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Omanalys av flamskyddsmedel i svenska vattendrag

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Sammanfattning

Syftet med den här studien var att få en ögonblicksbild av halterna av flamskyddsmedel i svenska vattendrag. Provtagningen ägde rum i oktober 2013, och resultaten från den provtagningen har rapporterats tidigare (Ahrens et al. 2014). Analysmetodiken har sedan dess förbättrats och det beslutades därför att provextrakten från den tidigare studien skulle analyseras på nytt. Resultaten från omanalysen presenteras i denna rapport.

Totalt analyserades 61 flamskyddmedel i denna studie. Det högsta antalet ämnen detekterades i Nyköpingsån (22) och Indalsälven (16). De mest frekvent förekommande ämnena var ∑TDCIPP/TEHP (kvantifierade som en totalhalt tillsammans) som detekterades i alla 25 proverna från norr till söder, följt av TCEP (detekterad i 15 prover) och TBBPA (detekterad i 11 prover). Högst sammanlagd koncentration av flamskyddsmedel uppmättes i Nyköpingsån (240 ng L^{-1}), Fyrisån (230 ng L^{-1}) och Indalsälven (140 ng L^{-1}). Generellt var koncentrationerna av flamskyddsmedel högre i södra Sverige än i norra vilket sannolikt kan förklaras av den högre populationstätheten i söder. Den dagliga tillförseln av flamskyddsmedel från vattendragen till Östersjön uppskattades. Indalsälven och Nyköpingsån uppvisade de högsta värdena med 5,2 och 4,9 kg/dag. Båda dessa vattendrag hade en likartad fördelning av flamskyddsmedel med TEBP-Anh (~30% av ΣFRs), TCBPA (~23% av ΣFRs) och TBBPA (~30% av ΣFRs) som dominerande ämnen. Detta indikerar att det främst är dessa tre flamskyddsmedel som transporteras till Östersjön via svenska vattendrag.

Eftersom denna studie ger en ögonblicksbild av mängden flamskyddsmedel i svenska vattendrag måste resultaten tolkas med försiktighet. Denna typ av studie är dock användbar för att få en generell uppfattning om föroreningsnivåer och för att upptäcka platser med förhöjd förorening, s.k. hot-spots. För att få en bättre insikt i föroreningssituationen krävs ytterligare studier med en annan provtagningsstrategi, t.ex. provtagning under längre tidsperioder (och under olika årstider) och mer frekvent provtagning alternativt tids- /flödesproportionell provtagning.

Re-analysis of organic flame retardants in Swedish rivers

Omanalys av flamskyddsmedel i svenska vattendrag

Jakob Gustavsson, Erik Ribéli, Karin Wiberg, Minh Anh Nguyen, Sarah Josefsson, Lutz Ahrens

Rapport till Naturvårdsverket
Överenskommelse NV-2213-15-018

Uppsala, 2016-05-13

Summary

Flame retardants (FRs) are used in everyday products such as furniture and electronics to provide fire protection. The intensive use of FRs has led to their wide spread in the environment. Many chemicals have been found to have bioaccumulative, persistent and toxic properties which have led to a ban of some of these FR compounds based on international agreements. For example, Penta- and octa-polybrominated diphenyl ethers (BDEs) have been included in the Stockholm Convention. However, most FRs are not restricted, and in many cases it is not known to which extent they are used or to which degree they are polluting the environment. The aim of this study was to provide a snapshot of the current FR pollution in Swedish rivers and streams. In total, 25 rivers and streams were sampled along the east coast of Sweden from north to south. The sampling was done in October 2013 and results from this pre-study were presented previously (Ahrens et al. 2014). Since then, the analytical method for FRs has been improved, and here we report on the re-analysis of the extracts from the previous study.

In total 61 (including 7 PBDEs, 35 AFRs, 19 OPFRs), mainly novel FRs, were included in the analytical method. The highest number of FRs was detected in Nyköpingsån (22) and Indalsälven (16). The most frequently detected FRs were ∑tris(1,3-dichloroisopropyl) phosphate/tris(2-ethylhexyl) phosphate) (ΣTDCIPP/TEHP, quantified as the sum of both) detected in all 25 samples from north to south, followed by tris(2-chloroethyl) phosphate (TCEP) (detected in 15 samples) and tetrabromobisphenol-A (TBBPA) (detected in 11 samples). The highest FR concentrations were observed in Nyköpingsån, Fyrisån and Indalsälven with ∑FR concentrations of 240, 230 and 140 ng L^{-1}, respectively. It is evident that FR concentrations in general are higher in the south than in the north, likely explained by the higher population density in the south. Daily loads of ∑FRs transported from Swedish rivers into the Baltic Sea were estimated to be in total 15 kg/day. Indalsälven and Nyköpingsån showed highest total daily loads with 5.2 and 4.9 kg/day, respectively. The composition profiles of these two rivers showed a similar pattern with 3,4,5,6-Tetrabromophthalic anhydride (TEBP-Anh, ~30% of the ∑FR), Tetrachlorobisphenol-A (TCBPA, ~23% of the ∑FR) and TBBPA (~30% of the ∑FR) as the major FRs indicating that these are the three main FRs transported into the Baltic Sea from Swedish rivers.

Since this study only provides a snapshot of current conditions, care needs to be taken in the interpretation of the results. This type of screening study is, however, useful for getting a general idea on pollution levels and revealing of tentative hot spots. For better insight into the pollution situation, another sampling strategy is neded, e.g. covering longer time periods (and different seasons) and using more frequent sampling or time/flow-proportional sampling.

Sammanfattning

Flamskyddsmedel används i många produkter och varor, som t.ex. möbler och elektronik, för att förebygga bränder. Den omfattande användandningen har lett till att flamskyddsmedel numera är vitt spridda i miljön. Många kemikalier har konstaterats vara bioackumulativa, svårnedbrytbara och giftiga vilket har lett till att vissa har förbjudits för användning genom internationella avtal, t.ex. ingår penta- och okta-bromerade difenyletrar (BDE) numera i Stockholmskonventionen. Dock är det många kemikalier som inte regleras på detta sätt, och i många fall vet man inte hur mycket de används och därmed inte heller hur mycket som hamnar i miljön. Syftet med den här studien var att få en ögonblicksbild av halterna av flamskyddsmedel i svenska vattendrag. Provtagningen ägde rum i oktober 2013, och resultaten från den provtagningen har rapporterats tidigare (Ahrens et al. 2014). Analysmetodiken har sedan dess förbättrats och det beslutades därför att provextrakten från den tidigare studien skulle analyseras på nytt. Resultaten från omanalysen presenteras i denna rapport.

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1. Introduction

Flame retardants are industrially produced chemical compounds added to a variety of everyday life products to provide fire protection, such as furniture, building insulation, electronics and textiles (Barber et al. 2012). FRs can be either additive or reactive. Additive FRs are those added to the material it aims to protect after polymerization, while reactive FRs are included in the polymerization of the material and hence are chemically bond to the material. Reactive FRs are less likely than additive FRs to leach from the material due to chemical bonding (Schlabach et al. 2011, Barber et al. 2012). Nowadays, the most frequently used FRs are halogenated and phosphorous FRs (Bergman et al. 2012).

Many FRs are causing concerns with aspect on their impact on the environment due to their persistence, toxicity, and potential to bioaccumulate. Polybrominated diphenyl ethers (PBDEs) have been extensively used as additive FRs in the past with peak production and usage in the 1960s and 1970s. The technical products Penta- and OctaBDE are included in the Stockholm Convention, meaning that they are no longer allowed to be used globally (Boon et al. 2002, Schlabach et al. 2011). The third existing BDE commercial mixture, DecaBDE, have been proposed for listing under the Stockholm Convention (URL1). This restriction of historically used FRs have led to the development of new types of FRs, many having similar properties as the restricted ones, and therefore they may pose a risk for both environmental and human health (Bergman et al. 2012, Stapleton et al. 2012). On the other hand, it has been shown that incorporation of FRs in flammable materials has led to significantly reduced incidents of fire- and smoke-related fatalities (Birnbaum et al. 2004, Reiner et al. 2009).

In this report, the FRs are divided into three different groups: PBDEs, alternative FRs (AFRs), and organophosphorous FRs (OPFRs). PBDEs consist of two phenyl rings linked together by an oxygen atom. There are 209 possible congeners differing between each other in the degree of bromination (number of substituted bromine atoms) and in the substitution pattern (Birnbaum et al. 2006). Among the AFRs many have a similar structure as the PBDEs, containing one or two phenyl rings with one or more hydrogens substituted with bromine. However, differently structured AFRs exist as well, e.g., hexabromocyclododecane (HBCDD) and dibromoethyl-dibromocyclohexane (DBE-DBCH) (Birnbaum et al. 2006, Bergman et al. 2012). Organophosphorous FRs (OPFRs) contain a phosphate group covalently bound to different functional groups (e.g. ethyl in triethyl phosphate, TEP, and phenyl in triphenyl phosphate, TPHP). Some OPFRs also contain functional groups that are halogenated (e.g. 2-chloropropyl in tris(2-chloropropyl) phosphate, T2CPP).

The aim of the current project was to investigate the presence of a selected number of 61 FRs in Swedish rivers and streams. The sampling was performed in October 2013 by the POPs laboratory at the Department of Aquatic Sciences and Assessment (IVM) at the Swedish University of Agricultural Sciences (SLU), Uppsala. The results have been published in a a NV-report in 2014 (Ahrens et al. 2014). Since then, the POPs laboratory has improved their method for analyzing FRs, primarily through an upgraded analytical instrument, inclusion of a clean-up step for the sample extracts and adding ~50 additional FRs to the instrumental method. In this study, the extracts from the previous study were re-analyzed for selected novel organic FRs (*n*=61). FR concentrations were reported in surface water from 25 Swedish rivers and streams and loadings into the recipient Baltic Sea were estimated.

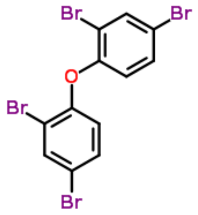
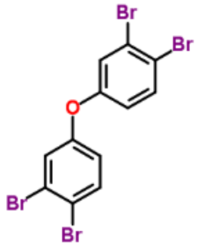
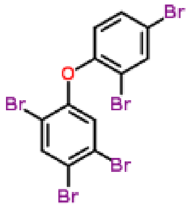
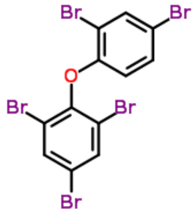
2. Materials and methods

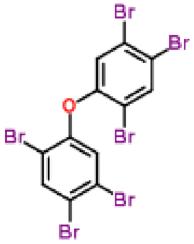
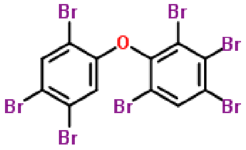
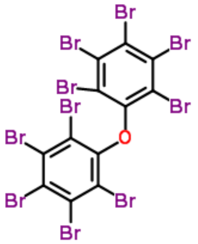
2.1 Chemicals

The target FRs (*n*=61) included BDE47, BDE77, BDE99, BDE100, BDE153, BDE183, BDE209, ATE, BATE, BEH-TBP, BTBPE, α-DBE-DBCH, β-DBE-DBCH, EH-TBB, HBB, *α*-HBCDD, β-HBCDD, γ-HBCDD, OBTMPI, PBT, TBBPA, α-TBCO, β-TBCO, TBX, a-DP, s-DP, TBCT, *o*-TCP, *m*-TCP, and *p*-TCP (purchased from Wellington laboratories, Ontario, Canada), 2,4,6-TBP, 2,4-DBP, 2,6-DBP, DBNPG, PBB-Acr, PBBBr, PBEB, PBP, PBPAE, TBNPA, TEBP-Anh, TCBPA, EHDPP, TBOEP, TCEP, TCIPP, TDCIPP, TEHP, TNBP, TPHP, TPP, TBPP (Sigma-Aldrich, Saint Louis, MO, USA), DBS (Mdpi, Basel, Switzerland), PBCH and TTBNPP (BOC Sciences, Shirley, NY, USA), and V6, TPeP, TiPPP, T2CPP, T3CPP and RDP (Accustandard, New Haven, CT, USA). The samples were spiked with the isotopically labelled internal standard (IS) BDE28, BDE99 and BDE153. This was done in order to be able to identify and correct for potential losses during sample processing. An injection standard (InjS) Mirex was added to all samples prior to analysis. The ISs and Mirex were purchased from Wellington laboratories, Ontario, Canada. Petroleum ether and alumina (active neutral 90), both used for clean-up, were purchased from Merck KGaA, Darmstadt, Germany. CAS-numbers, systematic names, structures and molecular formulas are shown in Table 1 (PBDEs), Table 2 (AFRs) and Table 3 (OPFRs).

The FRs analyzed in this study cover a wide range of physicochemical properties with for example log octanol-water partition coefficient (K_{OW}=$C_{\text{octanol}}/C_{\text{water}}$)-values ranging from 1.06 (DBNPG) up to 13.0 (OBTMPI). However, the majority of FRs (61%) have log K_{OW}-values between 4 and 8. The OPFRs are in general more water soluble with lower log K_{OW}-values, ranging from 1.4 to 10.4 with 58% of them between log K_{OW} 2 and 6. Physicochemical properties including molecular weights, log K_{OW}, log organic carbon-water partition coefficients (K_{OC}), vapor pressures (V_P), and acid dissociation constants (pK_a) are compiled in Table 1 (PBDEs), Table 2 (AFRs) and Table 3 (OPFRs).

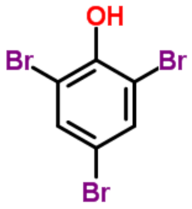
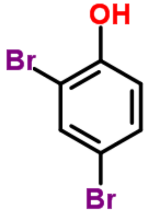
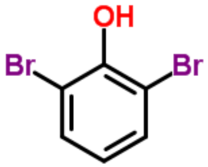
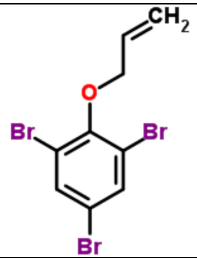
Table 1 Structure, CAS no. and physicochemical properties of PBDEs analysed in this project[a]

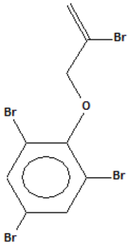
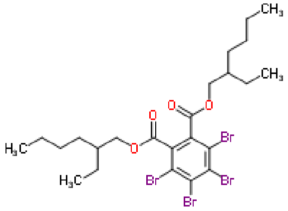
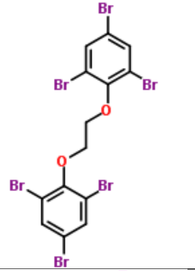
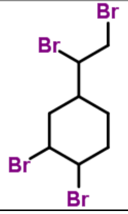
Abbreviation	**Name**	**Structure**	**Molecular formula**	**CAS no.**	**MW**	**log K_{OW}**	**log K_{OC}**	**V_P (Pa)**	**pK_a**
BDE47	2,2',4,4'-Tetrabromodiphenyl ether		C12H6Br4O	5436-43-1	485.8	6.77	4.73	3.21E-05	na
BDE77	3,3',4,4'-Tetrabromodiphenyl ether		C12H6Br4O	93703-48-1	485.8	7.61	5.19	3.21E-05	na
BDE99	2,2',4,4',5-Pentabromodiphenyl ether		C12H5Br5O	32534-81-9	564.7	6.84[b]	4.76	1.44E-04	na
BDE100	2,2',4,4',6-Pentabromodiphenyl ether		C12H5Br5O	189084-64-8	564.7	7.66	5.22	3.25E-06	na

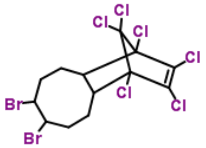
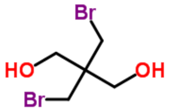
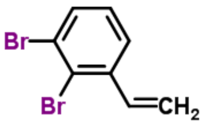
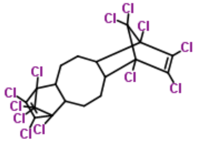
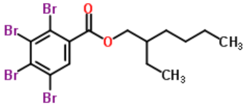
BDE153	2,2',4,4',5,5'-Hexabromodiphenyl ether		$C_{12}H_4Br_6O$	68631-49-2	643.6	8.55	5.71	3.83E-07	na
BDE183	2,2',3,4,4',5',6-Heptabromodiphenyl ether		$C_{12}H_3Br_7O$	207122-16-5	722.5	9.44	6.20	4.39E-08	na
BDE209	Decabromo diphenyl ether		$C_{12}Br_{10}O$	109945-70-2	959.2	12.11	7.68	6.23E-10	na

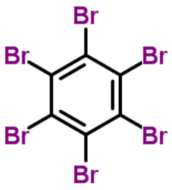
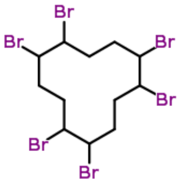
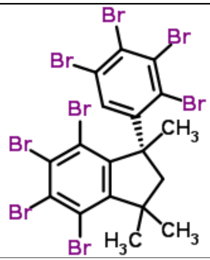
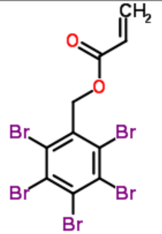
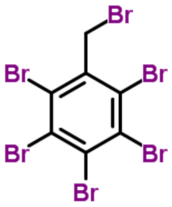
[a]MW = molecular weight; K_{OW} = octanol-water partition coefficient; K_{OC} = organic carbon-water partition coefficient; Vp = vapour pressure. Values modelled with EPI Suite (US EPA) and structures adopted from Chemspider chemical structure database. [b]Indicates experimental value from EPIsuite. Acid dissociation (pKa) values from Bergman et al. (2012). na = not available.

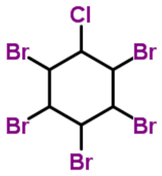
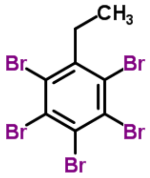
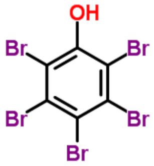
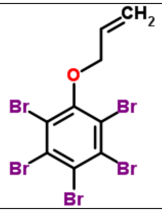
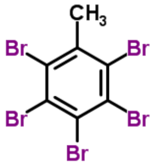
Table 2 Structure, CAS no. and physicochemical properties of AFRs analysed in this project[a]

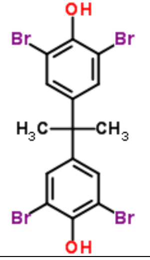
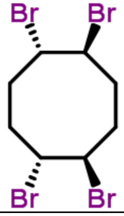
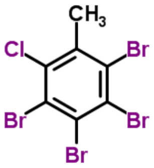
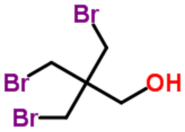
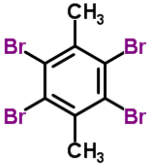
Abbreviation	**Name**	**Structure**	**Molecular formula**	**CAS no.**	**MW**	**log K_{OW}**	**log K_{OC}**	**V_P (Pa)**	**pK_a**
2,4,6-TBP	2,4,6-Tribromophenol		C6H3Br3O	118-79-6	330.8	4.13[b]	3.38	0.0404	6.32 ± 0.23
2,4-DBP	2,4-Dibromophenol		C6H4Br2O	615-58-7	251.9	3.22[b]	2.87	2.14	7.86
2,6-DBP	2,6-Dibromophenol		C6H4Br2O	608-33-3	251.9	3.36[b]	2.95	0.574	na
ATE	Allyl 2,4,6-tribromophenyl ether		C9H7Br3O	221-913-2	370.9	5.59	4.07	0.0135	na

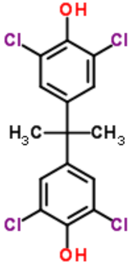
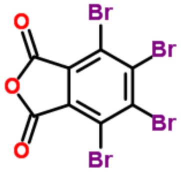
BATE	2-Bromoallyl 2,4,6-tribromophenyl ether		C9H6Br4O	na	449.76	5.98	4.29	9.8E-4	na
BEH-TEBP	Bis(2-ethyl-1-hexyl)tetrabromo-phthalate		C24H34Br4O4	26040-51-7	706.1	11.95	7.40	2.28E-09	na
BTBPE	1,2-Bis(2,4,6-tribromophenoxy) ethane		C14H8Br6O2	37853-59-1	687.6	9.15	6.10	3.17E-08	na
DBE-DBCH	1,2-Dibromo-4-(1,2-dibromoethyl)-cyclohexane		C8H12Br4	3322-93-8	427.8	5.24	4.55	0.014	na

DBHCTD	Hexachlorocyclo-pentadienyl-dibromocyclooctane		C13H12Br2Cl6	51936-55-1	540.8	7.91	6.87	1.42E-05	na
DBNPG	Dibromoneopentyl alcohol		C5H10Br2O2	3296-90-0	261.9	1.06[b]	0.69	8.56E-04	13.57
DBS	Dibromostyrene		C8H6Br2	31780-26-4	261.9	4.68	4.06	2.05	na
DP	Dechlorane Plus		C18H12Cl12	13560-89-9	653.73	11.27	9.78	9.41E-08	na
EH-TBB	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate		C15H18Br4O2	183658-27-7	549.9	8.75	5.70	4.58E-06	na

HBB	Hexabromobenzene		C6Br6	87-82-1	551.5	6.07[b]	5.27	2.24E-06	na
HBCDD	Hexabromocyclo-dodecane		C12H18Br6	3194-55-6	641.7	7.74	6.72	2.25E-06	na
OBTMPI	4,5,6,7-Tetrabromo-1,1,3-trimethyl-3-(2,3,4,5-tetrabromophenyl)-indane		C18H12Br8	1084889-51-9	867.5	13.03	11.31	2.05E-10	na
PBB-Acr	Pentabromobenzyl acrylate		C10H5Br5O2	59447-55-1	556.7	6.89	4.67	1.76E-05	na
PBBBr	Pentabromobenzyl-bromide		C7H2Br6	38521-51-6	565.5	7.33	6.36	8.45E-05	na

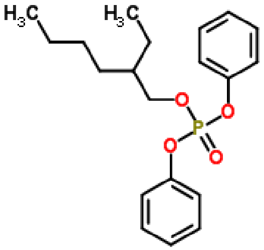
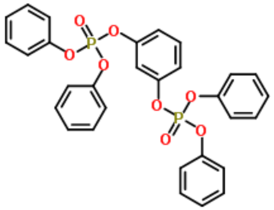
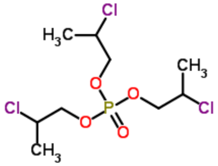
PBCH	Pentabromochloro-cyclohexane		C6H6Br5Cl	87-84-3	513.1	4.72[b]	4.10	4.61E-04	na
PBEB	Pentabromoethyl-benzene		C8H5Br5	85-22-3	500.6	7.48	6.49	6.2E-04	na
PBP	Pentabromophenol		C6HBr5O	608-71-9	488.6	5.96	4.39	6.77E-06	4.43 ± 0.33
PBPAE	Pentabromophenyl allyl ether		C9H5Br5O	604782	528.7	7.37	5.06	1.15E-04	na
PBT	Pentabromotoluene		C7H3Br5	87-83-2	486.6	6.99	6.07	1.95E-05	na

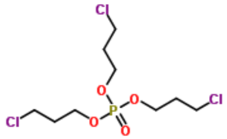
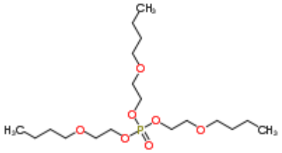
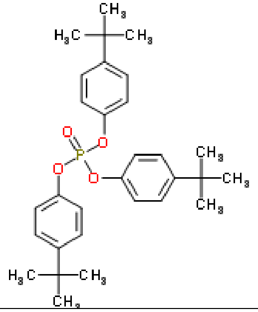
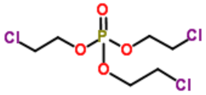
TBBPA	Tetrabromo-bisphenol A		C15H12Br4O2	79-94-7	543.9	6.25	5.42	9.05E-07	7.5/8.5 ± 0.10
TBCO	(1R,2R,5S,6S)-1,2,5,6-Tetrabromocyclo-octane		C8H12Br4	3194-57-8	427.8	5.24	4.55	9.43E-03	na
TBCT	1,2,3,4-Tetrabromo-5-chloro-6-methylbenzene		C7H3Br4Cl	39569-21-6	442.2	6.74	5.85	3.72E-03	na
TBNPA	Tribromoneopentyl alcohol		C5H9Br3O	1522-92-5	324.8	2.25	1.76	5.56E-03	13.73
TBX	2,3,5,6-tetrabromo-p-xylene		C8H6Br4	23488-38-2	421.8	6.65	5.77	5.52E-03	na

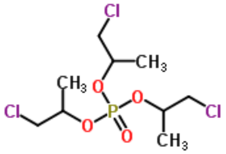
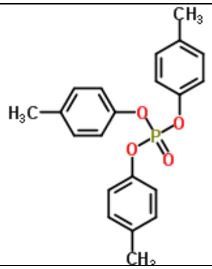
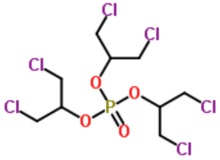
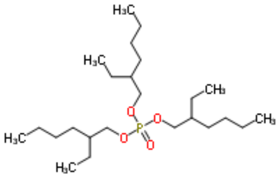
TCBPA	Tetrachloro-bisphenol A		C15H12Cl4O2	27360-90-3	366.1	6.22	4.84	3.84E-07	na
TEBP-Anh	3,4,5,6-Tetrabromophthalic anhydride		C8Br4O3	632-79-1	463.7	5.63	3.58	2.71E-06	na

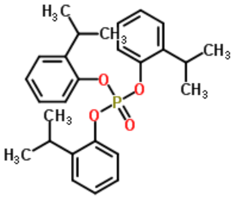
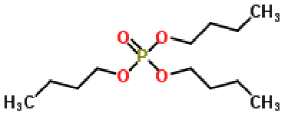
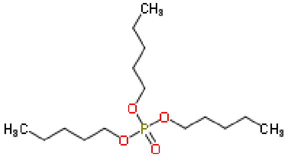
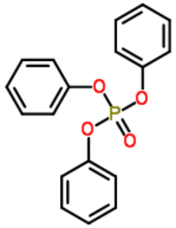
[a]MW = molecular weight; K_{OW} = octanol-water partition coefficient; K_{OC} = organic carbon-water partition coefficient; Vp = vapour pressure. Values modelled with EPI Suite (US EPA) and structures adopted from Chemspider chemical structure database except for BATE, which was drawn manually in EPIsuite. [b]Indicates experimental value from EPIsuite. Acid dissociation (pKa) values from Bergman et al. 2012. na = not available.

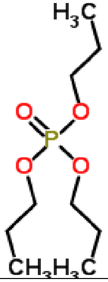
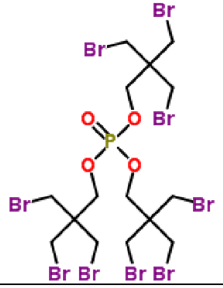
Table 3 Structure, CAS no. and physicochemical properties of OPFRs analysed in this project[a]

Abbreviation	Name	Structure	Molecular formula	CAS no.	MW	log K_{OW}	log K_{OC}	V_P (Pa)	pK_a
EHDPP	2-Ethylhexyl diphenyl phosphate		C20H27O4P	1241-94-7	362.4	5.73[b]	3.87	4.45E-03	na
RDP	Resorcinol bis(diphenyl phosphate)		C30H24O8P2	57583-54-7	574.47	7.41	4.80	2.74E-06	na
T2CPP	tris(2-Chloropropyl) phosphate		C9H18Cl3O4P	6145-73-9	327.57	2.89	2.63	7.02E-03	na

T3CPP	Tri(3-chloropropyl) phosphate		C9H18Cl3O4P	26248-87-3	327.57	3.11	2.75	6.38E-04	na
TBOEP	Tri(2-butoxyethyl) phosphate		C18H39O7P	78-51-3	398.5	3.75^b	2.83	1.65E-04	na
TBPP	Tris(4-tert-butylphenyl) phosphate		C30H39O4P	78-33-1	494.6	10.43	6.47	2.74E-06	na
TCEP	Tris(2-chloroethyl) phosphate		C6H12Cl3O4P	115-96-8	285.5	1.44^b	1.83	5.22E-02	na

TCIPP	Tri(1-chloro-2-propyl) phosphate		C9H18Cl3O4P	13674-84-5	327.6	2.59[b]	2.46	7.53E-03	na
TCP	Tritolyl phosphate		C21H21O4P	1330-78-5	368.4	6.34	4.21	4.65E-06	na
TDCIPP	Tris(1,3-dichloroisopropyl) phosphate		C9H15Cl6O4P	13674-87-8	430.9	3.65[b]	3.05	3.82E-05	na
TEHP	Tris(2-ethylhexyl) phosphate		C24H51O4P	78-42-2	434.6	9.49	6.28	8.09E-05	na

TiPPP	Tri(2-Isopropylphenyl) phosphate		C27H33O4P	64532-95-2	452.54	9.07	5.72	2.74E-06	na
TNBP	Tributyl phosphate		C12H27O4P	126-73-8	266.3	4[b]	3.24	0.466	na
TPeP	Tripentyl phosphate		C15H33O4P	2528-38-3	308.4	5.29	3.96	2.23E-03	na
TPHP	Triphenyl phosphate		C18H15O4P	115-86-6	326.3	4.59[b]	3.24	4.72E-07	na

TPP	Tripropyl phosphate		C9H21O4P	513-08-6	224.2	1.87[b]	2.06	3.08	na
TTBNPP	Tris(tribromo-neopentyl) phosphate		C15H24Br9O4P	19186-97-1	1020	8.05	5.48	2.74E-06	na

[a] MW = molecular weight; K_{OW} = octanol-water partition coefficient; K_{OC} = organic carbon-water partition coefficient; Vp = vapour pressure; pKa = acid dissociation coefficient. Values modelled with EPI Suite (US EPA) and structures adopted from Chemspider chemical structure database. [b] Indicates experimental value from EPIsuite. pKa-values from Bergman et al., (2012). na = not available.

2.2 Sampling sites

Different water bodies were included covering both small and large streams as well as streams in both remote and urban areas (for details see Ahrens et al. (2014)). A map with the selected sampling sites is shown in Figure 1.

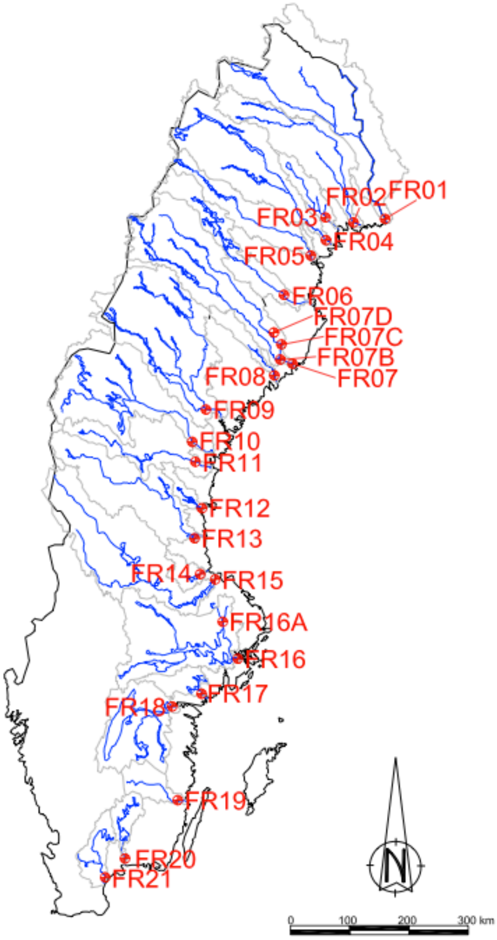


Figure 1 Sampling sites for FRs. Rivers are displayed in blue, watersheds in grey. Figure adopted from previous report (Ahrens et al. 2014).

2.3 Sample collection

Grab water samples were collected from the middle of the streams, standing on bridges using a stainless steel bucket connected to a polypropylene rope. Sample containers (12 L, stainless steel) and all other metal sampling equipment were subsequently pre-cleaned with ethanol, Millipore water and acetone. In addition to sampling for FR analysis, samples for determination of total organic carbon (TOC) and suspended particulate matter (SPM) were collected as well. Water temperature and pH were measured in the field after each sampling. The sampling was conducted October 1-9 and October 25 (Fyrisån) 2013. Details about the sampling are given in Table A1 in the Appendix. All extractions were performed within one month after the sampling (for details see Ahrens et al. 2014)).

2.4 Extraction of FRs

Water samples were extracted using solid-phase extraction (SPE) by passing the water through glass columns packed with the sorbent Amberlite XAD-2, glass wool and glass beads (used to keep the sorbent in place). All samples were spiked with 8 ng IS directly into the sample containers before being extracted. Figure 2 shows a schematic of the extraction set up. After extraction, the columns were dried with an N_2-gas flow and eluted with dichloromethane (DCM). Further treatment of the extract included volume reduction and removal of water residues with sodium sulfate (for details see Ahrens et al. (2014)).

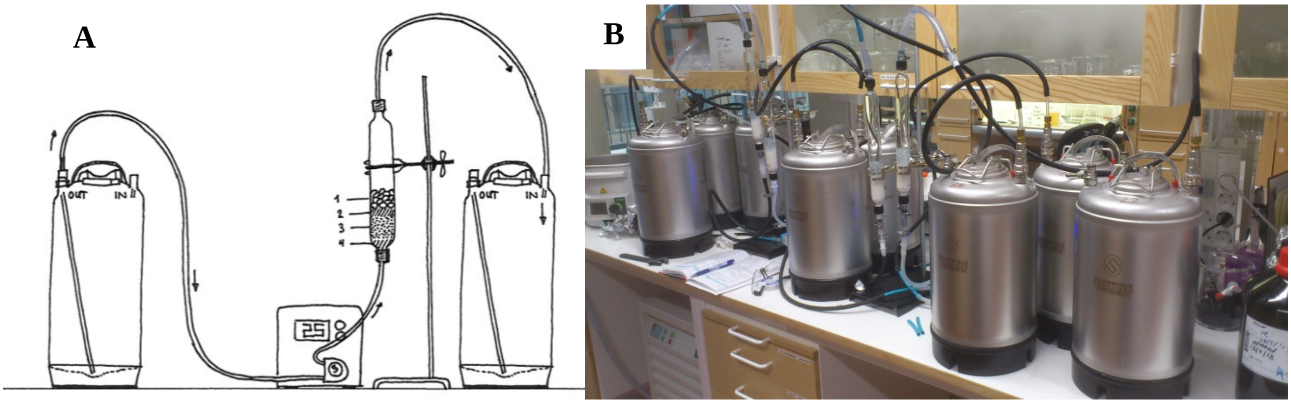


Figure 2 A) Schematic of the extraction set up for the FRs. 1: glass beads; 2 and 4: glass wool; 3: XAD-2. **B)** Photograph of the SPE set up with four extractions running in parallel. Figure adopted from previous report (Ahrens et al. 2014).

2.5 Clean-up

In the previous study, no clean-up step was included (Ahrens et al. 2014). Due to a larger number of target analytes in this study, it was necessary to clean the samples to reduce the background noise during instrumental analysis. Extracts were split in two equal parts and clean-up was conducted on one of the parts (the other part saved for potential future usage). For the clean-up, 1 g activated alumina (deactivation 6%) was packed in glass columns. Conditioning and elution were both done with 20 mL petroleum ether/DCM (95/5, v/v), respectively. Solvent was exchanged to toluene and reduced to 0.5 mL. Before analysis, the injection standard (Mirex, 5 ng) was added, and the samples were stored at -20 °C until instrumental analysis.

2.6 Instrumental analysis and quantification

The analysed FRs listed in Table 1 (PBDEs), Table 2 (AFRs), and Table 3 (PBDEs) were analysed using gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) according to in-house methods (IVM, SLU). The calibration curve was set up for in total 61 FR using calibration solutions at concentrations between 0.5 and 2100 ng mL^{-1} depending on the instrumental detection limits of the different FRs. All FRs were quantified by the isotope dilution method.

Quantification was performed using the isotope dilution method and the software QQQ MassHunter from Agilent. For a peak to be classified as a positive identification, retention time agreement within $\pm$ 0.5 min of the reference compound in the calibration solution was demanded, the signal to noise (S/N) ratio had to be ≥ 3, and the quantifier/qualifier ratio had to be within ± 20% of the ratio in the calibration standard.

The method detection limit (MDL) and method quantification limit (MQL) were calculated using two field blanks. If a compound was not detected in the blanks, then the instrumental detection limit (IDL) was used (determined from spiked river extracts). If a compound was not detected in the blanks and no IDL was available, then the lowest calibration point was used as the detection limit. MDLs and MQLs were calculated from field blank concentrations using eq. 1:

$$MDL = mean_{blanks} + 3 * SD_{blanks} \qquad (1)$$

where $mean_{blanks}$ is the mean value of the blanks, and SD_{blanks} is the standard deviation of the blanks. MQL was calculated from the MDL, using eq. 2:

$$MQL = \frac{10 \cdot MDL}{3} \qquad (2)$$

The stability of the FRs during storage was evaluated during a 31 days test. Pure solvent was spiked with native FRs and stored at -20°C. The spiked solvent was prepared 50 days before the first analysis (time 0) and then once per week the following 31 days to check for potential degradation over time.

3. Results and discussion

3.1 Quality assurance and quality control (QA/QC)

The MDLs and MQLs for the FRs are listed in Table 4. Several FRs were occasionally detected in field blanks (e.g. TCBPA, TBOEP, and pTCP) which resulted in higher MDLs for these FRs. Possible contamination sources for FRs are indoor air/particles, dust, and the Millipore water (12 L) used for the field blanks.

Table 4 Blank concentrations, method detection limits (MDLs), and method quantification limits (MQLs) for FRs detected in samples[a]

Compound	Blank (ng, n=5)	MDL (ng L^{-1})	MQL (ng L^{-1})
BDE47	n.d.	0.0059	0.020
BDE77	n.d.-0.18	0.042	0.14
BDE100	n.d.	0.0028	0.0093
BDE99	n.d.	0.0088	0.029
BDE153	n.d.	0.018	0.059
BDE183	n.d.	0.17	0.57
TBX	n.d.	0.010	0.034
TBCT	n.d.	0.077	0.26
PBT	n.d.-0.72	0.088	0.29
TEBP-Anh	n.d.	18	61
HBB	n.d.-0.34	0.038	0.13
TCBPA	n.d.-160	28	92
PBB-Acr	n.d.-1.3	0.23	0.76
TBBPA	n.d.	1.3	4.3
BTBPE	n.d.	0.15	0.49
sDP	n.d.-12	1.8	6.0
aDP	n.d.-29	4.6	15
2,4,6-DBP	n.d.	0.8	2.5
TTBNPP	n.d.-6.0	2.9	9.7
TNBP	n.d.-7.0	3.2	10.8
TCEP	n.d.-4.5	0.68	2.3
ΣT2CPP/T3CPP/TCIPP	n.d.-33	4.6	15
ΣTDCIPP/TEHP	n.d.-0.78	0.082	0.27
TBOEP	n.d.-250	44	150
EHDPP	n.d.-59	5.4	18
oTCP	n.d.-5.0	0.61	2.0
mTCP	n.d.-22	2.5	8.4
pTCP	n.d.-74	8.6	29
TiPPP	n.d.-25	3.5	12
TPHP	120	37	120

[a] n.d. = not detected

The recoveries of the internal standards were low with a high standard deviation (BDE28: 8±9 %, BDE99: 26±33 % and BDE153: 22±30 %). This might be explained by the not optimized sample preparation and long storage time of the sample extracts. Internal standards (dissolved in toluene) were spiked directly into the water sample in the sample container followed by shaking before being extracted. Since the time of this work, the method has been improved by adding a rinsing step of the sample container and tubing with organic solvent to minimize sorption of FRs to surfaces. Losses during sample preparation, storage, and analyses were corrected by isotope dilution quantification method.

The stability of flame retardants during storage in pure solvent was tested over a time period of 31 days. Results for selected PBDEs are shown in Figure 3 while results for AFRs and OPFRs can be found in Figure A1 in the Appendix. Results showed a stable peak area over time with no clear degradation (Figure 3A). When utilizing an internal standard, variation from the instrumental analyses is corrected, resulting in an even more stable peak area over time (Figure 3B).

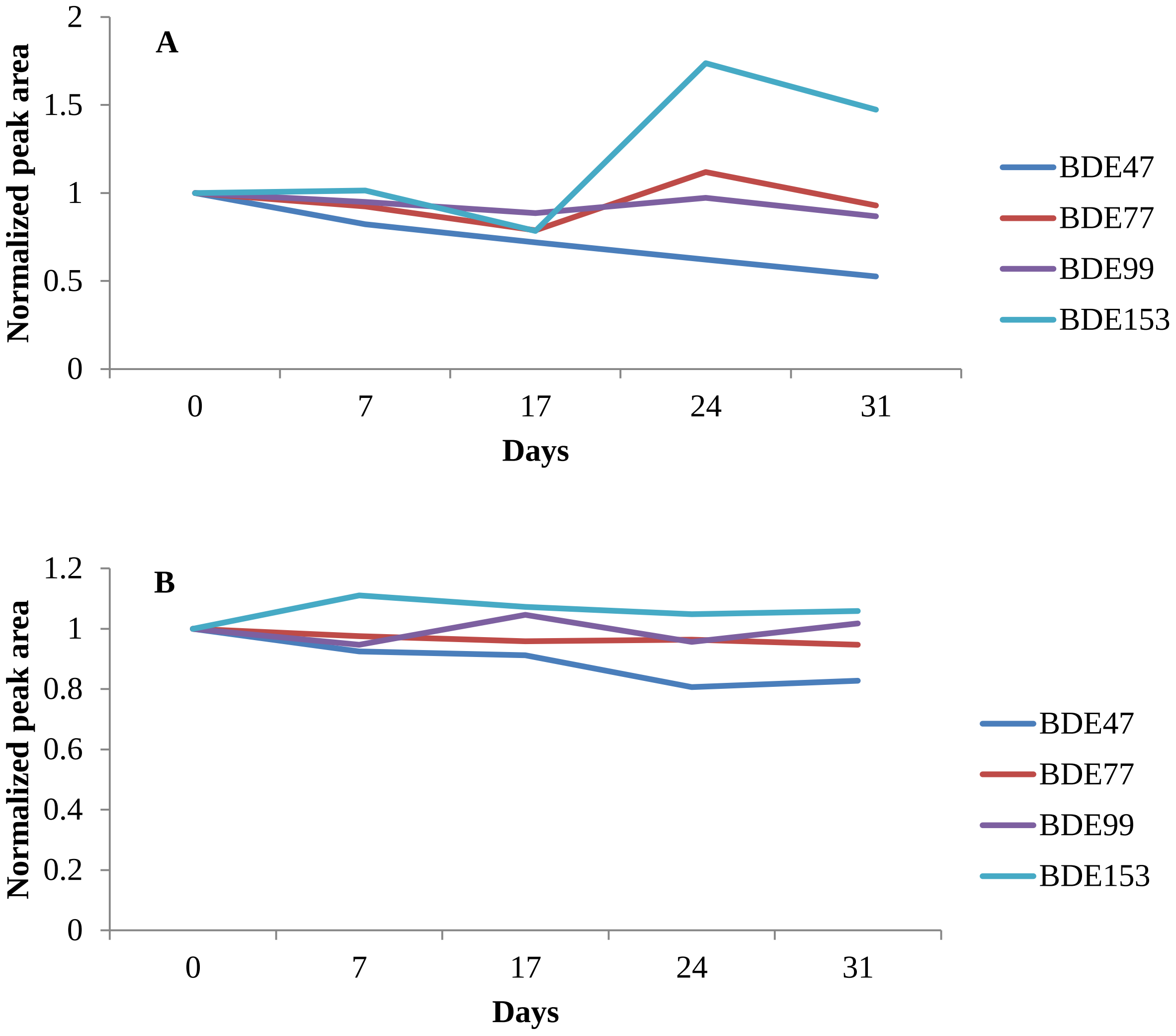


Figure 3 Results from stability test for A) PBDEs (no internal standards correction), and B) PBDEs (including internal standards correction). Peak areas are normalized against peak area from the first measurement (day 0). Results for AFRs and OPFRs are shown in Figure A1 in the Appendix.

3.2 River and stream results

Out of the 61 targeted FRs, 29 were detected in at least one of the samples. 2,4,6-TBP and TPHP both showed chromatographic interferences and retention time shift and could not be quantified in this study. Instead, results from the previous studies were used included in this study. All analysed samples contained at least one FR above the detection limit (Figure 5). The highest number of FRs were detected in Nyköpingsån (22) followed by Indalsälven (16), Skellefteälven (14) and Delångersån (14). In general, a larger number of FRs were detected in the south than in the north, likely explained by the higher population density in the south.

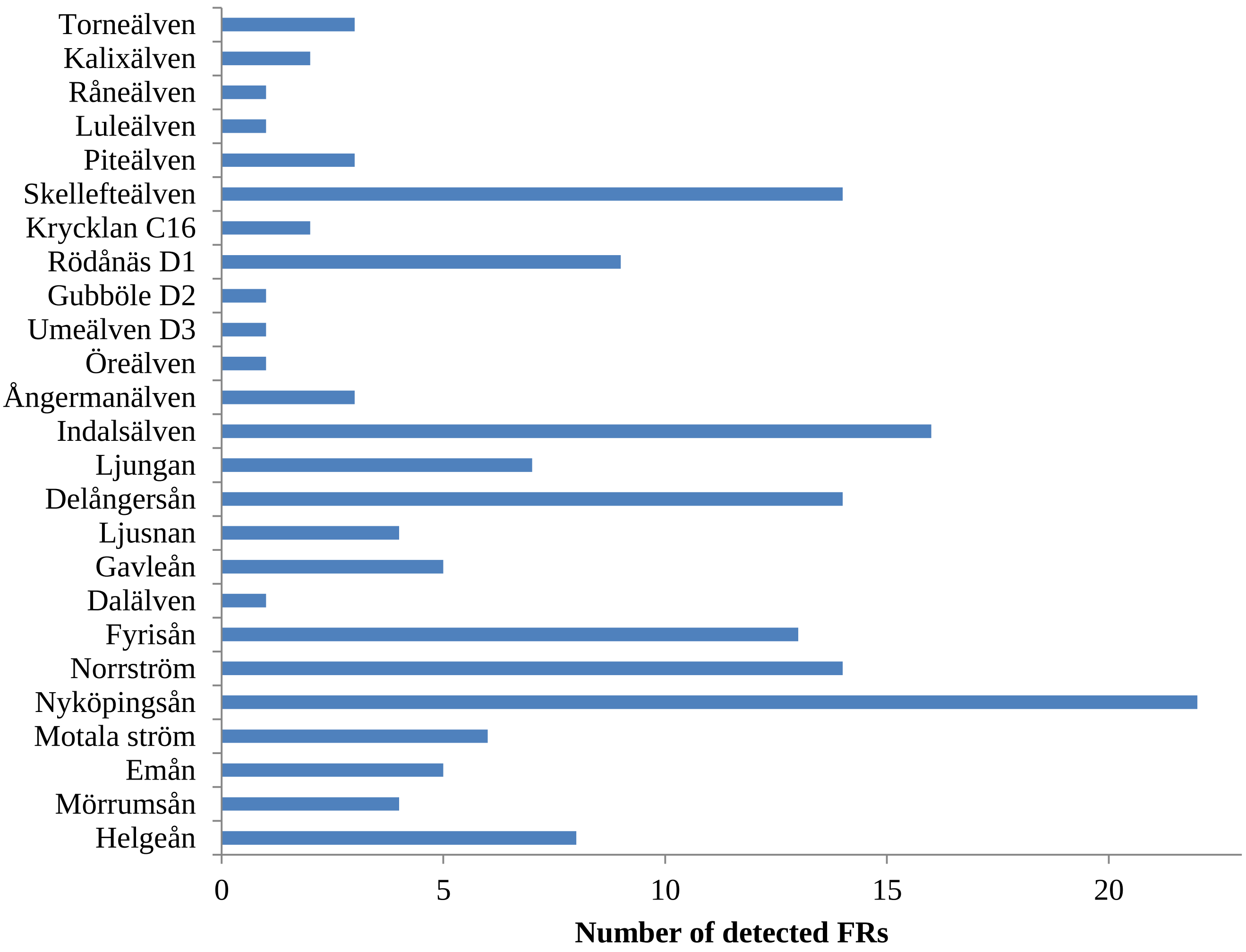


Figure 5 Number of detected FRs in Swedish streams from north to south.

The most frequently detected FR was ∑TDCIPP/TEHP detected in all analysed samples (Figure 6). ∑TDCIPP/TEHP could not be chromatographically separated and were therefore determined as the total sum concentration of the two. ∑TDCIPP/TEHP were detected in all samples, both in urban and more remote areas in northern Sweden. This indicates an extensive use of at least one of them in combination with a potential for long range atmospheric transport (LRAT). The second most frequently detected FR was TCEP, which was detected in samples from all over Sweden, also indicating a potential of LRAT.

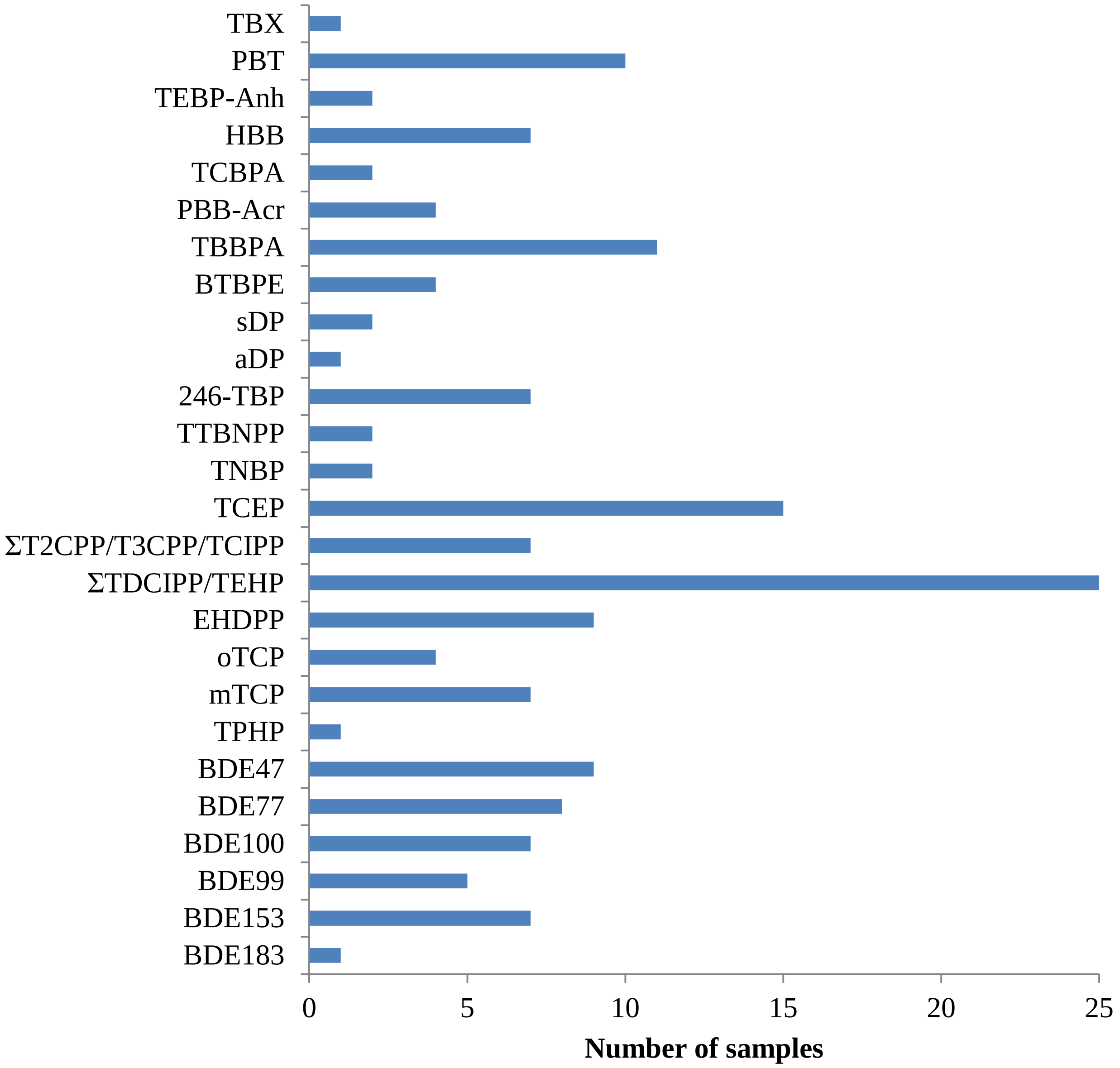


Figure 6 Detection frequency of FRs in Swedish rivers.

The ΣFR concentration in Swedish rivers ranged from 0.1 ng L^{-1} (Råneälven, Luleälven, Gubböle D2 and Dalälven) up to 240 ng L^{-1} (Nyköpingsån) (Tables A2-A4 in the Appendix). The average ΣFR concentration in the rivers was 44 ng L^{-1} (median = 23 ng L^{-1}). In general, ΣFR concentrations were lower in the north (in average 6.4 ng L^{-1}, Torneälven-Ångermanälven) compared to the south (on average 74 ng L^{-1}, Ljungan-Helgeån, Figure 5). Previously, ΣFR concentrations of up to 1000 ng L^{-1} (including 7 PBDEs and 5 AFRs) in water near suspected sources in Norway have been reported (Andersson et al. 2013). In another study, ΣFR concentrations of 590 ng L^{-1} for 4 OPFRs were found in a drinking water treatment plant (Lacorte et al. 2012). In Austrian rivers, ΣFR concentrations of 9 OPFRs have been reported between 140-920 ng L^{-1} (Gans et al. 2007). One possible explanation for the high FR concentration detected in Fyrisån could be that the sample was taken just downstream the Uppsala municipality waste water treatment plant (WWTP). For the sampling site Nyköpingsån, no larger WWTP is located upstream.

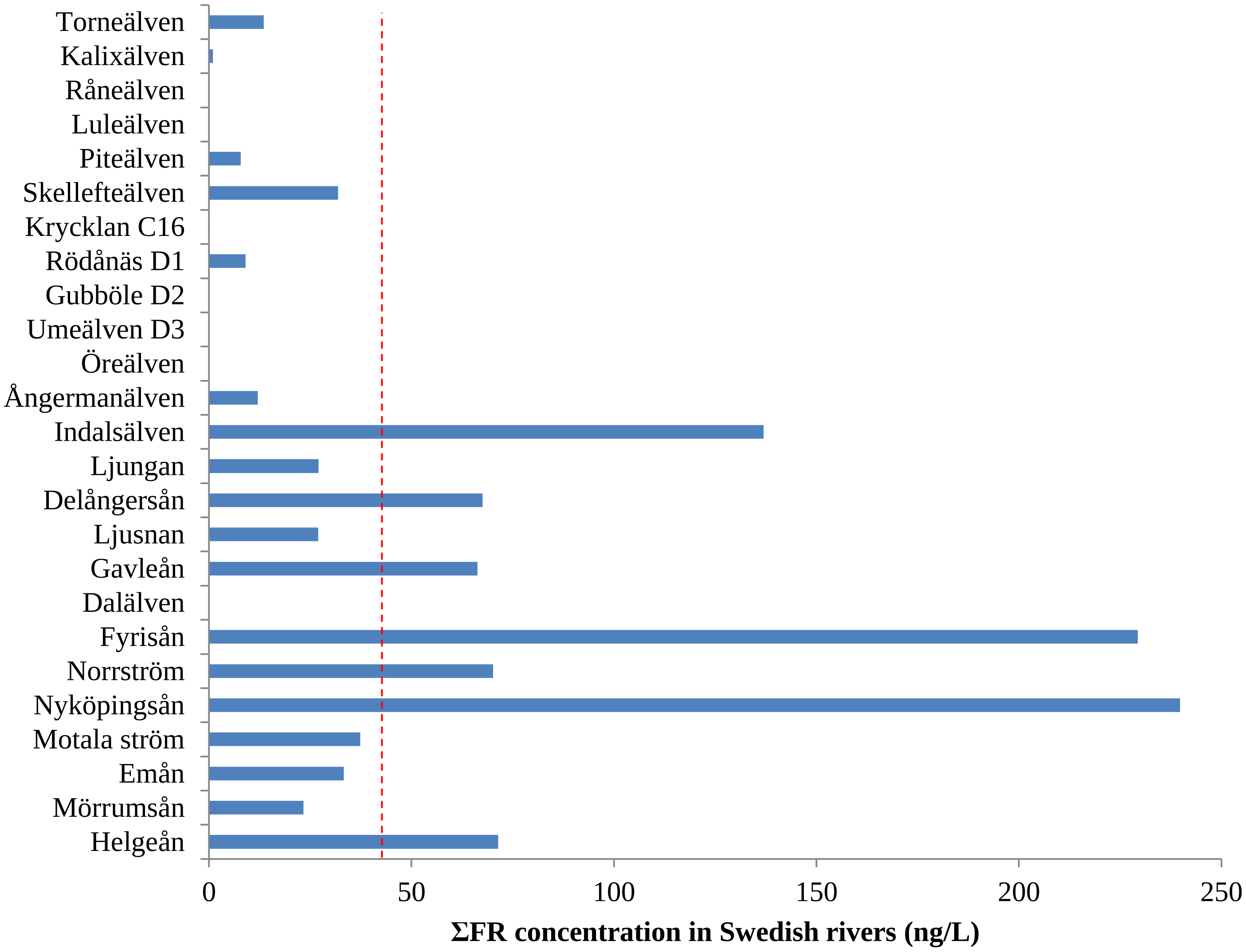


Figure 7 ∑FR concentrations (ng L^{-1}) in Swedish rivers from north to south. The dotted line represents the average concentration of all rivers.

The composition profiles of the detected FRs (above MDL) are shown in Figure 8. Two of the rivers with the highest concentrations, Indalsälven and Nyköpingsån (Figure 5), showed similar profiles with TEBP-Anh, TCBPA and TBBPA as dominant FRs. This similar pattern indicates common dominating source type(s) e.g. industry effluents, airports, or landfills. Composition similarities were also observed for the northern rivers Råneälven, Luleälven, Umeälven, Öreälven and Dalälven with only ∑TDCIPP/TEHP detected, and Torneälven and Piteälven with mainly TCEP and EHDPP detected.

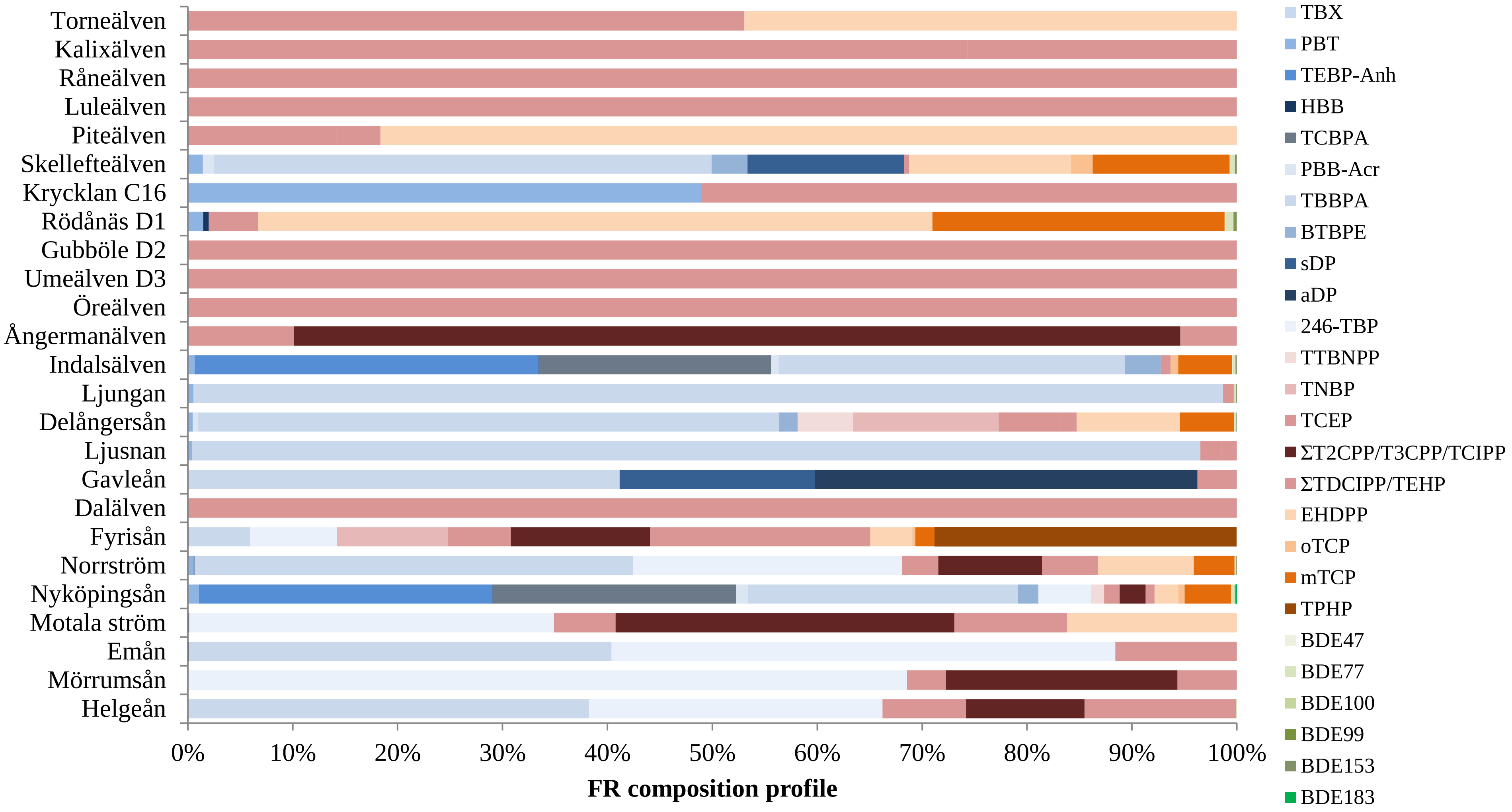


Figure 8 Composition profiles of FRs (above MDL) in the river samples (AFRs are represented with blue colors, OPFRs with red/orange/brown colors, and BPDEs with green colors).

Estimated daily loads of FRs are shown in Figure 9. The daily loads are estimated based on the snapshot concentrations obtained from the analysis of grab samples together with the daily average riverine water discharge (data from 2002 to 2012 obtained from SMHI via Datavärdskapet för sjöar och vattendrag, IVM, SLU). Since only a snapshot picture is obtained through one-time grab sampling, the results have to be interpreted with care and be seen as indicative rather than conclusive. The total riverine input of the targeted FRs into the Baltic Sea was 15 kg/day. The FRs with the highest loads transported to the sea were TBBPA (4.6 kg/day), TEBP-Anh (3.1 kg/day) and TCBPA (2.3 kg/day). This corresponded to 32%, 21%, and 16% of the total FR load, respectively. Indalsälven and Nyköpingsån had the highest daily FR loads compared to the other rivers with ~5 kg/day and river. The legacy FRs (BDEs) contributed only with 0.4 % to the total load of FRs. This study included selected FRs and only Swedish rivers, thus the total load of FRs into the Baltic Sea is underestimated.

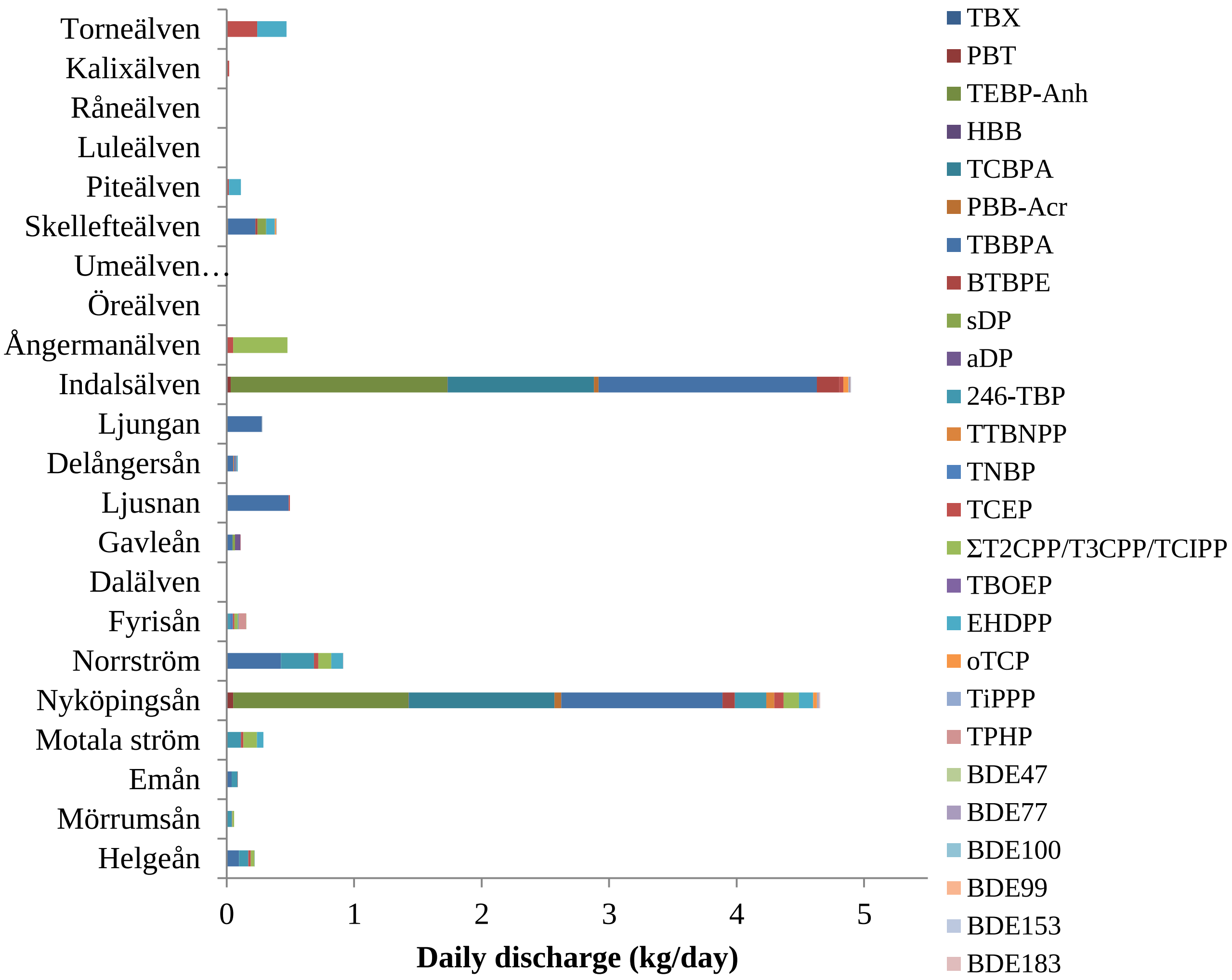


Figure 9 Daily discharges (kg/day) of FRs into the Baltic Sea from Swedish rivers.

3.3 Comparison with the previous study

In the previous study, only three FRs (i.e 2,4,6-TBP, TCIPP and TPHP) were quantified due to a limited number of compounds included in the instrumental method and high detection limits (Ahrens et al. 2014). When the extracts were reanalysed with the updated method, in total 27 FRs were detected above detection limits. One of the compounds (TCIPP) quantified in the previous study was included in this study. The other two (246-TBP and TPHP) both showed poor chromatographyand were therefore not quantified in this studyInstead concentrations determined in the previous study were used. In both studies TCIPP was detected at the highest concentration in Fyrisån. However, the obtained concentration of ΣTCIPP/T2CPP/T3CPP was about 80 times lower in the second analysis than during the first. One important difference between the first and the second study is the inclusion of a clean-up step before the reanalysis. During method development a 46% loss of TCIPP was observed during clean-up using alumina which can partly explain the lower concentration determined in the reanalysis. Other possible explanations could be degradation during the long storage, matrix effects during instrumental analysis, and interferences with coeluting compounds.

4. Conclusions and future perspectives

In this and the previous study (Ahrens et al. 2014) a screening of Swedish rivers and streams was performed with the aim of getting a broad overview of the current status of flame retardant pollution in Swedish rivers and streams.

The highest number of the 61 analysed FRs were detected in Nyköpingsån (22), Indalsälven (16), and Skellefteälven (11). The most frequently detected FRs were ∑TDCIPP/TEHP detected in all 25 samples from north to south, followed by TCEP (detected in 15 samples) and TBBPA (detected in 11 samples). The highest FR concentrations were observed in Nyköpingsån, Fyrisån and Indalsälven with total FR concentrations of 240, 230 and 140 ng L^{-1}, respectively. It is evident that FR concentrations in general were higher in the south than in the north, likely explained by the higher population density in the south. Indalsälven and Nyköpingsån showed the highest total daily loads (5.2 and 4.9 kg/day, respectively) compared to the other rivers . The compositional profiles of these two rivers showed a similar pattern with TEBP-Anh, TCBPA and TBBPA as the dominant FRs and these were also the three main FRs transported into the Baltic Sea from Swedish rivers. Since this study was performed as a screening study and only provides a snapshot picture of current condition care needs to be taken when interpreting the results. Further studies are needed to verify some conclusions, especially regarding hot spots.

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Appendix

Table A1 Sampling details for the sampling sites. The ID numbers correspond to the locations given in Figure 1. Adopted from Ahrens et al., 2014

ID no.	**Site**	**Date**	**Time**	**POP-can no.**	**TOC (mg/L)**	**T (air) (°C)**	**T (water) (°C)**	**pH**	**U (mV)**	**Coordinates (RT90)**	
										X	**Y**
FR01	Torneälven	2013-10-01	10:15	6	4.1	3.0	5.7	7.0	−0.8	7 330 503	1 880 556
FR02	Kalixälven	2013-10-01	11:15	1	5.8	6.0	7.6	7.2	−7.6	7 325 285	1 833 885
FR03	Råneälven	2013-10-01	14:00	5	8.1	5.0	10.2	7.1	−5.5	7 338 361	1 779 226
FR04	Luleälven	2013-10-01	16:30	3	3.1	6.0	9.4	7.3	−16.2	7 290 561	1 786 921
FR05	Piteälven	2013-10-02	09:30	4	4.4	8.0	6.8	6.5	12.3	7 264 163	1 755 232
FR06	Skellefteälven	2013-10-02	12:11	8	3.8	10.0	10.3	7.1	−5.2	7 190 964	1 736 256
FR06	Skellefteälven DUPLICATE	2013-10-02	12:11	9	3.8	10.0	10.3	7.1	−3.4	7 190 964	1 736 256
FR07	Umeälven	2013-10-03	08:02	7	4.7	2.0	7.9	7.9	−3.4	7 087 353	1 718 699
FR07B	Umeälven [Gubböle]	2013-10-02	18:50	15	4.5	8.0	8.2	8.2	−3.4	7 092 989	1 701 914
FR07C	Vindelälven [Rödånäs]	2013-10-02	16:15	11	4.2	11.0	9.1	9.1	−18	7 115 827	1 701 376
FR07D	Vindelälven [Krycklan, 16]	2013-10-02	15:23	14	13.4	11.0	7.2	7.2	−11.8	7 127 639	1 697 343
FR08	Öreälven	2013-10-03	09:30	10	16.3	3.0	8.5	6.4	26.2	7 061 011	1 691 347
FR09	Ångermanälven	2013-10-03	13:55	2	6.5	13.0	9.6	6.7	4.2	7 007 585	1 573 842
FR010	Indalsälven	2013-10-03	16:55	12	5.9	12.0	10.3	7.3	−13.2	6 934 786	1 580 851
FR011	Ljungan	2013-10-09	13:45	25	7.2	12.0	10.7	6.9	−4.2	6 917 403	1 559 911
	Ljungan BLANK	2013-10-09	13:45	30	N/A	12.0	N/A	N/A	N/A	6 917 403	1 559 911
FR012	Delångersån	2013-10-04	11:45	13	6.7	11.0	10.2	6.8	3.2	6 836 677	1 567 893
FR013	Ljusnan	2013-10-09	17:45	26	7.4	13.0	11.6	6.9	1.5	6 789 337	1 568 698
FR014	Gavleån	2013-10-09	19:50	28	11.8	12.0	9.8	6.8	−2.6	6 729 091	1 572 721
FR015	Dalälven	2013-10-09	21:10	29	6.3	10.0	10.3	6.8	8.3	6 717 372	1 589 704
FR016	Norrström	2013-10-06	18:50	22	9.5	12.0	13.1	7.4	−28.0	6 580 773	1 628 741
FR016A	Fyrisån	2013-10-25	11:00	31	10.5	10.0	11.1	7.0	−0.3	6 636 135	1 604 086

ID no.	**Site**	**Date**	**Time**	**POP-can no.**	**TOC (mg/L)**	**T (air) (°C)**	**T (water) (°C)**	**pH**	**U (mV)**	**Coordinates (RT90) X**	**Y**
FR016A	Fyrisån DUPLICATE	2013-10-25	11:00	32	10.4	10.0	11.1	7.0	−0.3	6 636 135	1 604 086
FR017	Nyköpingsån	2013-10-06	17:00	21	13.6	14.0	9.9	7.5	−32.2	6 523 002	1 564 896
FR018	Motala Ström	2013-10-06	15:35	20	8.0	14.0	11.8	7.4	−27.2	6 496 919	1 518 441
	Motala Ström BLANK	2013-10-06	15:35	17	N/A	14.0	N/A	N/A	N/A	6 496 919	1 518 441
FR019	Emån	2013-10-06	12:30	23	11.0	13.0	11.0	7.3	−15.3	6 335 205	1 539 225
FR019	Emån DUPLICATE	2013-10-06	12:30	24	10.8	13.0	11.0	7.3	−15.3	6 335 205	1 539 225
FR020	Mörrumsån	2013-10-06	09:50	19	12.0	13.0	10.6	7.1	−7.2	6 230 020	1 434 417
FR021	Helgeån	2013-10-06	07:20	18	11.2	11.0	11.2	7.6	−32.2	6 202 819	1 400 869
	Helge ån BLANK	2013-10-06	07:20	16	N/A	11.0	N/A	N/A	N/A	6 202 819	1 400 869

Table A2 Levels of detected alternative flame retardants (AFRs) in Swedish rivers (ng L^{-1})[a]

Sample ID	River	TBX	PBT	TEBP-Anh	HBB	TCBPA	PBB-Acr	TBBPA	BTBPE	sDP	aDP	246-TBP
FR01	Torneälven	< 0.010	< 0.088	< 18	< 0.038	< 28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR02	Kalixälven	< 0.010	< 0.088	< 18	< 0.038	< 28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR03	Råneälven	< 0.010	< 0.088	< 18	< 0.038	< 28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR04	Luleälven	< 0.010	< 0.088	< 18	< 0.038	< 28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR05	Piteälven	< 0.010	< 0.088	< 18	< 0.038	< 28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR06	Skellefteälven	< 0.010	0.46	< 18	< 0.038	< 28	(0.34)	15	1.1	(4.8)	< 4.6	< 0.80
FR07D	Krycklan C16	< 0.010	(0.10)	< 18	< 0.038	< 28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR07C	Rödånäs D1	< 0.010	(0.13)	< 18	(0.047)	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR07B	Krycklan Gubböle D2	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR07	Umeälven/Krycklan D3	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR08	Öreälven	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR09	Ångermanälven	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR010	Indalsälven	< 0.010	0.86	(45)	(0.047)	(30)	1.0	45	4.7	< 1.8	< 4.6	< 0.80
FR011	Ljungan	< 0.010	(0.15)	< 18	< 0.038	< 28	< 0.23	27	< 0.15	< 1.8	< 4.6	< 0.80
FR012	Delångersån	< 0.010	0.31	< 18	< 0.038	<28	(0.35)	37	1.2	< 1.8	< 4.6	< 0.80
FR013	Ljusnan	< 0.010	(0.12)	< 18	< 0.038	<28	< 0.23	26	< 0.15	< 1.8	< 4.6	< 0.80
FR014	Gavleån	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	27	< 0.15	12	24	< 0.80
FR015	Dalälven	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	< 0.80
FR016A	Fyrisån	< 0.010	(0.11)	< 18	(0.10)	<28	< 0.23	13	< 0.15	< 1.8	< 4.6	(19)
FR016	Norrström	< 0.010	0.40	< 18	(0.039)	< 28	< 0.23	29	< 0.15	< 1.8	< 4.6	(18)
FR017	Nyköpingsån	(0.022)	2.5	67	0.13	(56)	2.6	62	4.7	< 1.8	< 4.6	(12)
FR018	Motala ström	< 0.010	< 0.088	< 18	(0.050)	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	(13)
FR019	Emån	< 0.010	< 0.088	< 18	(0.041)	<28	< 0.23	13	< 0.15	< 1.8	< 4.6	(16)
FR020	Mörrumsån	< 0.010	< 0.088	< 18	< 0.038	<28	< 0.23	< 1.3	< 0.15	< 1.8	< 4.6	(16)
FR021	Helgeån	< 0.010	< 0.088	< 18	< 0.038	< 28	< 0.23	27	< 0.15	< 1.8	< 4.6	(20)

[a] Values in brackets were above MDL, but lower than MQL.

Table A3 Levels of detected organophosporous flame retardants (OPFRs) in Swedish rivers (ng L^{-1})[a]

Sample ID	River	TTBNPP	TNBP	TCEP	ΣT2CPP/T3CPP/TCIPP	ΣTDCIPP/TEHP	EHDPP	oTCP	mTCP	TPHP
FR01	Torneälven	< 2.9	< 3.2	6.6	< 4.6	0.56	(6.4)	< 0.61	< 2.5	< 37
FR02	Kalixälven	< 2.9	< 3.2	(0.72)	< 4.6	(0.25)	<5.4	< 0.61	< 2.5	< 37
FR03	Råneälven	< 2.9	< 3.2	< 0.68	< 4.6	(0.12)	<5.4	< 0.61	< 2.5	< 37
FR04	Luleälven	< 2.9	< 3.2	< 0.68	< 4.6	(0.14)	<5.4	< 0.61	< 2.5	< 37
FR05	Piteälven	< 2.9	< 3.2	(1.1)	< 4.6	0.32	(6.4)	< 0.61	< 2.5	< 37
FR06	Skellefteälven	< 2.9	< 3.2	< 0.68	< 4.6	(0.17)	(4.9)	(0.66)	(4.2)	< 37
FR07D	Krycklan C16	< 2.9	< 3.2	< 0.68	< 4.6	(0.11)	<5.4	< 0.61	< 2.5	< 37
FR07C	Rödånäs D1	< 2.9	< 3.2	< 0.68	< 4.6	0.42	(5.8)	< 0.61	(2.5)	< 37
FR07B	Krycklan Gubböle D2	< 2.9	< 3.2	< 0.68	< 4.6	(0.12)	<5.4	< 0.61	< 2.5	< 37
FR07	Umeälven/Krycklan D3	< 2.9	< 3.2	< 0.68	< 4.6	(0.18)	<5.4	< 0.61	< 2.5	< 37
FR08	Öreälven	< 2.9	< 3.2	< 0.68	< 4.6	(0.18)	<5.4	< 0.61	< 2.5	< 37
FR09	Ångermanälven	< 2.9	< 3.2	(1.2)	10	0.65	<5.4	< 0.61	< 2.5	< 37
FR010	Indalsälven	< 2.9	< 3.2	(0.86)	< 4.6	0.43	<5.4	(1.0)	(7.0)	< 37
FR011	Ljungan	< 2.9	< 3.2	< 0.68	< 4.6	(0.27)	<5.4	< 0.61	< 2.5	< 37
FR012	Delångersån	(3.6)	(9.4)	3.9	< 4.6	1.1	(6.7)	< 0.61	(3.5)	< 37
FR013	Ljusnan	< 2.9	< 3.2	(0.54)	< 4.6	0.40	<5.4	< 0.61	< 2.5	< 37
FR014	Gavleån	< 2.9	< 3.2	(1.0)	< 4.6	1.5	<5.4	< 0.61	< 2.5	< 37
FR015	Dalälven	< 2.9	< 3.2	< 0.68	< 4.6	(0.10)	<5.4	< 0.61	< 2.5	< 37
FR016A	Fyrisån	< 2.9	24	14	30	48	(9.2)	(0.67)	(4.3)	(66)
FR016	Norrström	< 2.9	< 2.9	2.4	(6.9)	3.7	(6.4)	< 0.61	(2.7)	< 37
FR017	Nyköpingsån	(3.0)	< 2.9	3.5	(5.9)	2.1	(5.4)	(1.4)	11	< 37
FR018	Motala ström	< 2.9	< 2.9	(2.2)	(12)	4.0	(6.0)	< 0.61	< 2.5	< 37
FR019	Emån	< 2.9	< 2.9	(1.2)	< 4.6	2.7	<5.4	< 0.61	< 2.5	< 37
FR020	Mörrumsån	< 2.9	< 2.9	(0.87)	(5.1)	1.3	<5.4	< 0.61	< 2.5	< 37
FR021	Helgeån	< 2.9	< 2.9	5.7	(8.1)	10	<5.4	< 0.61	< 2.5	< 37

[a] Values in brackets were above MDL, but lower than MQL.

Table A4 Levels of detected polybrominated diphenylethers (PBDEs) in Swedish rivers (ng L^{-1})[a]

Sample ID	River	BDE47	BDE77	BDE100	BDE99	BDE153	BDE183
FR01	Torneälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR02	Kalixälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR03	Råneälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR04	Luleälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR05	Piteälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR06	Skellefteälven	0.020	(0.14)	(0.0080)	(0.019)	(0.034)	< 0.17
FR07D	Krycklan C16	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR07C	Rödånäs D1	(0.0077)	(0.067)	< 0.0028	0.011	0.018	< 0.17
FR07B	Krycklan Gubböle D2	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR07	Umeälven/Krycklan D3	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR08	Öreälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR09	Ångermanälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR010	Indalsälven	0.048	0.34	0.027	0.055	0.12	< 0.17
FR011	Ljungan	(0.0077)	(0.048)	(0.0031)	< 0.088	(0.021)	< 0.17
FR012	Delångersån	(0.014)	(0.12)	(0.0078)	< 0.088	(0.040)	< 0.17
FR013	Ljusnan	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR014	Gavleån	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR015	Dalälven	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR016A	Fyrisån	0.03	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR016	Norrström	(0.012)	(0.088)	(0.0051)	(0.016)	(0.028)	< 0.17
FR017	Nyköpingsån	0.10	0.64	0.050	0.12	0.15	(0.20)
FR018	Motala ström	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR019	Emån	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR020	Mörrumsån	< 0.0059	< 0.042	< 0.0028	< 0.088	< 0.018	< 0.17
FR021	Helgeån	(0.0061)	(0.062)	(0.0029)	< 0.088	< 0.018	< 0.17

[a] Values in brackets were above MDL, but lower than MQL.

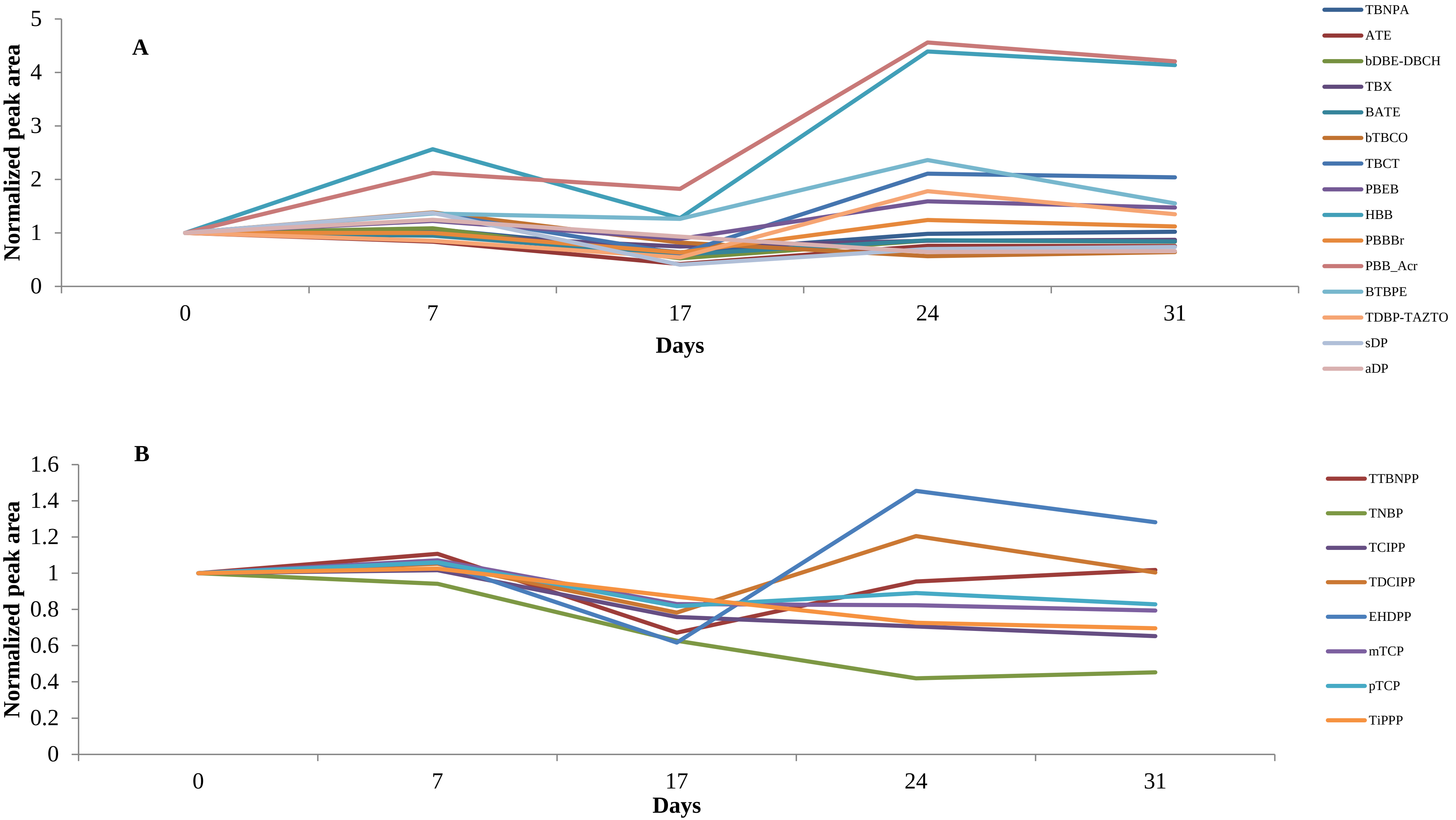

Figure A1 Results from stability test for A) AFRs in pure solvent (no internal standards correction), and B) OPFRs in pure solvent (no internal standards correction). Peak areas are normalized against peak area from the first measurement (day 0).