



Norsk institutt for luftforskning
Norwegian Institute for Air Research

Content and migration of chemical additives from plastic products

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Contents

Contents	3
Summary	4
1 Introduction.....	5
2 Samples	5
3 Methods	6
3.1 Part 1 Measurements of extractable content of chemical additives in plastic products.....	6
3.2 Part 2 Measurements of migration of chemical additives to dust particles	6
3.3 Part 3 Measurements of emission of chemical additives to air	7
4 Chemical analysis	7
5 Results.....	8
5.1 Part 1.....	8
5.2 Part 2.....	10
6 Conclusion	12
Annex A	14

Summary

NILU has, on behalf of the Norwegian Environment Agency, performed chemical analyses of a selection of chemical additives in plastic products. The main goal was to identify the content and migration of the chemical additives in and from the products to air and surfaces of the products at room temperature.

The study was split in three parts. In part 1, the content of the chemical additives in seven groups of plastic products was analysed and quantified by cutting the products in smaller pieces and extracting in solvent. In part 2 and 3, four of the product groups with highest content were selected to study the migration of the chemical additives to the surfaces of the products and the air. Part 2 and 3 was conducted in closed metal containers containing the products and passive air samplers based on ABN adsorbent. The release to surfaces was studied using wipes of the surfaces after two weeks in the closed container. Analyses were performed on gas chromatography coupled to mass spectrometer (GC-MS) using internal standards for identification and quantification of the content in all samples.

The results showed that OPFRs, nBFRs and TBBPA were detected as extractable content of and in surface wipes of all the studied project groups.

1 Introduction

NILU – Norwegian Institute for Air Research on behalf of the Norwegian Environment Agency, has performed chemical analyses of a selection of chemical additives in plastic products.

The main goal of the study was to identify the extractable content and migration of the chemical additives in and from the products to air and surfaces of the products at room temperature.

In recent years, studies have shown that chemical additives are present in indoor matrices (e.g. house dust). The sources for the additives are not yet well characterized. A better understanding of the content and release of chemical additives in and from plastic products is crucial for chemical regulation and reduced exposure for humans and the environment.

2 Samples

All the plastic products in the study (n=28) were selected and purchased by the Norwegian Environment Agency. A complete list of all samples is given in Table 1.

Table 1: Plastic product groups and specific products included in each group in this study with information on those groups selected for part 2-3.

Sample nr.	Product group	Specific product name (in Norwegian)	Part 1	Part 2+3
1	Extension cords	Luxorparts UTP-nettverkskabel; Skjøteledning, jordet 3 m; Exibel CAT-6 nettverkskabel; Grenuttak 3-veis, 5m kabel	Yes	No
2	Sockets	Elko RS Jordet stikkontakt 2-veis utenpåliggende; ELKO RS16 stikkontakt dobbel på vegg; Stikkontakt 2-veis m/jord vegg elko polarhvit; Eletra 1+2 way adapter 16/2.5A	Yes	No
3	Flooring	Vinylgulv starfloor click 55 modern oak white; Vinylgulv starfloor click 55 composite black; Marmoleum Click Scarlet; Marmoleum Click Trace of Nature linoleumsgulv; Concept 690 Pinnacles gulvbelegg; Vareprøve parkett laminat	Yes	Yes
4	Wall paper	Vareprøve : vinyltapet blåmønstret; vinyltapet beige; vinyltapet beige m/oransje mønster; vinyltapet, grønn m/ mønster	Yes	Yes
5	PC mouse	liglo M610 Trådløs Ergo Mus Sort; Mousetrapper Advance 2.0 svart; Logitech M705 Marathon Mouse U; Eletra Wired Mouse EM100	Yes	Yes
6	PC	Aspire Aspire 3 A314-32 14" HD; ASUS Chromebook 15 C523NA 15,6" FHD	Yes	Yes

7	Upholstery	Pølle dia. 20 x 40cm; Skumkube 40x40x40cm; Skumkube 8x8x8cm; Skumpute	Yes	No
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3 Methods

3.1 Part 1 Measurements of extractable content of chemical additives in plastic products

In the first part of the study, the extractable content of the targeted chemical additives in the seven product groups was measured. This was done by cutting representative parts of each product in small pieces and extracting the pieces in acetone:hexane (1:1) using ultrasonication. The extract was taken to instrumental analyses without any clean-up steps. Solvent was exchanged for the specific analyses.

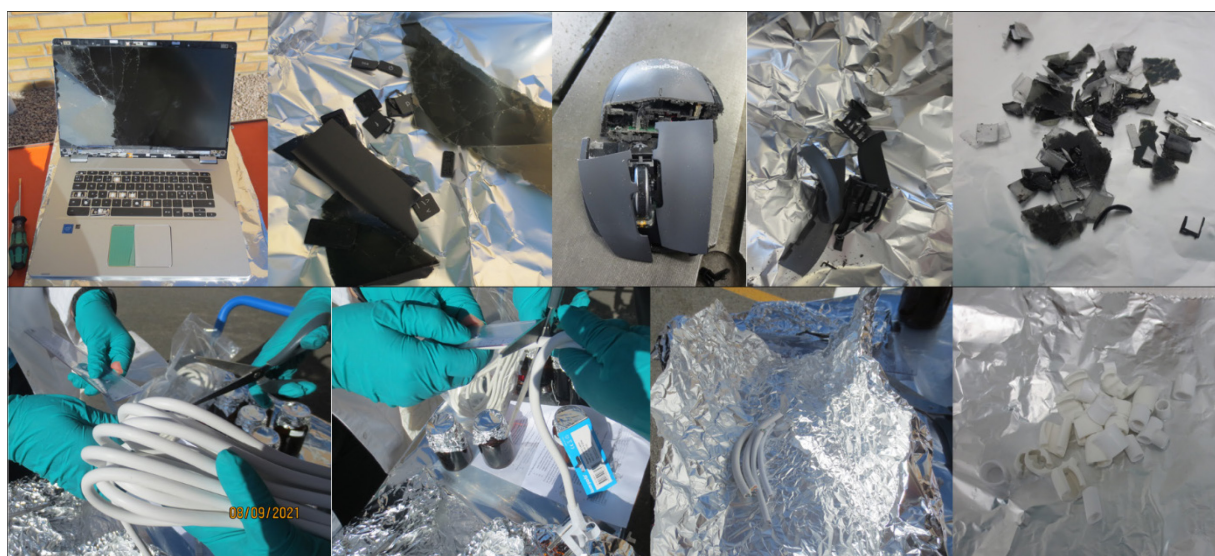


Figure 1 Part 1 – Sample preparation for measurements of extractable content of chemical additives in plastic products.

3.2 Part 2 Measurements of migration of chemical additives to dust particles

In the second part of the study, the release of chemical additives to particles on the surface of the products was measured. Four of seven product groups were selected based on the results from part 1:

- Flooring
- Wall paper
- PC mouse
- PC

The study was performed inside metal (plastic free) containers. The metal containers were pre-cleaned in soap followed by hexane and acetone before any products were placed inside them. The products of each product groups were placed in one metal container. As control of contamination from the container or leakage of indoor air, also two empty containers were included. The containers were sealed and left in room temperature for two weeks. After two weeks the containers were opened and a wipe sample was taken of the product surfaces and the inside walls of the containers. The wipe samples were collected using glass fiber filters (142 mm) soaked in solvent (iso-propanol). The glass

fiber filters were pre-cleaned at 450°C before sampling. The wipes from one container were packed together in alumina foil, placed in two sealed plastic bags and stored cold until sample preparation. The wipes were extracted in hexane:acetone (1:1) using ultra sonication. The extracts were filtered before instrumental analysis.

3.3 Part 3 Measurements of emission of chemical additives to air

In the third part of the study, the emission of chemical additives to air was measured. Four of seven product groups were selected based on the results from part 1:

- Flooring
- Wall paper
- PC mouse
- PC

The study was performed together with Part 2, inside pre-cleaned metal containers. The products were placed in rinsed metal containers together with a passive air sampler. Some of the products were cut in smaller parts to fit the containers (e.g. floor and PC). The passive air samplers used in this study were based on ABN adsorbent. Before exposure, the ABN was pre-cleaned and packed to minimize risk of contamination. One ABN tube was placed inside the metal container together with the products, making sure they were not in direct contact. The containers were sealed and the passive air samplers were exposed for two weeks in room temperature. As control of contamination from the container or leakage of indoor air, passive air samplers were also deployed inside two empty containers. After two weeks the containers were opened and the passive air samplers were packed in alumina foil, placed in two sealed plastic bags and stored cold until sample preparation. The ABN samplers were then extracted in hexane:acetone (1:1). The extracts were filtered before instrumental analysis.

4 Chemical analysis

The extracts from part 1-3 were analyzed for organophosphorous flame retardants (OPFRs, n=22), polybrominated flame retardants (PBDEs, n=25), novel brominated flame retardants (nBFRs, n=14), TBBPA (2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol), short- and medium chain chlorinated paraffins (SCCPs/MCCPs) and dechloranes (n=10). The full list of targeted compounds is given in Annex A.

Shortly, the instrumental analyses for PBDEs and nBFRs were performed on gas chromatography (GC) coupled to a high resolution mass spectrometer (HRMS) operated in electron impact ionization (EI) mode. OPFRs were analyzed on an ultra-high-pressure liquid chromatograph (UHPLC) coupled to a triple quadrupole MS equipped with an electrospray ionization source (ESI) operated in positive mode. TBBPA was analyzed on a Vanquish UHPLC coupled to an Q Exactive Plus Orbitrap high-resolution mass spectrometer (HRMS) with ESI ion source operated in negative mode. SCCPs/MCCPs and dechloranes on an Agilent GC coupled to HR-qTOF in electron capture negative ion (ECNI) mode.

5 Results

5.1 Part 1

The targeted chemical additives detected at concentrations above the analytical limit of detection (LOD) in the products groups are listed in Table 2-3 (name, CAS-number, EC-number, quantified concentrations). In total, ten of the targeted chemical additives were detected in at least one product group. Four of these were detected at high concentrations and in more than one product group: TBEP, TPHP, EHDP and TBBPA (Figure 2). In addition to the targeted compounds, phthalates were also observed in four of the product groups (i.e. extension cords, flooring, wall paper and upholstery). Further identification and quantification of these were not a part of this study.

Table 2: Summary of results in part 1 of the study. Presented are the five OPFRs detected in the individual product groups (ng/g).

	Tris(2-butoxyethyl) phosphate (TBEP)	Triphenyl phosphate (TPP/TPHP)	2-ethylhexyl diphenyl phosphate (EHDP)	2-isopropyl-phenyl diphenyl phosphate (2IPDPPP)	mmm-Tritolyl phosphate (TMTP)
CAS	78-51-3	115-86-6	1241-94-7	64532-94-1	563-04-2
EC-number	201-122-9	204-112-2	214-987-2	248-848-2	209-241-8
LOD (ng/g)	654	1374	652	627	627
	Concentrations (ng/g)				
Extension cords	<LOD	<LOD	<LOD	<LOD	13306
Sockets	<LOD	<LOD	<LOD	<LOD	<LOD
Flooring	775 216	2196	<LOD	<LOD	<LOD
Wall paper	346695	6200	10283	<LOD	<LOD
Upholstery	<LOD	9941	<LOD	<LOD	<LOD
PC mouse	<LOD	72840	2747	<LOD	<LOD
PC*	<LOD	15092-436366	<LOD	<LOD-760	<LOD

*Two PCs analysed separately.

Table 3: Summary of results in part 1 of the study. Presented are the five halogenated compounds detected in the individual product groups (ng/g).

	2,2',6,6'-tetrabromo-4,4'-isopropylidene-diphenol (TBBPA)	1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE)	1,1'-(ethane-1,2-diyl)bis[pentabromo-benzene] (DBDPE)	Syn-dechlorane plus (syn-DP)	Anti-dechlorane plus (anti-DP)
CAS	79-94-7	37853-59-1	84852-53-9	135821-03-3	135821-74-8
EC-number	201-236-9	253-692-3	284-366-9	NA	NA
LOD (ng/g)	8	0,2	1,5	1.0	1.0
	Concentrations (ng/g)				
Extension cords	<LOD	<LOD	<LOD	<LOD	13306
Sockets	528	<LOD	<LOD	<LOD	<LOD
Flooring	<LOD	<LOD	<LOD	<LOD	<LOD
Wall paper	<LOD	<LOD	<LOD	<LOD	<LOD
Upholstery	<LOD	<LOD	<LOD	<LOD	<LOD
PC mouse	18225	191	1209	5,2	26
PC*	18-210	<LOD	<LOD	<LOD	<LOD

*Two PCs analysed separately.

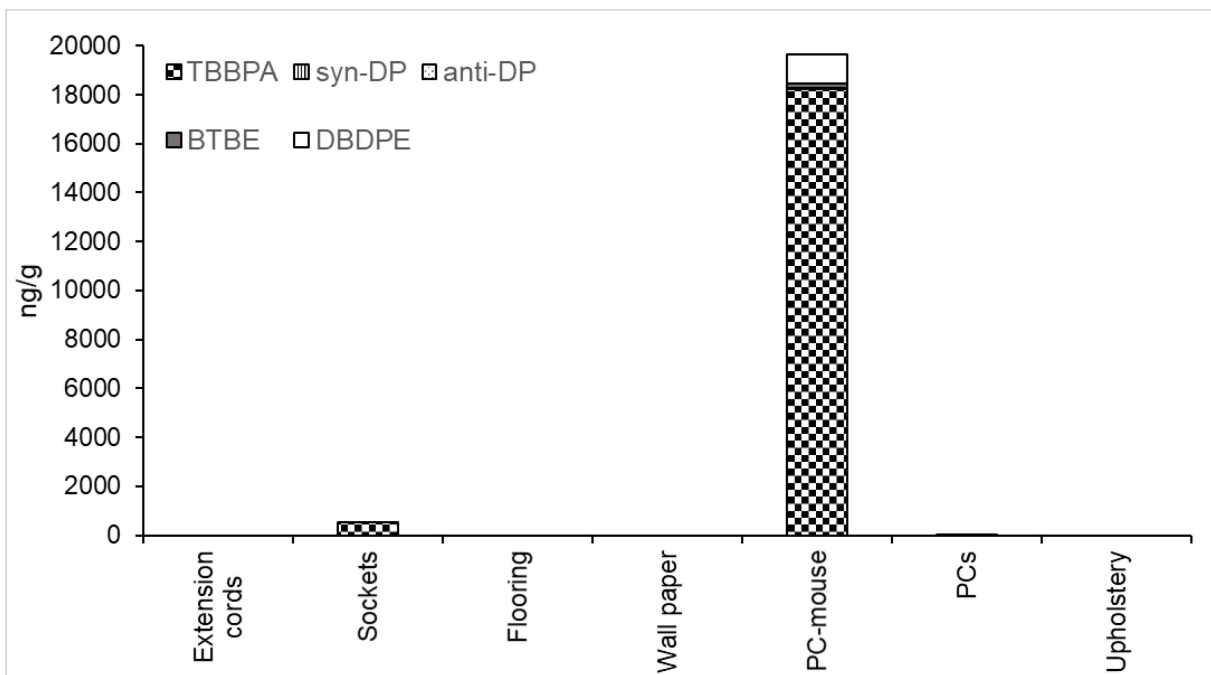
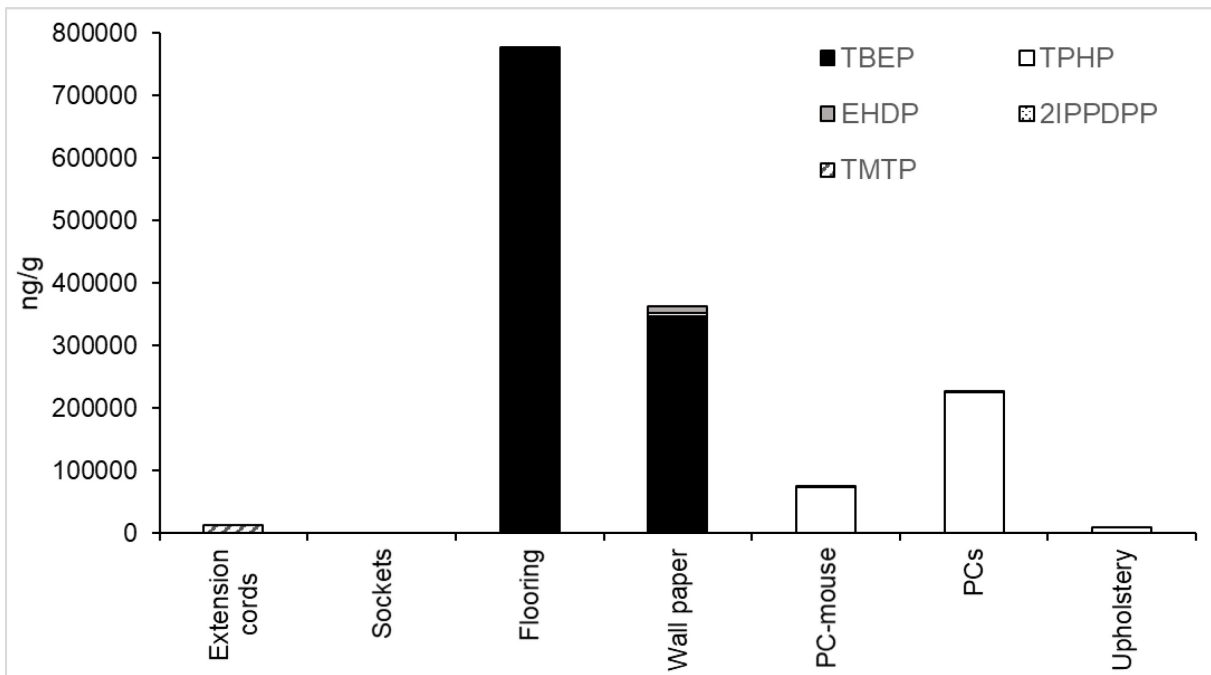


Figure 2 Profiles and concentrations (ng/g) of OPFRs (above) and brominated flame retardants (below) in the selected product groups.

5.2 Part 2

The chemical additives detected above the LOD in the wipe samples are listed in Table 4-5 (name, CAS-number, EC-number, quantified concentrations). In total, 21 of the targeted chemical additives were detected in at least one of the four product groups included in part 2. Five of these were detected at high concentrations and in more than two product group: TBEP, TPHP, EHDP, TCPP and TBBPA (Figure 3).

Table 4: Summary of results in part 2 of the study. Presented are the eleven halogenated compounds detected in wipe samples (ng/sample).

	α -Tetrabromoethylcyclohexane (α -TBECH/DBE-DBCH)	β -Tetrabromoethylcyclohexane (β -TBECH/DBE-DBCH)	γ/δ -Tetrabromoethylcyclohexane (γ/δ -TBECH/DBE-DBCH)	2-Bromoallyl-2,4,6-tribromophenyl ether (BATE/TBP-BAE)	Pentabromotoluene (PBT)
CAS	3322-93-8	3322-93-8		99717-56-3	87-83-2
EC-number	222-036-8	222-036-8		NA	201-774-4
LOD (ng/sample)	0.2	0.2	0.2	0.05	0.06
	Concentrations (ng/sample)				
Flooring	<LOD	<LOD	0.7	0.1	0.1
Wall paper	2.0	0.8	<LOD	0.2	0.2
PC mouse	<LOD	<LOD	<LOD	<LOD	<LOD
PC*	<LOD	<LOD	<LOD	<LOD	<LOD

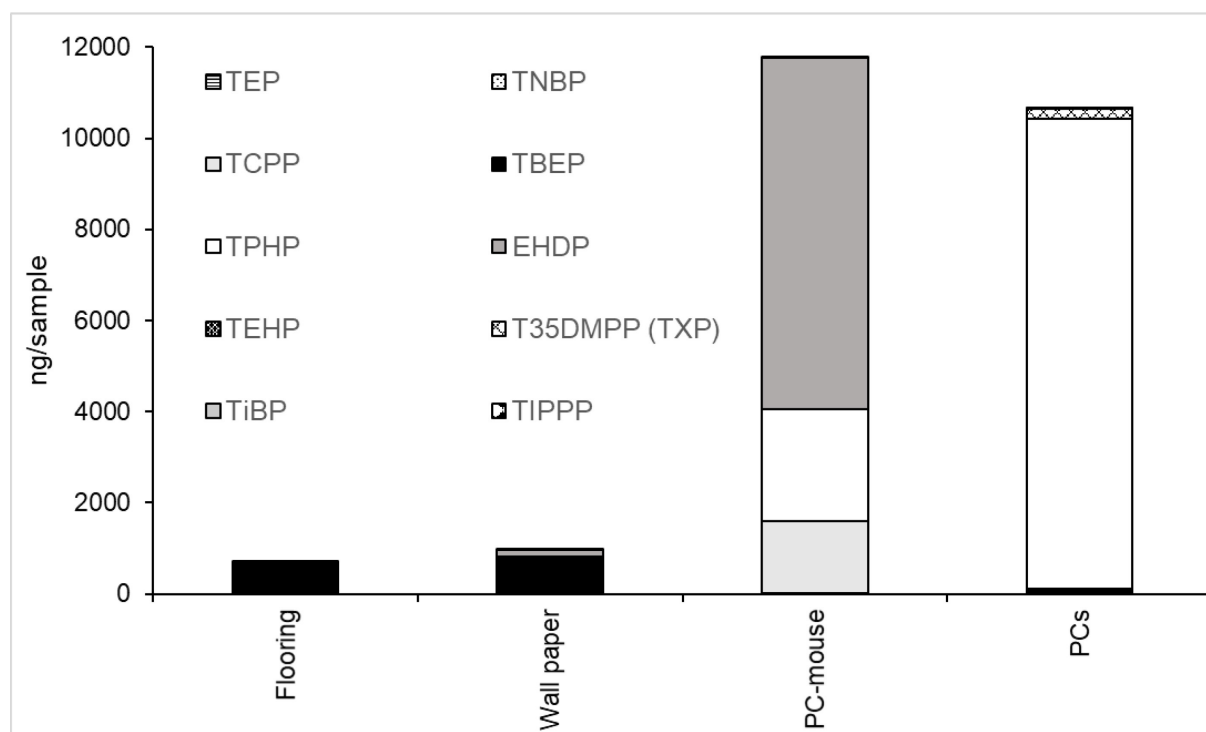
	Pentabromoethylbenzene (PBEB)	Hexabromobenzene (HBB)	2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE/TBP-DBPE)	1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE)	Bis(2-ethylhexyl)tetra-bromophthalate (TBPH / BEH-TBP)
CAS	85-22-3	87-82-1	35109-60-5	37853-59-1	26040-51-7
EC-number	201-593-0	201-773-9	252-372-0	253-692-3	247-426-5
LOD (ng/sample)	0.03	0.2	0.03	0.1	0.5
	Concentrations (ng/sample)				
Flooring	0.1	<LOD	<LOD	<LOD	<LOD
Wall paper	0.2	0.2	0.15	<LOD	<LOD
PC mouse	<LOD	<LOD	<LOD	0.08	<LOD
PC*	<LOD	<LOD	<LOD	0.2	1.4

	2,2',6,6'-tetrabromo-4,4'-isopropylidene-diphenol (TBBPA)
CAS	79-94-7
EC-number	201-236-9
LOD (ng/sample)	0.03
	Concentrations (ng/sample)
Flooring	0.9
Wall paper	0.5
PC mouse	22.4
PC*	5.6

Table 5: Summary of results in part 2 of the study. Presented are the ten OPFRs detected in wipe samples (ng/sample).

	Tris(2-butoxyethyl) phosphate (TBEP/TBOEP)	Triphenyl phosphate (TPHP)	2-ethylhexyl diphenyl phosphate (EHDP)	Tri-n-butyl phosphate (TnBP)	Triethyl phosphate (TEP)
CAS	78-51-3	115-86-6	1241-94-7	126-73-8	78-40-0
EC-number	201-122-9	204-112-2	214-987-2	204-800-2	201-114-5
LOD (ng/g)	654	1374	652		
Concentrations (ng/sample)					
Flooring	659	<LOD	7.2	<LOD	<LOD
Wall paper	772	37	161	4.1	<LOD
PC mouse	<LOD	2462	7689	2.5	<LOD
PC*	82	10315	10	2.7	4.3

	Tris(2-chloro-isopropyl) phosphate (TCPP)	Tris(2-ethylhexyl) phosphate (TEHP)	Trixylyl phosphate (TXP/T35DMPP)	Triisobutyl phosphate (TiBP)	Tris(4-isopropylphenyl) phosphate (TIPPP)
CAS	13674-84-5	78-42-2	25155-23-1	126-71-6	2502-15-0 68937-41-7
EC-number	237-158-7	201-116-6	246-677-8	204-798-3	219-703-0 273-066-3
LOD (ng/g)					
Concentrations (ng/sample)					
Flooring	39	<LOD	<LOD	<LOD	<LOD
Wall paper	<LOD	<LOD	<LOD	3.4	<LOD
PC mouse	1598	<LOD	<LOD	0.9	<LOD
PC*	14	5.6	201	0.6	6.7



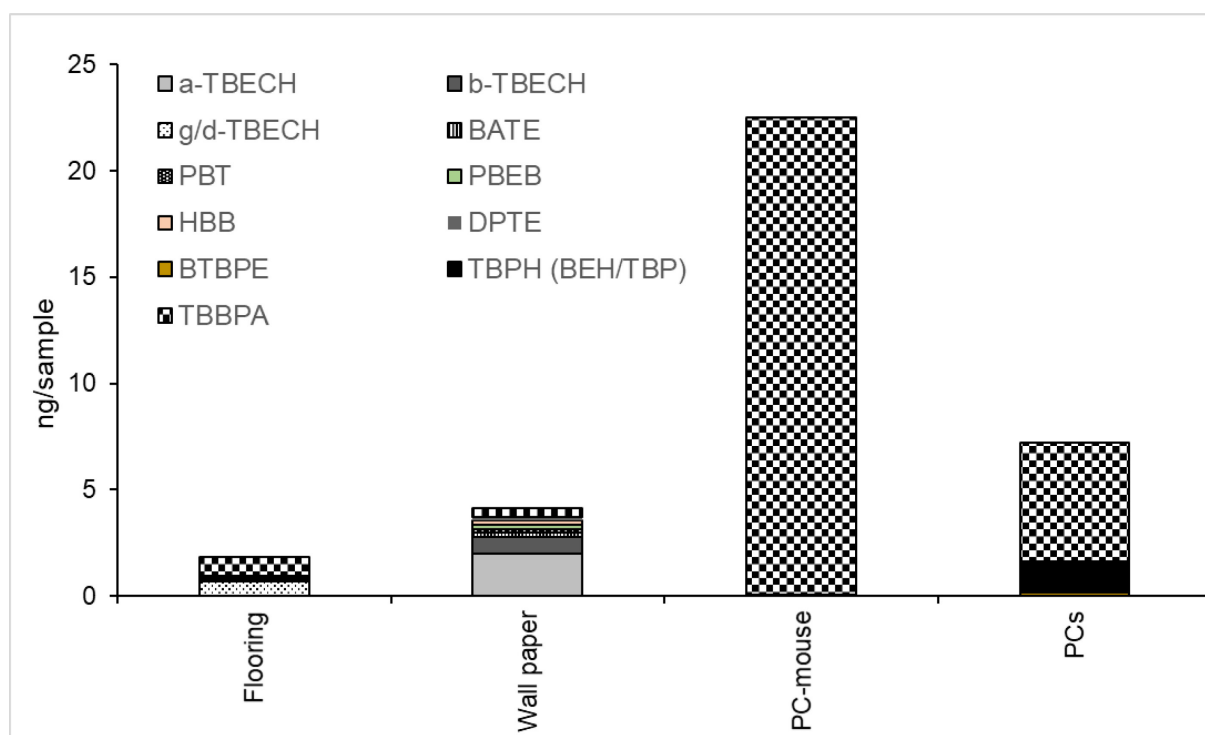


Figure 3 Profiles and concentrations (ng/sample) of OPFRs (above) and brominated flame retardants (below) in the selected product groups

Table 6: Detected compounds in the four prioritized product groups.

	Flooring	Wall paper	PC mouse	PC
Content	TBEP, TPHP	TBEP, EHDP, TPHP	TPHP, EHDP, TBBPA, Syn-DP, anti-DP, BTBPE, DBDPE	TPHP, 2IPDP, TBBPA
Surface wipes	TBEP, TCPP, EHDP, TBBPA, g/d-TBECH, BATE, PBT, PBEB	TBEP, EHDP, TPHP, TNBP, TiBP, TBBPA, a-TBECH, b-TBECH, BATE, PBT, PBEB, HBB, DPTE	EHDP, TPHP, TCPP, TNBP, TiBP, TBBPA, BTBPE	TPHP, T35DMPP(TXP), TBEP, TCPP, EHDP, TIPPP, TEHP, TEP, TNBP, TiBP, TBBPA, BTBPE, TBPH(BEH/TBP)

6 Conclusion

OPFRs, nBFRs and TBBPA were detected as extractable content of and in surface wipes of all the studied product groups. The highest concentrations were detected for TBEP, TPHP, EHDP and TBBPA. The highest numbers of detected compounds were found in the PC-mouse group. The reason for this may be that the group contained both normal PC-mouse and ergonomic PC-mouse containing both hard and soft parts. This means that the brominated flame retardants may originate from another part of the mouse than the OPFRs. More detailed studies are therefore recommended for the PC-mouse group, but also for the other groups to identify in which part of the product the chemicals are added. For that, the approach used in part 1 of this study is recommended.

The results of the wipes samples shows that the chemical additives also migrate to particles on the surface of the products and particles settled on the walls of a sampling container. More detailed

studies are needed to identify their potential to migrate also to airborne particles as none of the targeted compounds were detected in the air samples of this study.

Surprisingly, neither SCCPs nor MCCPs were detected in any of the product groups. CPs have been detected at high concentrations in extension cords and sockets in earlier projects performed by NILU for the Norwegian Environment Agency

Annex A

Targeted chemicals in the study.

Full name	Alternative name	Abbreviation	CAS no	EC no
Novel brominated flame retardants - nBFRs				
Allyl 2,4,6-tribromophenyl ether	2-(allyloxy)-1,3,5-tribromobenzene	ATE (TBP-AE)	3278-89-5	221-913-2
α -Tetrabromoethyl-cyclohexane	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	α -TBECH (DBE-DBCH)	3322-93-8 1232836-48-4	222-036-8
β -Tetrabromoethyl-cyclohexane		β -TBECH (DBE-DBCH)	3322-93-8 1232836-49-5	
γ/δ -Tetrabromoethyl-cyclohexane		γ/δ -TBECH (DBE-DBCH)		
2-Bromoallyl-2,4,6-tribromophenyl ether		BATE (TBP-BAE)	99717-56-3	
Pentabromotoluene	2,3,4,5,6-pentabromotoluene	PBT	87-83-2	201-774-4
Pentabromoethylbenzene	2,3,4,5,6-pentabromoethylbenzene	PBEb	85-22-3	201-593-0
1,2,3,4,5-pentabromobenzene		PBBZ	608-90-2	
Hexabromobenzene	1,2,3,4,5,6-hexabromobenzene	HBB	87-82-1	201-773-9
2,3-dibromopropyl-2,4,6-tribromophenyl ether	1,3,5-tribromo-2-(2,3-dibromopropoxy)benzene	DPTE (TBP-DBPE)	35109-60-5	252-372-0
2-ethylhexyl-2,3,4,5-tetrabromobenzoate		EHTBB	183658-27-7	814-310-6
1,2-bis(2,4,6-tribromophenoxy)ethane	FireMaster 680	BTBPE	37853-59-1	253-692-3
Bis(2-ethylhexyl)-tetrabromophthalate		TBPH (BEH-TBP)	26040-51-7	247-426-5
Decabromodiphenylethane	1,1'-(ethane-1,2-diyl)bis-[pentabromobenzene]	DBDPE	84852-53-9	284-366-9
2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol		TBBPA	79-94-7	201-236-9
Polybrominated diphenylethers - PBDEs				
2,2',4-TriBDE		BDE-17	147217-75-2	874-730-0
2,4,4'-TriBDE		BDE-28	41318-75-6	868-402-6
2,2',4,4'-TetBDE		BDE-47	5436-43-1	690-137-8
2,2',4,5'-TetBDE		BDE-49	243982-82-3	
2,3',4,4'-TetBDE		BDE-66	189084-61-5	621-543-5
2,3',4',6-TetBDE		BDE-71	189084-62-6	620-888-9
3,3',4,4'-TetBDE		BDE-77	93703-48-1	621-837-3
2,2',3,4,4'-PenBDE		BDE-85	182346-21-0	621-547-7
2,2',4,4',5-PenBDE		BDE-99	60348-60-9	690-282-7
2,2',4,4',6-PenBDE		BDE-100	189084-64-8	690-350-6
2,3',4,4',6-PenBDE		BDE-119	189084-66-0	620-889-4
3,3',4,4',5-PenBDE		BDE-126	366791-32-4	

Full name	Alternative name	Abbreviation	CAS no	EC no
2,2',3,4,4',5'-HexBDE		BDE-138	182677-30-1	621-550-3
2,2',4,4',5,5'-HexBDE		BDE-153	68631-49-2	690-275-9
2,2',4,4',5,6'-HexBDE		BDE-154	207122-15-4	
2,3,3',4,4',5-HexBDE		BDE-156	405237-85-6	
2,2',3,4,4',5',6-HepBDE		BDE-183	207122-16-5	
2,2',3,4,4',6,6'-HepBDE		BDE-184	117948-63-7	
2,3,3',4,4',5',6-HepBDE		BDE-191	446255-30-7	
2,2',3,3',4,4',5,6'-OctBDE		BDE-196	446255-39-6	
2,2',3,3',4,4',6,6'-OctBDE		BDE-197	117964-21-3	
2,2',3,3',5,5',6,6'-OctBDE		BDE-202	67797-09-5	
2,2',3,3',4,4',5,5',6-NonBDE		BDE-206	63936-56-1 63387-28-0	264-565-7
2,2',3,3',4,4',5,6,6'-NonBDE		BDE-207	437701-79-6	
DecaBDE		BDE-209	1163-19-5	214-604-9
Organophosphorous flame retardants - OPFRs				
Triethyl phosphate		TEP	78-40-0	201-114-5
Tri(2-chloroethyl)phosphate		TCEP	115-96-8	204-118-5
Tripropyl phosphate		TPrP (TPP)	513-08-6	208-151-6
Tris(2-chloroisopropyl)phosphate		TCPP (TCIPP)	13674-84-5	237-158-7
Triisobutyl phosphate		TiBP (TBP)	126-71-6	204-798-3
Butyl diphenyl phosphate		BdPhP	2752-95-6	220-398-1
Triphenyl phosphate		TPP (TPhP)	115-86-6	204-112-2
Dibutyl phenyl phosphate		DBPhP	2528-36-1	219-772-7
Tri-n-butyl phosphate		TnBP (TBP)	126-73-8	204-800-2
Tris(1,3-dichloro-2-propyl)-phosphate		TDCPP (TDCIPP)	13674-87-8	237-159-2
Tris(2-butoxyethyl) phosphate		TBEP (TBOEP)	78-51-3	201-122-9
Tricresyl phosphate	Tris(methylphenyl) phosphate	TCP	1330-78-5	215-548-8
2-ethylhexyldiphenyl phosphate		EHDP (EHDPP)	1241-94-7	214-987-2
Trixylyl phosphate		TXP (T35DMPP)	25155-23-1	246-677-8
Tris(4-isopropylphenyl) phosphate		TIPPP	2502-15-0 68937-41-7	219-703-0 273-066-3
Tris(2-ethylhexyl)phosphate		TEHP	78-42-2	201-116-6
2-isopropylphenyl diphenyl phosphate		2IPDPDP	64532-94-1 28108-99-8	248-848-2
ooo-Tritolyl phosphate		TOTP	78-30-8	201-103-5
Isodecyl diphenyl phosphate		IDDP	29761-21-5	249-828-6
mmm-Tritolyl phosphate	Tri-m-tolyl phosphate	TMTTP	563-04-2	209-241-8
4-isopropylphenyl diphenyl phosphate	Diphenyl p-isopropylphenyl phosphate	4IPDPDP	55864-04-5	
ppp-Tritolyl phosphate		TPTP	78-32-0	201-105-6

Full name	Alternative name	Abbreviation	CAS no	EC no
Tris(2-isopropylphenyl) phosphate		T2IPPP	64532-95-2	
Bis(4-isopropylphenyl) phenyl phosphate		B4IPPPP	55864-07-8	
Dechloranes				
Syn-Dechlorane plus	Syn-dodecachloropenta-cyclooctadecadiene	syn-DP	135821-03-3	
Anti-Dechlorane plus	Anti-dodecachloropenta-cyclooctadecadiene	anti-DP	135821-74-8	
Dechlorane 601		Dec-601	13560-90-2	
Dechlorane 602		Dec-602	31107-44-5	250-472-9
Dechlorane 603		Dec-603	13560-92-4	
Dechlorane 604		Dec-604	34571-16-9	252-097-6
Dibromo-aldrin		Dba	20389-65-5	660-975-9
Chlorinated paraffins				
Short-chain chlorinated paraffins		SCCPs	85535-84-8	
Medium-chain chlorinated paraffins		MCCPs	85535-85-9	

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