage

TDCPP	118 days variation in % of the value reported
JDS 11	78.9
JDS 12	57.6
JDS 16	66.5

Table 32: TDCPP – dissolved phase summary

TDCPP (ng L^{-1})-	all samples	Danube	tributaries
$N_{analyzed}$	71	57	14
$N_{positive}$	70	56	14
min	2.83	5.93	2.83
mean	11.3	11.4	10.8
max	28.4	22.2	28.4
C50	11.0	11.2	7.49
C90	17.4	15.3	27.2

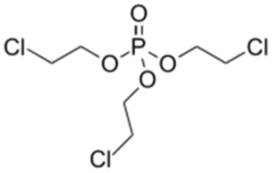
3.7 Tris(2-chloroethyl) phosphate (TCEP) CAS No. 115-96-8

Among the chlorinated OPCs investigated during JDS 3 TCEP got a comparable low production/use volume in Europe of 2040 tons annually (year 1995, Van der Veen, De Boer 2012). Nowadays the production/use figure should be much lower, since TCEP, due to its comparably high aquatic toxicity and its classification as human carcinogen in the EU, has been more and more substituted, mainly by TCPP (Regnery, Puettmann 2010).

TCEP was quantified in all 71 samples.

The results we obtained for TCEP in the dissolved phase can be considered slightly underestimated, since the decrease during our stability experiments was moderate (37-50%), (Table 34). The log K_{ow} of 1.44 (Table 33) suggests that the dissolved phase concentrations reported can be interpreted as total water concentrations.

Table 33: TCEP – properties and application

Properties and application: Tris(2-chloroethyl) phosphate (TCEP) CAS No. 115-96-8		
log K_{ow} #	1.44	
Ws #	7.0 g L^{-1}	
Vp #	8.2 Pa	
Applications&, $	FR, P, L, I	

Bollmann et al (2012) from SRC physProp Database Demo 2010
& FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance
$ Bollmann et al (2012) from Marklund et al., 2013

The downstream concentration in the Danube (Figure 7) displays a uniform distribution with slightly higher concentrations in the upper stretch and 2 isolated peaks in the middle and lower stretch (JDS 43 and JDS 67). Concentrations were similar to TDCPP in a range between 4.0 and 33.3 ngL^{-1} (JDS 43) with an average concentration of 10.7 ngL^{-1}. The concentrations in the tributaries in the lower stretch are partially higher, (Rivers Iskar, Jantra, Lom and Arges) with a range of 2.4 – 41.4 ngL^{-1} (River Iskar), and an average of 13.4 ngL^{-1} (Table 35).

No impact from the tributaries Iskar, Jantra, Lom and Arges displaying higher concentrations was observed at the Danube sites downstream, again due to low discharges compared to the Danube itself.

The concentration rise observed between JDS7 and JDS8 suggests higher concentrations in the River Inn (60% contribution to discharge)

Figure 7: TCEP – downstream profile dissolved phase

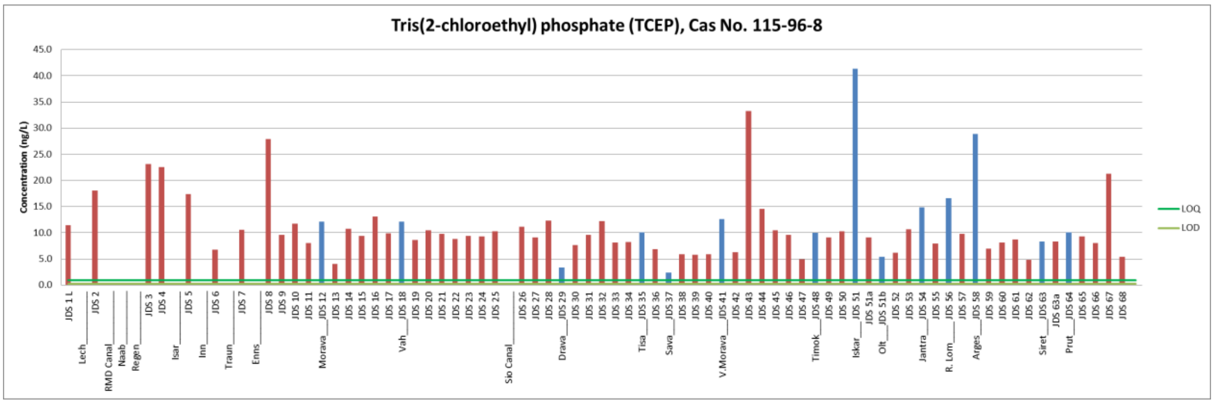


Table 34: TCEP – stability during storage

TCEP	118 days variation in % of the value reported
JDS 11	72.8
JDS 12	49.7
JDS 16	62.2

Table 35: TCEP – dissolved phase summary

TCEP (ng L^{-1})$^{-}$	all samples	Danube	tributaries
N_{analyzed}	71	57	14
N_{positive}	71	57	14
min	2.36	4.03	2.36
mean	11.2	10.7	13.4
max	41.4	33.3	41.4
C50	9.57	9.38	11.1
C90	20.6	18.7	35.1

3.8 Triphenyl phosphate (TPhP) CAS No. 115-86-6

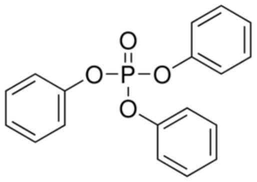
With 20,000 – 30,000 tons of annual usage/production in Europe (year 2000), TPhP is used in similar quantities as TCPP. It is one of the most effective flame retardant used in polymers. (Van der Veen, De Boer 2012)

TPhP is the most acute toxic of the various triaryl phosphates to fish, shrimps and daphnids. The acute toxicity index of TPhP for fish (96 h LC50) ranges from 0.36 mg/l in rainbow trout to 290 mg/l in bluegills (Danish EPA 1999).

TPhP was detected in 68 of 71 samples.

The results we obtained for TPhP in the dissolved phase may be underestimated for some sites, as indicated by the heterogeneous decrease observed during our stability experiments of 7, 24 and 89% (Table 37). As suggested by a log K_{ow} of 4.59 (Table 36), the dissolved phase concentrations reported can be interpreted as fairly representative for the total water concentrations. For comparison: During JDS 3, where dissolved phase and SPM associated concentrations were analysed separately, Endrin (higher log Kow of 5.2, SRC Physprop database 2014) was still present to > 80% in the dissolved phase.

Table 36: TPhP – properties and application

Properties and application: Triphenyl phosphate (TPhP) CAS No. 115-86-6		
log K_{ow} #	4.59	
Ws #	$1.9*10^{-3}$ g L^{-1}	
Vp #	$8.4*10^{-4}$ Pa	
Applications&, $	FR, P, H, L	

Bollmann et al (2012) from SRC physProp Database Demo 2010
& FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance
$ Bollmann et al (2012) from Marklund et al., 2013

The downstream concentration in the Danube (Figure 8) shows a prevalence of TPhP in the upper stretch with some isolated peaks in the middle and lower stretch at JDS 51a and JDS 66. Concentrations range between 0.29 and 5.6 ngL^{-1} (JDS2), with an average of 1.36 ngL^{-1} in the Danube. The concentrations in the tributaries are partially higher, ranging from 0.23 to 7.62 ngL^{-1} (Morava), with an average (dominated by the Rivers, Morava, Tisa, Jantra and Arges) of 7.62 ngL^{-1} (Table 38).

The partially higher concentrations in some of the tributaries do not seem to impact the concentrations in the Danube downstream its influence due to the low contribution (1.7%, 8.4%, <1% ,< 1%) to the total discharge.

The rising concentration between JDS 1 and JDS 2 suggest higher concentrations in the River Lech 40% contribution to discharge), while the drop in concentration between JDS6 and JDS7/8 cannot be explained with dilution from the Rivers Traun and Enns, contributing onlt 10 and 15% the discharge of the Danube River.

Figure 8: TPhP – downstream profile dissolved phase

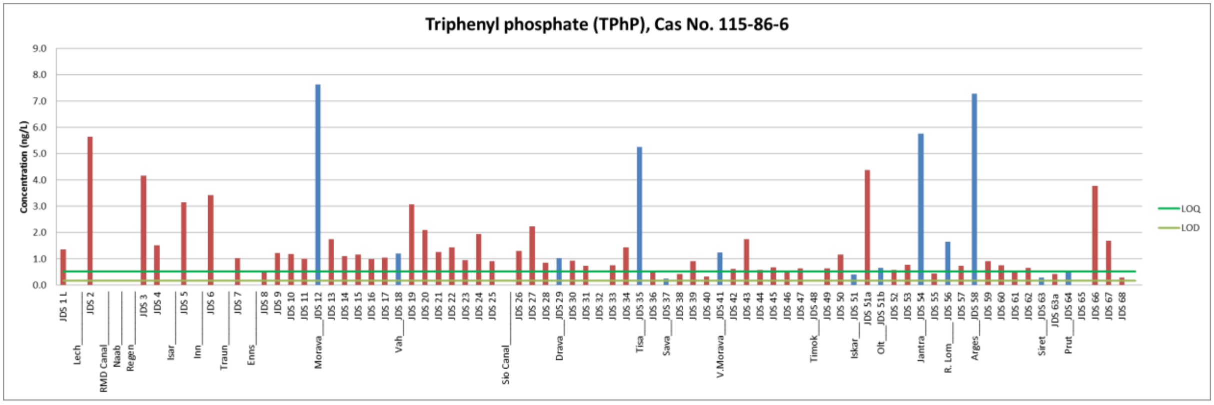


Table 37: TPhP– stability during storage

TPhP	**118 days variation in % of the value reported**
JDS 11	97.2
JDS 12	10.9
JDS 16	65.7

Table 38: TPhP– dissolved phase summary

TPhP (ng L^{-1})-	**All samples**	**Danube**	**tributaries**
N $_{analyzed}$	71	57	14
N $_{positive}$	68	55	14
min	0.24	0.29	0.24
mean	1.58	1.36	2.40
max	7.62	5.64	7.62
C50	1.01	0.99	1.11
C90	4.18	3.26	7.45

3.9 **Tris (methylphenyl) phosphate (TMPP) CAS no. 1330-78-5**

Also Tricresylphosphate, (TCP, TCrP), Tritolyl phosphate.

The commercial TMPP is a mixture of the isomers tri-o-cresyl phosphate (CAS no. 78-30-8), tri-m-cresyl phosphate (CAS no. 563-04-2), and tri-p-cresyl phosphate (CAS no. 78-32-0). There is a significant difference in toxicity between the isomers. The o-isomer is very toxic and is usually excluded as much as possible from the commercial products.

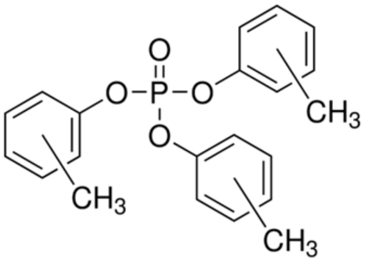
As a consequence of the physico-chemical properties of TMPP, there is a high potential for bioaccumulation. However, this seems not to occur in practice, owing to its rapid degradation. Freshwater algae are relatively sensitive to TMPP, the 50% growth inhibitory concentration ranging from 1.5 to 5.0 mg/l. Among fish species, the rainbow trout is adversely affected at concentrations below 1 mg/l, with sign of chronic poisoning, but the tidewater silverside is more resistant (LC50 is 8,700 mg/l). TMPP does not inhibit cholinesterase activity in fish and frogs, but it has a synergistic effect on organophosphorus insecticide activity (Danish EPA 1999).

TMPP (CAS No. of the technical mixture is 1330-78-5) concentration was measured as a sum of its orto-meta- and para-isomers (CAS Nos. 78-30-8, 563-04-2, 78-32-0).

TMPP was detected in 12 sites of 71 sites.

The results we obtained for TMPP in the dissolved phase can be considered slightly underestimated, since the decrease during our stability experiments was moderate (0-44%), (Table 40). The log K_{ow} of 5.11 (Table 39) suggests that the dissolved phase concentrations reported can be interpreted as slightly underestimated total water concentration. During JDS 3, where dissolved phase and SPM associated concentrations were analysed separately, Endrin (comparable log Kow of 5.2, SRC Physprop database 2014) was still present to > 80% in the dissolved phase.

Table 39: TMPP - Properties and application

Properties and application: Tris (methylphenyl) phosphate (TMPP) CAS no. 1330-78-5		
log K_{ow} #	5.11	
Ws #	$3.6*10^{-4}$ g L^{-1}	
Vp #	$8.0 * 10^{-5}$Pa	
Applications&, $	FR, H, L, I P in PVC@	

Bollmann et al (2012) from SRC physProp Database Demo 2010
& FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance
$ Bollmann et al (2012) from Marklund et al., 2003
@ Danish EPA 1999

The downstream concentration in the Danube (Figure 9) shows a prevalence of TMPP in the upper stretch and middle stretch in between JDS6 and JDS24. Further downstream no TMPP was found except in traces at JDS 49. In the positive samples concentrations ranged between 0.81 and 10.8 ngL^{-1} (JDS24), with an average of 4.96 ngL^{-1} in the Danube. The only positive tributary was the Morava with 12.8 ngL^{-1}, representing the maximum concentration found (Table 41).

Figure 9: TMPP – downstream profile dissolved phase

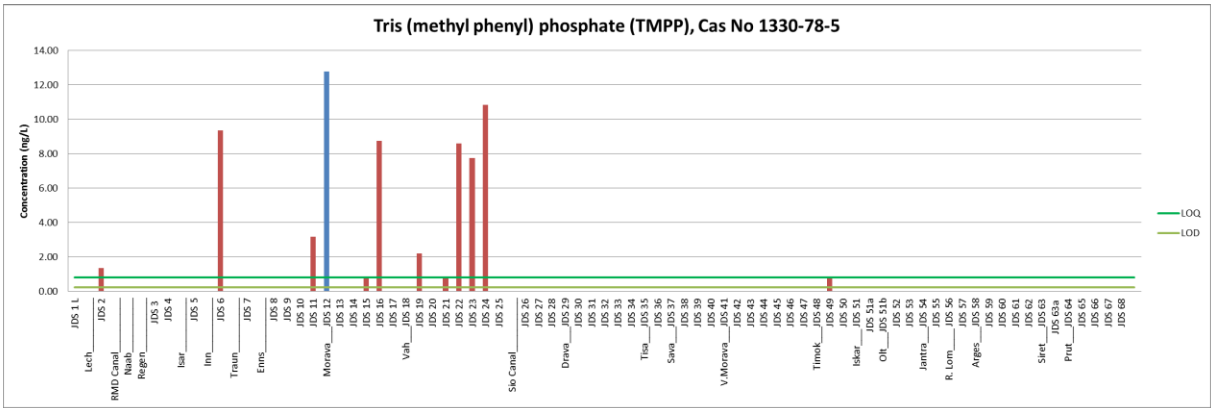


Table 40: TMPP – stability during storage

TMPP	**118 days variation in % of the value reported**
JDS 11	89.3
JDS 12	56.1
JDS 16	118

Table 41: TMPP – dissolved phase summary

TMPP (ng L^{-1})$^{-}$	**all samples**	**Danube**	**tributaries**
N$_{\text{analyzed}}$	71	57	14
N$_{\text{positive}}$	12	11	1
min	0.806	0.806	12.8
mean	5.61	4.96	12.8
max	12.8	10.8	12.8
C50	5.46	3.17	12.8
C90	12.2	10.5	-

***Note**: Due to weaknesses of the analytical methods applied, the results presented in the following chapters 3.10, 3.11, 3.12, may be considered only as indicative for the presence of the compounds discussed, and do not quantitatively reflect their actual concentrations. The reason why we present these data in spite of their poor quality is because even the supposingly underestimated concentrations (e.g. for T35DMPP and T2iPPP) lie in the upper range of the concentrations observed for the OPCs quantified in a reliable way. This suggests the need for further methodological development to obtain quantitative results for these compounds that would allow rank them according to their actual relevance within the OPCs investigated.*

3.10 Tris(3,5-dimethylphenyl) phosphate (T35DMPP) CAS No. 25653-16-1

Also Tri-3,5-xylenyl phosphate (TXP).

Tris(dimethylphenyl) phosphate, Trixylenyl phosphate (CAS No. 25155-23-1) is a substance of very high concern for human health because it is rated carcinogenic, mutagenic or toxic for reproduction According to Nobile (1980), who investigated the composition of two TXP products, the isomers (in decreasing order of abundance) 2,5- (19074-59-0) > 2,3-(65695-97-8) > 3,5-(25653-16-1, the one we used as surrogate standard) > 2,4-(3862-12-2) > 3,4-(3862-11-1) were present in the products. The 2,6-isomer (CAS no 121-06-2) was not present (ECHA, accessed 2. July 2014)

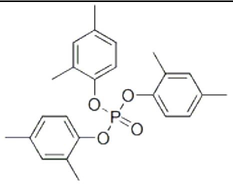
We used T35DMPP standards for quantification. Chromatograms displayed one native peak with the corresponding mass fragments and retention time. However, since we got no other isomers from the family of Tris(dimethylphenyl)phosphates available, we actually cannot say, whether we quantified only the less abundant isomer T35DMPP (CAS No. 25653-16-1), or if the results include other isomers of the technical mixture (CAS No. 25155-23-1)

T35DMPP was detected in 17 of 71 samples.

Indicated through the high losses we observed during the stability experiment (97 – 99%).-results presented for T35DMPP must be considered as significantly underestimated. This can be due to high decomposition rates, but may also be due to adsorption in the sample containers (log K_{ow} is 7.8, Table 42). Investigations on the latter aspect are on-going.

The high log K_{ow} suggests also that in the water column T35DMPP is mainly associated with SPM, this means that the total water concentration again is significantly underestimated by analysing the dissolved phase only. For comparison DDT with a log K_{ow} of 6.91 was found between 20 to 80% associated with SPM during JDS2. This means, that the resulting underestimation for TDMPP during this study, both from storage losses and the association with SPM, may range up to several orders of magnitude.

Table 42: T35DMPP - Properties and application

Properties and application: Tris(3,5-dimethylphenyl) phosphate (T35DMPP) CAS No. 25653-16-1		
log Kow #	7.98	
Ws #	0.89* 10-3 g L^{-1}	
Vp #	0.0000000206 mm Hg	
Applications $	Flame retardants compositions, hydraulic fluid (steel works, furnaces, mines); polyvinyl chloride plasticizer	
# Bollmann et al (2012) from SRC physProp Database Demo 2010 $ TOXNET Toxicology Data Network , http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:%2225653-16-1%22, accessed 1st July 2014		

The downstream concentration in the Danube shows a prevalence of T35DMPP in the upper stretch and the middle stretch until JDS 27. Further downstream no T35DMPP was found except in traces at JDS 49.

In the positive samples in the Danube concentrations ranged between 0.75 and 53.8 ngL^{-1} (JDS16), with an average of 13.9 ngL^{-1}. The only two positive tributaries were the Morava and Vah with 3.13 and 3.28 ngL^{-1} respectively.

Figure 10: T35DMPP – downstream profile dissolved phase

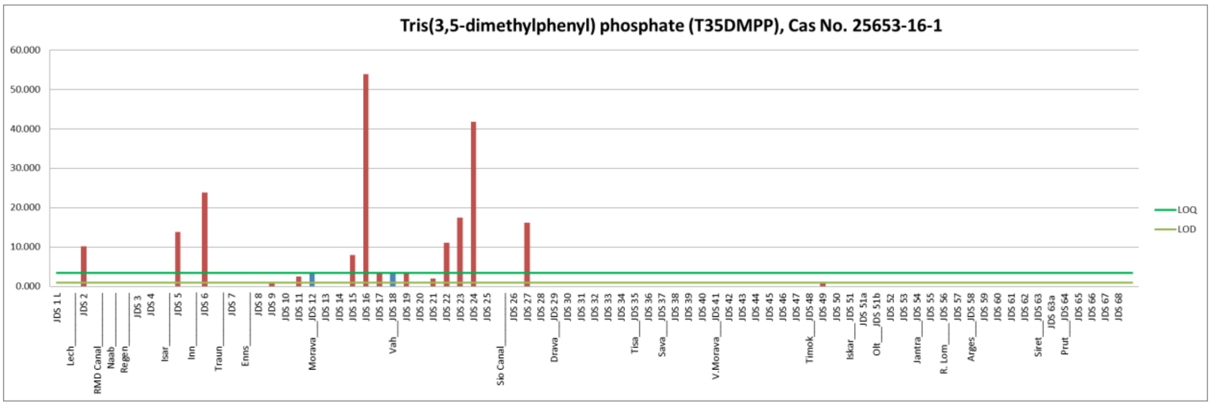


Table 43: T35DMPP – stability during storage

T35DMPP	118 days variation in % of the value reported
JDS 11	2.7
JDS 12	2.2
JDS 16	0.5

Table 44: T35DMPP– dissolved phase summary

T35DMPP (ng L^{-1})$^{-}$	all samples	Danube	tributaries
N $_{\text{analyzed}}$	71	57	14
N $_{\text{positive}}$	17	15	2
min	0.758	0.758	3.13
mean	12.7	13.9	3.20
max	53.8	53.8	3.28
C50	8.01	10.2	3.20
C90	44.2	46.6	-

3.11 Tris(2-isopropylphenyl) phosphate (T2*i*PPP) CAS No. 64532-95-2

Tris(2-isopropylphenyl)phosphate is considered as neurotoxic. http://www.chemicalbook.com/ChemicalProductProperty_EN_CB4141576.htm.

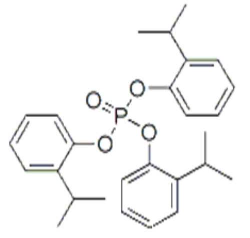
We used T2*i*PPP standards for quantification. Similar to T35DMPP above, chromatograms displayed one native peak with the corresponding mass fragments and retention time. However, since we got no other isomers from the family of Tris(isopropylphenyl) phosphate (T*i*PPP) available, we actually cannot say, whether we quantified only T2*i*PPP (CAS No.64532-95-2) only, or if the results include other isomers of the technical mixture of T*i*PPP(CAS No 68937-41-7).

T2*i*PPP was detected in 8 of 71 samples. We can present only indicative values with a potential of serious underestimation. The quantification for T2*i*PPP is even more critical than for T25DMPP.

The only site where we obtained stability data displayed a loss of 81% during the storage period (Table 46). Therefore, from the viewpoint of sample stability the results presented for T2*i*PPP must be considered as significantly underestimated. Losses may be the result of high decomposition rates, but may also be due to adsorption in the sample containers (log Kow is 9.07, Table 45).Investigations on the latter aspect are on-going.

The high log Kow suggests also that in the water column T2*i*PPP is quasi entirely associated with SPM, this means that the total water concentration again is significantly underestimated by analysing the dissolved phase only. This means, that the resulting underestimation of the total water concentration for T2*i*PPP during this study, both from storage losses and the association with SPM, may range up to several orders of magnitude.

Table 45: T2*i*PPP - Properties and application

Properties and application: Tris(2-isopropylphenyl) phosphate (T2*i*PPP) CAS No. 64532-95-2		
log Kow $	9.07	
Ws #	2.6 * 10-8 g/L-1	
Vp $	2.06*10-8 mm Hg (for T4*i*PPP)	
Applications&,$	FR in PVC cables, P used in PVC and phenolic resins, flexible PU, cellulosic resins, synthetic rubber, polycarbonate blends. Lubricants; H, F,L; cutting fluids; construction materials; surface treatment; extinguishing agents; adhesives, binding agents	

TNPP European Risk Assessment Report – Annex 2. http://echa.europa.eu/documents/10162/13630/trd_rar_annex2_france_tnpp_en.pdf, accessed 1st July 2014
& FR: flame retardant, P: plasticizer, H: hydraulic fluid, F: floor covering, L: lacquer/paint/glue, A: anti-foaming agent, I: industrial processes, Fu: fungus resistance
$TOXNET Toxicology Data Network, http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:@rn+26967-76-0, accessed 1st July 2014

The downstream concentration profile in the Danube shows a prevalence of T2*i*PPP in the upper stretch and middle stretch until JDS 27. Further downstream no T2*i*PPP was found (Figure 11).

In the positive samples in the Danube concentrations ranged between 6.54 and 26.8 ngL^{-1} (JDS24), with an average of 15.1 ngL^{-1}. No T2*i*PPP (LOD of 5 ngL^{-1}) was detected in the tributaries (Table 47).

Figure 11: T2*i*PPP – downstream profile dissolved phase

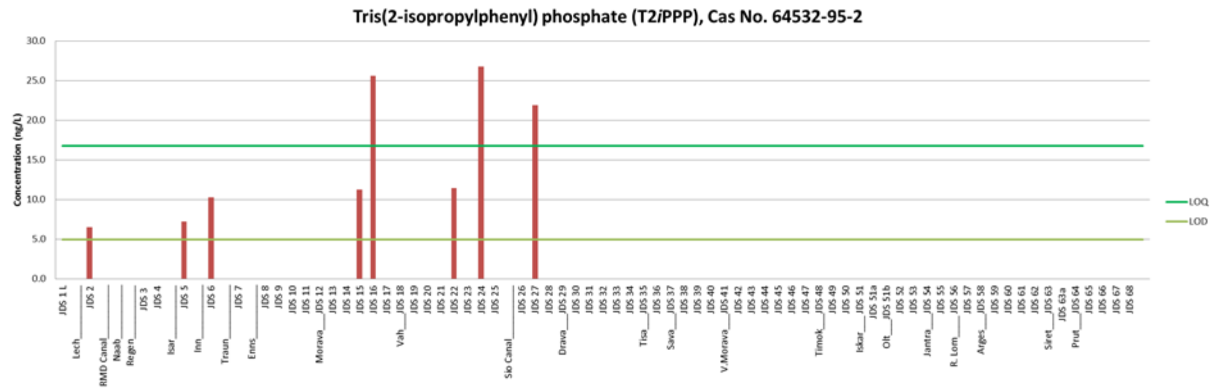


Table 46: T2*i*PPP – stability during storage

T2*i*PP	**118 days variation in % of the value reported**
JDS 11	-
JDS 12	-
JDS 16	18.8

Table 47: T2*i*PPP – dissolved phase summary

T2*i*PP (ng L^{-1})-	**all samples**	**Danube**	**tributaries**
N analyzed	71	57	14
N positive	8	8	0
min	6.54	6.54	-
mean	15.1	15.1	-
max	26.8	26.8	-
C50	11.4	11.4	-
C90	-	-	-

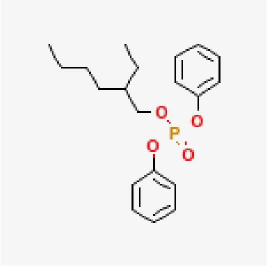
3.12 2-ethylhexyl diphenyl phosphate (EHDP) CAS no.1241-94-7

EHDP is considered neurotoxic (http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:%221241-94-7%22, accessed 1st July 2014).

EHDP losses were acceptable during the storage experiment (Table 50), and also the log Kow of 5.73 (Table 48) suggests that EHDP is mainly associated with the dissolved phase. However, an underestimation of the concentration of a factor 3-4 must be considered because of insufficient extraction efficiency of the solid phase employed for extraction (2.9.7).

EHDP was detected in 21 of 71 samples. We can present only indicative values with a potential of underestimation.

Table 48: EDHP Properties and application

Properties and application: 2-ethylhexyl diphenyl phosphate (EHDP) CAS no.1241-94-7		
log K_{ow} #	5.73	
Ws #	1.9 mg L-1	
Vp #	0.00005 mm	
Applications $	Most important mixed alkyl aryl phosphate. Considered nontoxic. Plasticizer for food-wrapping films, tubing for skinless sausages, and for other meat packaging. Main component in certain non-flammable hydraulic fluids used in large aircraft. Plasticizer for PVC and PVC copolymers	

SRC physProp Database, assessed 1st July 2014
$ TOXNET Toxicology Data Network http://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:%221241-94-7%22, accessed 1st July 2014

The downstream concentration profile in the Danube shows a prevalence of EHDP in the upper stretch and middle stretch, with some minor amounts detected also along the lower stretch.

In the 17 positive samples in the Danube EHDP concentrations ranged between 0.079 and 5.92 ngL^{-1} (JDS6), with an average of 1.61 ngL^{-1}. In the 4 tributaries Morava, Tisa, Rusensky Lom and Prut EHDP was detected between 0.38 and 1.8 ngL^{-1} (Morava), the average concentration was 0.88 ngL^{-1}

Figure 12: EHDP – downstream profile dissolved phase

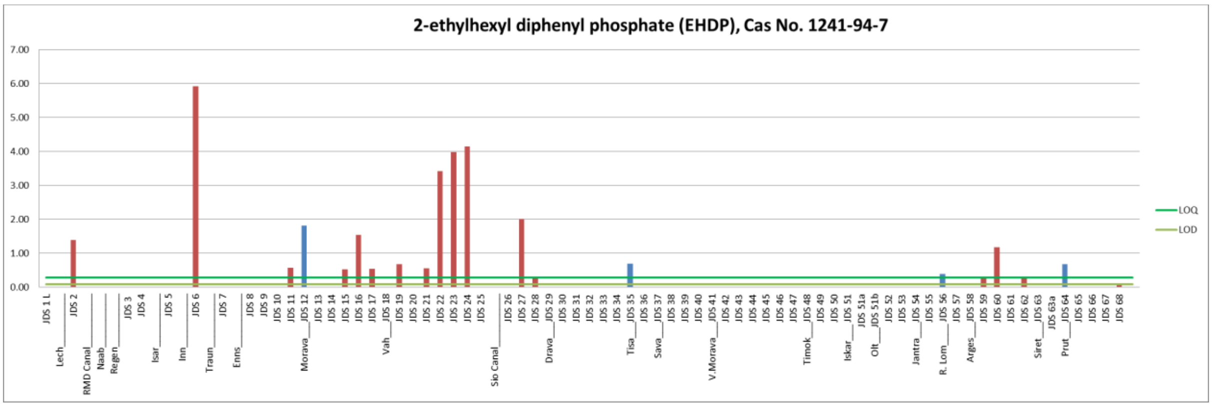


Table 49: EHDP - dissolved phase summary

EHDP	**all samples**	**Danube**	**tributaries**
N analyzed	71	54	14
N positive	21	17	4
min	0.0790	0.0790	0.380
mean	1.47	1.61	0.888
max	5.92	5.92	1.80
C50	0.680	0.680	0.683
C90	4.11	4.50	-

Table 50: EDHP - stability during storage

EDHP	**118 days variation in % of the value reported**
JDS 11	14.9
JDS 12	101
JDS 16	146

3.13 **Summary OPCs in the dissolved phase**

3.13.1 Spatial distribution

The observed downstream concentration profiles of the OPC's during the survey display some similarities between specific groups of compounds.

TDCPP, TCPP (with some isolated maxima), T*n*BP, T*i*BP, and T*n*PP are present in comparable concentrations along the whole Danube.

TBEP and TPhP are more abundant in the upper stretch with a decreasing trend downstream but still present in considerable amounts.

TMPP, T35DMPP, T2*i*PPP and EHDP (to lesser extent) were almost exclusively detected in fairly variable concentrations in the upper/middle stretch, but not further downstream than JDS 27 (rkm 1434).

For most OPCs the concentrations in the tributaries, from which samples were available, do not differ too much from the Danube itself. However, from the upper stretch, where the several tributaries contribute more to the total discharge, were available. Consequently the picture remains incomplete.

Remarkable concentrations in the investigated tributaries that were above those in the Danube itself (tributaries in the order of concentration) were seen only for T*i*BP (Arges >Vah), T*n*BP (Vah>>Iskar>Arges, Prut), TBEP (Arges), TPhP (Morava, Arges, Jantra, Tisa), TCPP (Timok> Arges, Iskar), TDCPP (Arges, Morava, Iskar), TCEP (Iskar, Arges). Thereby one order of magnitude of concentration difference was never exceeded.

As a consequence of the low contributions of the tributaries to the overall discharge of the Danube, the partially higher concentrations in the tributaries display no visible impact on the concentration downstream their confluence.

Also along the Danube itself an overall low impact of the few sites with higher concentrations on the sites downstream is observed. The few ‘hot spots’ display only local impact. It has to be taken into consideration that the higher concentrations observed locally might as well be due to incomplete mixing, rather than representing a representative value for the whole water column. The overall low variability points to a situation with diffuse emissions along the whole Danube and its tributaries. That would fit to the fact that OPCs are mainly used in open applications and enter the aquatic environment from diffuse urban sources rather than from industrial hotspots.

For those OPCs that were found predominantly in the upper middle stretch (TMPP, T35DMPP, T2*i*PPP, EHDP) one might assume that they entered more recently into production and are therefore released mainly in zones of a higher industrialization, while the diffuse emissions from the open use are still low. In such a scenario they would be simply diluted further downstream. In addition TMPP, T35DMPP, T2*i*PPP, EHDP got the highest log Kows (5.11, 7.98, 9.07 and 5.73). As a consequence their higher association with settling material would privilege a higher sedimentation rates and provides an efficient removal mechanism from the water column.

In summary, the concentration differences we observed for the investigated OPCs do identify any local emission source of concern for the Danube catchment, which would require specific action.

3.13.2 Ranking and potential impact on aquatic biota

As mentioned above, the concentration data of T35 TMPP, T2*i*PPP and EHDP are underestimated by the methodology applied. This has to be considered when looking into their ranking within the observed concentration ranges for OPCs.

In terms of concentrations TCPP clearly dominates, both in the Danube and in the tributaries

In the 57 samples from Danube the ranking of the concentrations detected (number of positive samples, average, range) are as follows:

TCPP (57pos, **av103**, 45-594ng/L) >> T*i*BP (57pos, **av19**, 6.8-48 ng/L) > T2iPP (8pos, **av15.1**, 6.5-27 ng/L) ≥ TBEP (56pos, **av14**, 2-54ng/L) ≥ T35DMPP(15pos, **av14**, 0.76-54 ng/L) ≥ TDCPP (56pos, **av11.4**, 6-22 ng/L) ≥ TCEP (57pos, **av11**, 4-33 ng/L) > TMPP(11pos, **av5.0**, 0.81-10.8 ng/L) ≥ T*n*BP (57pos, **av4.3**, 0.42-9.4ng/L) > EDHP (17pos, **av1.6**, 0.079-5.9 ng/L) ≥ TPhP (55pos, **av1.4**, 0.3-5.6 ng/L) > T*n*PP (55pos, **av0.35**, 0,075-2.1 ng/L)

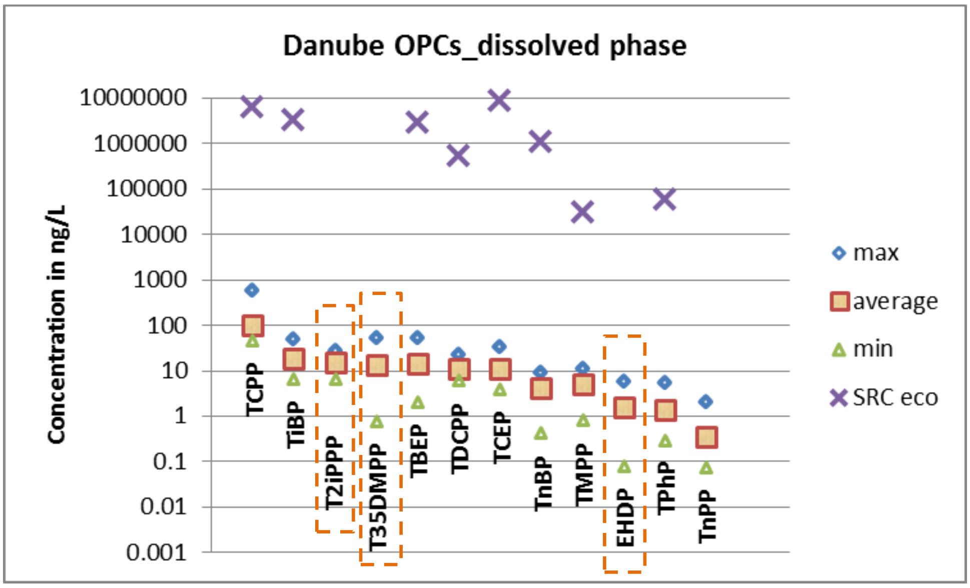
In Figure 13 the ranking for the Danube River is displayed. The compounds that we believe are underestimated by the analytical approach applied are marked with a dashed box.

In the 14 samples from tributaries the ranking of the concentrations detected (number of positive samples, average, range) are as follows:

TCPP (14pos, **av151**, 28-603ng/L) >> T*i*BP (14pos, **av23**, 2.5-97ng/L) > TBEP (10pos, **av15.4**, 1.3-93ng/L) ≥ TCEP (14pos, **av13**, 2.4-41ng/L) ≥ TMPP(1pos, **12.8** ng/L) ≥ TDCPP (14pos, **av10.8**, 8-28ng/L) ≥ T*n*BP (57pos, **av10.6**, 0,26-70ng/L) > T35DMPP(2pos, **av3.2**, 3.1-3.3ng/L) > TPhP (14pos, **av2.4**, 0.24-7.6ng/L) > EDHP (4 pos, **av0.89**, 0.38-1.8ng/L) > T*n*PP (13pos, **av0.42**, 0,085-1.0ng/L) >T2iPP (0pos).

In Figure 14 the ranking for the tributaries is displayed. The compounds we believe are underestimated are marked with a dashed box.

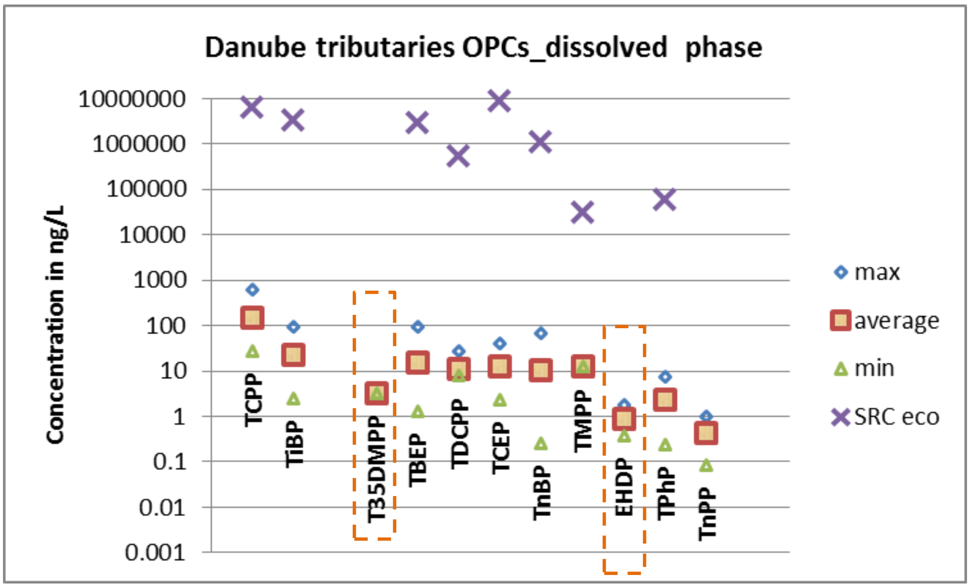
Figure 13: Summary of concentration ranges and average of OPCs in the Danube



In terms of concentrations TCPP clearly dominates, both in the Danube and in the tributaries, the other OPCs were at ranging one and more orders of magnitude lower in concentration.

In order to get an indication about in how far the ranking of the concentrations reflects the actual risk for aquatic biota, we compare the concentrations with the so called *'Serious Risk Concentration for surface waters, SRCeco'* which is derived from a risk assessment approach employing acute and chronic toxicity test data for number of aquatic organisms (Table 51, Verbrueggen et al. 2005). The *SRCeco*, as far as available, is displayed together with the concentrations in Figure 13 and Figure 14.

Figure 14: Summary of concentration ranges and average of OPCs in the Danube tributaries



It appears that the concentrations of those OPCs where *SRCeco* values are available are currently several orders of magnitude below their effect levels for aquatic biota. However, in terms of ranking the OPCs, the picture changes. TCPP, although dominating the concentration in the dissolve phase, is now ranking behind TDCPP, TPhP and TMPP, the later one dominating by far the ranking. The situation in the tributaries is analogue (Figure 15). For T35DMPP, T2*i*PPP and EHDP no *SRCeco* values were available.

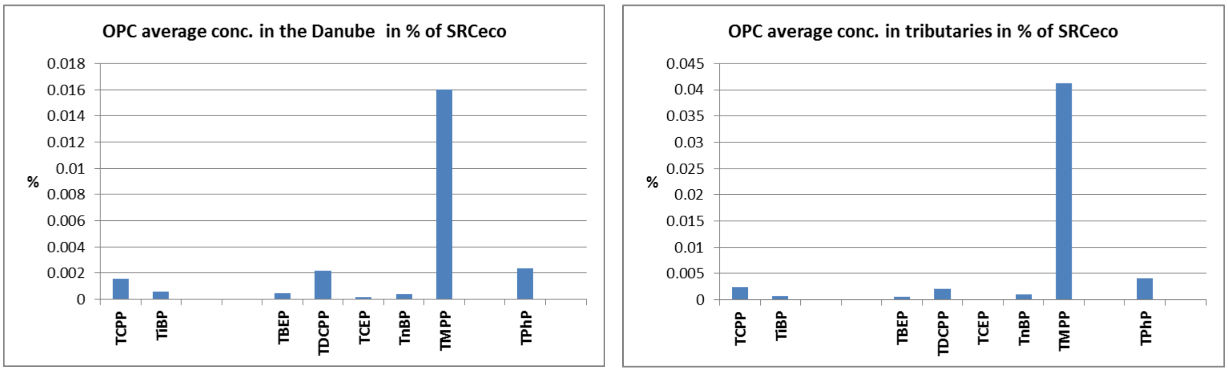
From this, and since the chlorinated OPCs have been phased out to a large extent, it can be concluded that in particular TMPP and to a lesser extent TPhP may deserve future attention what regards their temporal trends in the effluents into the Danube basin.

Table 51: Serious risk concentration for selected OPCs in surface waters

Compound	Serious Risk Concentration for surface waters, SRC Eco[$] (mg/L)
TCPP	6.5
T*i*BP	3.4
T2*i*PPP	no data
T35DMPP	no data
TBEP	2.9
TDCPP	0.52
TCEP	8.6
T*n*BP	1.1
TMPP	0.031
EHDP	no data
TPhP	0.06
T*n*PP	no data

[$]SRC eco from Verbrueggen et al 2005

Figure 15: average OPC concentrations in % of the Serious Risk Concentration



3.14 Comparison with other surface waters in Europe

In Table 52 the OPC concentrations obtained from this study are resumed, in comparison with data available from literature. It should be kept in mind, however, that the JDS3 data can only be considered as a snapshot, and we do not have reliable information on the temporal variability on OPCs (as observed by Bollmann et al. (2012) in various European Rivers) in the Danube.

The comparison with the data from Martinez Carballo et al (2007), obtained from the Danube around Vienna suggests lower concentrations in 2013 for T*n*BP and TBEP, while the concentrations of TCPP and TDCPP were higher.

The comparison with the ranges available from other surface waters suggests that the concentrations obtained during JDS3 for OPCs in the Danube are within the (large) ranges typically observed. Also the dominance of TCPP can be seen in most of the other surface waters investigated.

Table 52: OPCs in surface waters, JDS3 results in comparison with literature data

OPCs in surface waters, JDS3 in comparison with literature data, concentrations in ng/L^{-1}											
Compound	T*n*PP	T*i*BP	T*n*BP	TCPP	TBEP	TDCPP	TCEP	TPhP	TMPP	Reference	Comment
Danube	0.075- 2.1; **0.35**	6.8-48; **19**	0.42-9.4; **4.3**	45-549; **103**	2-54; **14**	6-22; **11.4**	4.0-33: **11**	0.3-5.6; **1.4**	0.8-11; **5**	This study	Min-max; **average** of positive samples
Danube trib.	0.085-1.0; **0.42**	2.5-97; **23.4**	0.26-70; **10.6**	28 –603; **151**	1.3-93;**15.4**	3-28; **10.8**	2.4- 41,: **13**	0.24-7.6; **2.4**	< 0.24-13	This study	
Danube	----	-----	110, 20	43, 33	52, 24	7, < 3	23, 13	6 < 4.4 -	< 7.9	Martinez Carballo et al. 2007	Up and down Vienna (Nussdorf, Haslau)
Elbe	< 0.86	4.3 – 19.2	< 0.25-7.5	44.0 - 134	< 2 -94.3	6.4-31	9.3 – 35.5	< 1.2 -10.3	< 2.0	Bollmann et al. 2012	August 2010
		10 – 50		40 – 250	< 2 – 80		5 – 20				March – October 2010
				20-520; 72-217			<10-150; 52-66			ARGE Elbe 2000	1996
				<25-88			<25-100				1998
Mulde				160-450; 284 71-79			<10-150; 79 45-57			ARGE Elbe 2000	1996 Dessau 1998 Dessau
Saale				130-780; 205 <25-140			50-220; 112 <25-98			ARGE Elbe 2000	1996 Rosenburg 1998 Rosenburg
Schwarze Elster				33-720			30-52			ARGE Elbe 2000	1998 Gorsdorf
Weser	< 0.86	< 1.3 – 13.2		24.3 - 167	< 2-48.4	5.3-27	3.3 - 34	< 1.2	< 2.0	Bollmann et al. 2012	August 2010
Ems	< 0.86	4.81-11.1		89.9 - 175	38.9 – 42.7	8-35	11.5 – 34.2	< 1.2	< 2.0	Bollmann et al., 2012	August 2010
Rhine	< 0.86	16.8-84.0	6 - 28	74.8 – 159	28.5- 53.9	13-31	12.4 – 25.8	< 1.2	< 2.0	Bollmann et al. 2012	August 2010,
				30-150			5-500			Knepper et al. 1999	Colone
		30-50	30-120	80-100	80-140	13-36	80-100			Andresen et al. 2004	September 2002, instant extraction
Meuse	< 0.86	20.7		196	103	37	38.4	3.6	< 2.0	Bollmann et al. 2012	August 2010
Scheldt	< 0.86	5.04-5.23		164 - 570	< 2 - 72	19-67	19-69.9	< 1.2	< 2.0	Bollmann et al. 2012	August 2010
Ruhr		< LOD - 150	30 - 110	20-200	10 - 200	50	50	<10 - 40		Andresen et al. 2004	September 2002, instant extraction
Aire				113 – 26050 Average 6040		62-149	119 -316	6.3 - 22		Cristale et al. 2013	
Tiber	15-62	98 - 137	82-114	54-117	87-323	< 0.7	< 1.5-7	11-165	< 0.1	Bacaloni et al. 2007	June and November 2006, Rome
Spanish rivers	< 0.2	11 - 89	<10-50	28-430	< 10 - 2700	< 2-70	0.8-85	< 2 - 35		Garcia-Lopez et al. 2010	2009, no location
Lake Taihu	1,2-9.4		2.2-12	7.7-19		7.4-42	260-2406	<0.8-1.8		Yan et al. 2012	
Urban lakes		8-10	17 -32	85-126	<30-53		23-61			Regnery and Puettmann 2010	2007 – 2009, range of mean

4 Conclusions

Among the investigated OPCs, TCPP clearly dominates in concentration, both in the Danube and in the tributaries. Looking into their toxicities, the concentrations for OPCs are several orders of magnitude below their effect levels for aquatic biota. Under the toxicity aspect, TMPP and TPhP, although lower in concentration, are ranking at first place what concerns their potential impacts on aquatic biota and may deserve further attention regarding their temporal trends.

For most OPCs the concentrations in the tributaries do not differ much from the Danube itself. Consequently, the partially higher concentrations in the tributaries do not display discrete impacts on the concentration downstream their confluence, thus to the overall discharge of the Danube.

Generally the observed concentration differences do not reveal any local OPC emissions of concern for the Danube catchment, which would require action on hot spots or specific zones of emissions.

The comparison with data available from other surface waters suggests that the concentrations obtained during JDS3 for OPCs in the Danube are within the (large) ranges typically reported. Also the dominance of TCPP can be seen in most of the other surface waters investigated

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7 Supplementary material

Supplement 1: OCP concentration data

JDS3 code	*rkm*	T*n*PP	T*i*BP	T*n*BP	TCPP	TBEP	TDCPP	TCEP	TPhP	TMPP	T35DMPP	EHDP	T2*i*PPP
		ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
JDS 1 L	*2581*	0.36	11.1	3.97	107.5	25.4	15.9	11.4	1.4	< LOD	< LOD	< LOD	< LOD
JDS 2	*2415*	0.74	47.6	3.79	95.3	49.4	17.6	18.1	5.6	1.3	10.2	1.4	6.5
JDS 3	*2354*	0.46	23.3	1.79	165.9	34.5	21.5	23.2	4.2	< LOD	< LOD	< LOD	< LOD
JDS 4	*2285*	0.47	23.8	3.81	181.9	40.0	22.2	22.5	1.5	< LOD	< LOD	< LOD	< LOD
JDS 5	*2258*	0.65	19.7	5.1	116.7	42.0	18.4	17.4	3.1	< LOD	13.9	1.6	7.2
JDS 6	*2205*	0.85	17.0	1.77	64.2	22.8	10.4	6.8	3.4	9.3	23.8	5.9	10.3
JDS 7	*2120*	0.34	14.6	3.29	89.7	17.9	11.3	10.6	1.0	< LOD	< LOD	< LOD	< LOD
JDS 8	*2008*	0.35	12.9	2.8	238	53.6	12.0	27.9	0.49	< LOD	ST n.d.	< LOD	ST n.d.
JDS 9	*1942*	0.20	8.5	3.9	56.0	23.9	11.2	9.6	1.2	< LOD	1.2	< LOD	< LOD
JDS 10	*1895*	0.19	21.6	3.5	91.5	19.8	11.4	11.8	1.2	< LOD	< LOD	< LOD	< LOD
JDS 11	*1881*	0.15	16.3	4.1	58.3	22.0	9.4	8.1	1.0	3.2	2.6	0.56	< LOD
JDS 12	*1880*	0.30	12.0	5.1	133	7.0	26.0	12.2	7.6	12.8	3.1	1.8	< LOD
JDS 13	*1869*	0.07	13.8	3.1	45.4	19.8	6.6	4.0	1.7	< LOD	< LOD	< LOD	< LOD
JDS 14	*1852*	0.33	14.8	3.9	113	18.0	13.0	10.8	1.1	< LOD	< LOD	< LOD	< LOD
JDS 15	*1806*	0.17	15.2	4.0	59.1	19.3	10.3	9.4	1.2	0.86	8.0	0.52	11.2
JDS 16	*1794*	0.33	17.0	4.5	95.4	19.9	14.8	13.1	1.0	8.76	53.8	1.5	25.6
JDS 17	*1790*	0.81	17.3	6.2	57.9	18.4	11.2	9.9	1.0	< LOD	3.3	0.54	< LOD
JDS 18	*1766*	0.89	49.2	69.8	86.3	11.2	14.0	12.1	1.2	< LOD	3.3	0.93	< LOD
JDS 19	*1761*	0.14	16.0	3.9	52.4	16.4	11.1	8.6	3.1	2.19	3.2	0.68	< LOD
JDS 20	*1707*	0.15	18.0	9.4	99.5	15.3	11.5	10.5	2.1	< LOD	< LOD	< LOD	< LOD
JDS 21	*1660*	0.71	16.9	6.0	73.4	18.6	11.8	9.7	1.3	0.82	2.1	0.56	< LOD
JDS 22	*1632*	0.37	17.8	7.2	77.2	18.3	12.7	8.7	1.4	8.80	11.1	3.4	10.8
JDS 23	*1586*	0.34	26.3	5.7	146	9.3	7.8	9.3	1.0	7.92	17.4	4.0	< LOD
JDS 24	*1560*	0.11	15.3	5.0	79.5	17.5	12.4	9.2	2.0	11.10	41.7	4.2	25.3
JDS 25	*1533*	0.25	17.1	3.4	112	9.7	13.6	10.3	0.90	< LOD	< LOD	< LOD	< LOD
JDS 26	*1481*	0.17	18.1	3.5	123	9.6	13.7	11.1	1.3	< LOD	< LOD	< LOD	< LOD

JDS3 code	*rkm*	**TnPP**	**TiBP**	**TnBP**	**TCPP**	**TBEP**	**TDCPP**	**TCEP**	**TPhP**	**TMPP**	**T35DMPP**	**EHDP**	**T2iPPP**
		ng/L	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
JDS 27	*1434*	0.39	14.6	5.8	78.9	17.3	11.5	9.0	2.2	< LOD	16.1	2.01	20.2
JDS 28	*1384*	0.49	16.5	5.0	92.2	15.1	13.1	12.3	0.9	< LOD	< LOD	0.30	< LOD
JDS 29	*1379*	0.27	20.8	0.26	36.2	9.5	7.5	3.4	1.0	< LOD	< LOD	< LOD	< LOD
JDS 30	*1367*	0.26	17.4	3.1	73.5	7.7	10.9	7.7	0.9	< LOD	< LOD	0.19	< LOD
JDS 31	*1300*	0.16	18.7	4.6	83.6	4.3	10.9	9.6	0.7	< LOD	< LOD	< LOD	< LOD
JDS 32	*1262*	< LOD	9.5	3.3	582	< LOD	ST n. d.	12.3	< LOD	< LOD	ST n. d.	< LOD	ST n. d.
JDS 33	*1252*	0.38	30.1	0.4	81.6	7.6	11.6	8.1	0.74	< LOD	< LOD	< LOD	< LOD
JDS 34	*1216*	0.21	23.0	3.5	80.8	6.1	11.1	8.2	1.4	< LOD	< LOD	0.22	< LOD
JDS 35	*1215*	0.68	12.8	2.8	72.1	< LOD	7.3	10.1	5.2	< LOD	< LOD	0.69	< LOD
JDS 36	*1200*	0.22	22.9	2.4	65.7	4.1	9.2	6.9	0.50	< LOD	< LOD	< LOD	< LOD
JDS 37	*1170*	0.08	4.7	4.5	28.0	1.2	4.3	2.4	0.24	< LOD	< LOD	< LOD	< LOD
JDS 38	*1159*	0.24	15.8	4.1	57.4	5.0	7.7	5.9	0.41	< LOD	< LOD	< LOD	< LOD
JDS 39	*1151*	0.12	15.2	5.0	59.3	4.9	8.0	5.8	0.90	< LOD	< LOD	0.10	< LOD
JDS 40	*1107*	0.15	17.9	4.4	65.3	3.6	8.4	5.9	0.32	< LOD	< LOD	< LOD	< LOD
JDS 41	*1103*	0.17	23.6	2.9	83.8	< LOD	11.3	12.6	1.2	< LOD	< LOD	< LOD	< LOD
JDS 42	*1097*	0.19	14.8	4.1	61.0	4.4	8.3	6.3	0.62	< LOD	< LOD	< LOD	< LOD
JDS 43	*1071*	2.1	15.2	4.2	122	50.9	14.4	33.3	1.8	< LOD	< LOD	< LOD	< LOD
JDS 44	*1040*	0.26	15.4	2.0	103	10.9	11.3	14.6	0.58	< LOD	< LOD	< LOD	< LOD
JDS 45	*954*	0.27	14.4	3.8	112	10.7	11.6	10.5	0.67	< LOD	< LOD	< LOD	< LOD
JDS 46	*926*	0.18	15.3	4.2	117	8.6	11.7	9.6	0.48	< LOD	< LOD	< LOD	< LOD
JDS 47	*851*	0.12	18.8	3.7	67.2	3.7	7.4	4.9	0.63	< LOD	< LOD	< LOD	< LOD
JDS 48	*845*	< LOD	2.54	2.9	603	< LOD	7.5	10.0	< LOD	< LOD	ST n.d.	< LOD	ST n. d.
JDS 49	*834*	0.41	18.6	5.1	73.6	4.7	9.1	9.1	0.64	0.87	0.758	0.16	< LOD
JDS 50	*685*	0.25	22.3	3.7	112	5.7	10.6	10.3	1.2	< LOD	< LOD	< LOD	< LOD
JDS 51	*637*	0.40	36.7	19.2	282	2.5	19.3	41.4	0.40	< LOD	< LOD	< LOD	< LOD
JDS 51a	*606*	0.65	30.7	2.9	98.3	4.2	12.1	9.1	4.4	< LOD	< LOD	< LOD	< LOD

JDS3 code	*rkm*	**TnPP** **ng/L**	**TiBP** **ng/L**	**TnBP** **ng/L**	**TCPP** **ng/L**	**TBEP** **ng/L**	**TDCPP** **ng/L**	**TCEP** **ng/L**	**TPhP** **ng/L**	**TMPP** **ng/L**	**T35DMPP** **ng/L**	**EHDP** **ng/L**	**T2iPPP** **ng/L**
JDS 51b	*605*	0.65	16.2	2.7	167	3.5	3.5	5.4	0.66	< LOD	< LOD	< LOD	< LOD
JDS 52	*602*	0.26	24.7	4.2	68.9	3.3	8.2	6.2	0.58	< LOD	< LOD	0.18	< LOD
JDS 53	*550*	0.63	21.5	6.6	115	3.1	9.1	10.6	0.76	< LOD	< LOD	< LOD	< LOD
JJDS 54	*537*	0.13	15.4	2.4	74.2	< LOD	3.9	14.8	5.8	< LOD	< LOD	< LOD	< LOD
JDS 55	*532*	0.13	20.8	4.1	86.4	2.0	9.1	7.9	0.44	< LOD	< LOD	< LOD	< LOD
JDS 56	*498*	0.46	8.5	7.3	110	12.4	6.3	16.6	1.6	< LOD	< LOD	0.38	< LOD
JDS 57	*488*	0.27	21.1	4.4	85.4	4.2	10.3	9.8	0.74	< LOD	< LOD	< LOD	< LOD
JDS 58	*432*	1.0	97.1	12.1	304	93.0	28.4	28.9	7.3	< LOD	< LOD	< LOD	< LOD
JDS 59	*429*	0.73	22.9	4.6	107	2.2	10.1	7.0	0.91	< LOD	< LOD	0.27	< LOD
JDS 60	*378*	0.59	25.4	1.4	102	5.2	10.6	8.1	0.74	< LOD	< LOD	1.18	< LOD
JDS 61	*235*	0.09	18.7	5.2	123	8.4	11.3	8.7	0.47	< LOD	< LOD	< LOD	< LOD
JDS 62	*167*	0.08	22.4	4.2	122	3.0	9.8	4.8	0.64	< LOD	< LOD	0.27	< LOD
JDS 63	*154*	0.15	21.2	6.6	96.0	4.7	9.5	8.3	0.29	< LOD	< LOD	< LOD	< LOD
JDS 63a	*134*	0.19	24.4	6.0	103	3.4	10.8	8.4	0.41	< LOD	< LOD	< LOD	< LOD
JDS 64	*135*	0.22	7.4	11.0	34.9	8.9	2.8	10.0	0.55	< LOD	< LOD	0.68	< LOD
JDS 65	*130*	< LOD	6.8	5.9	294	6.0	9.8	9.4	< LOD	< LOD	< LOD	< LOD	< LOD
JDS 66	*18*	0.13	27.3	6.8	78.6	5.3	8.8	8.1	3.8	< LOD	< LOD	< LOD	< LOD
JDS 67	*26*	0.079	27.0	8.2	120	10.2	15.0	21.3	1.7	< LOD	< LOD	< LOD	< LOD
JDS 68	*107*	0.10	19	4.6	54	2.4	6.0	5.4	0.31	< LOD	< LOD	0.083	< LOD
LOD	*ng/L*	0.21	0.15	0.091	1.3	1.5	0.85	0.29	0.16	0.24	1.0	0.084	12

ST n.d. means that the surrogate standard got lost and no quantification was possible