ChEmiTecs

Occurrence in the environment of case-study chemicals - A literature study

Birgit Paulsson

Dept of Materials and Environmental Chemistry

Stockholm University

CHEMITECS REPORT P3-D5a-IR

IVL Svenska Miljöinstitutet · Stockholms universitet · KTH Vetenskap och konst · Umeå Universitet · CHALMERS

CHEMITECS REPORT P3-D5a-IR

Literature study in selected case-study chemicals – occurrence in the environment

BIRGIT PAULSSON

Dept of Materials and Environmental Chemistry

STOCKHOLM UNIVERSITY

May 2010

Table of contents

Background

This literature study is a presentation of existing data on the chemicals selected as test substances for the case studies within the ChEmiTecs programme (Table 1). The report is based on literature retrieved from the on-line data bases: SciFinder, Web of Science and Science Direct. It means that the references cited are all from peer reviewed articles. Search has been done on chemical group and/or CAS number and the keyword "occurrence" combined with words like: environment, vertebrates, mammals, birds, humans, etc. Some concluding remarks are presented in the end of the report.

Table 1. Chemicals selected as candidates for the case studies.

Chemical group	Name	CAS-number
Benzenediamine	1,4-Benzenediamine, N,N'-bis(1,4-dimethylpentyl)	3081-14-9
	N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine	793-24-8
Benzothiazole	N,N-dicyclohexylbenzothiazole-2-sulphenamide	4979-32-2
	N-cyclohexylbenzothiazole-2-sulphenamide	95-33-0
	Benzothiazole-2-thiol (*MBT, 2-Merkaptobenzothiazole*)	149-30-4
	Di(benzothiazol-2-yl) disulphide	120-78-5
	N-tert-butylbenzothiazole-2-sulphenamide	95-31-8
Benzotriazole	2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol	25973-55-1
	2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol	3147-75-9
	2-benzotriazol-2-yl-4,6-di-tert-butylphenol	3846-71-7
	2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol	3864-99-1
	2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	70321-86-7
Organo phosphates	Triphenyl phosphate	115-86-6
	Tris(2-chloro-1-methylethyl) phosphate	13674-84-5
	Tributyl phosphate	126-73-8
PFCs	Perfluorobutric acid	375-22-4
	Perfluorhexanoic acid	307-24-4
	Perfluoroheptanoic acid	375-85-9
	Perfluordecanoic acid	335-76-2
	Perfluorobutane sulfonate	29420-49-3
	Perfluorohexane sulfonate	3871-99-6
Phthalates	Di-"isononyl"phthalate (DINP)	28553-12-0

Benzenediamines

On the list of selected chemicals for the case-studies the group benzenediamines are represented by two substances, 1,4-Benzenediamine, N,N'-bis(1,4-dimethylpentyl) and N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine. No scientific articles were found when searching for their occurrence in the environment.

Benzothiazoles

The group of benzothiazoles (BT) is including five substances on the list of case study compounds (see Table 1). No authentic references were found for any of these chemicals regarding their accumulation in fish, birds, mammals or in human tissues and/or body fluids. Two studies on rats and humans report 2-mercaptobenzothiazole (Benzothiazole-2-thiol, 149-30-4) as a metabolite from ***a)*** 2-(thiocyanomethylthio)benzothiazole, TCMTB, a wood preservative (Manninen et al 1996) and ***b)*** BT-sulpheneamides (Fukuka et al 1995).

Several articles (including reviews) deal with various BTs in abiotic environment but mostly other BTs than those on the list. However, Kloepfer et al (2005) determined BTs in waste water, e. g. 2-mercaptobenzothiazole (Benzothiazole-2-thiol, 149-30-4) and Khoroshko et al (2005) identified 2-merkaptobenzothiazole (Benzothiazole-2-thiol, 149-30-4) in river water suggested as a metabolite of the wood preservative 2-(thiocyanomethyl)benzothiazole, TCMTB. Kumata et al (2000) describe measurements of N-cyclohexyl-2 benzothiazoleamine as a marker for N-cyclohexylbenzothiazole-2-sulphenamide (95-33-0), showing it to be a widely distributed (~ng/g to µg/g) compound in urban environment in Japan (road dust, runoff- and river-water particles, river sediments, aerosols).

Table 2. Scientific references found for two of the selected benzothiazoles in the abiotic environment

Name	CAS no	Use	Occurrence found	Conc. levels	Ref
N-cyclohexylbenzothiazole-2-sulphenamide	95-33-0	Vulcanization accelerator	Road dust, water particles, river sediment, aerosols (measured as another BT-amine)	∑BTs; ~ng/g to ~µg/g	Kumata et al 2000
Benzothiazole-2-thiol (2-mercapto benzothiazole, 2-MBT)	149-30-4	Corrosion inhibitor, Found as a metabolite	Wastewater (influent) River water	0.02 – 0.19 µg/L (∑BTs: ~ 3 µg/L) No conc.	Kloepfer et al 2005 Khoroshko et al 2005

Benzotriazoles

Five specific benzotriazoles (BZT) are on the list of case study compounds (Table 1). Only two references concerning occurrence in the environment were found. Reddy et al (2000) reported total BZT-concentrations in marine and freshwater sediments. Nakata et al (2009) analyzed marine organisms in Japan.

Table 3. Scientific references found for three of the selected benzotriazoles in the abiotic environment

Name	CAS no	Use	Occurrence found	Conc. levels (ng/g ww)	Ref
2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol	25973-55-1	UV-filter	Fish (whole, ssp.) Mullet (whole, exc. liver) Bass (liver, ssp.) Hammerhead shark (liver) Duck+mallard (liver)	< 62 8.7±4.9 2.4-19 55±46 < 0.15	Nakata et al 2009
2-benzotriazol-2-yl-4,6-di-tert-butylphenol	3846-71-7	UV-filter	Fish (whole, ssp.) Bass (liver, ssp.) Hammerhead shark (liver) Duck+mallard (liver)	< 0.09 < 0.05-0.41 7.0±7.5 <0.05	Nakata et al 2009
2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2yl) phenol	3864-99-1	UV-filter	Fish (whole, ssp.) Mullet (whole, exc. liver) Bass (liver, ssp.) Hammerhead shark (liver) Duck+mallard (liver)	< 0.51 1.7±0.79 4.1-2.5 13±9.9 2.6-3.4	Nakata et al 2009

Organophosphates

Triphenyl phosphates (TPP), tris(2chloro-1-methylethyl) phosphate (TCPP) and tributyl phosphate (TBP) are on the case compound study list (Table 1).The first two chemicals have been selected as representatives of substances applied in the electronic industry (use: flame retardants) and the last one a chemical used in concrete production (use: antifoaming agent).

The literature search resulted in a fair number of scientific articles about occurrence in the outdoor environment. One reference about accumulation of the compounds in fish, and human milk was found (Marklund-Sundkvist et al 2010) and one on urine metabolites of TPP, indicating the formation and excretion of diphenyl phosphate (Schindler et al 2009). About 10 different studies were found on indoor air/dust or from outdoor abiotic environment.

Table 4. References found for the selected organo phosphates in the abiotic environment

Name	CAS no	Use	Occurrence	Conc. levels	Ref
Triphenyl Phosphate, TPP	115-86-6,	Flame retardant	Air Indoor Dustt Water River River River Effluent Sedim. River Marine Herring ……..Perch ……..Salmon Freshw. Perch Human milk	0,5-0,8 ng/m3 7360 ng/g -10 ng/L 11-165 ng/L - ~ 2000 ng/L -170 ng/L -160 µg/kg 16 ng/g lw 72 ng/g lw 4.2 ng/g lw 150 ng/g lw 8.5 ng/g lw	Carlsson et al 1997 Stapleton et al 2009 Martinez-C. et al 2007 Bacaloni et al 2007 Andresen et al 2004 Martinez-C. et al 2007 Martinez-C. et al 2007 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010
Tris(2chloro-1-methylethyl) phosphate, TCPP	13674-84-5	Flame retardant	Air Indoor Indoor Indoor Indoor Dust Water River River Effluent Sedim. River Marine Herring ……..Perch ……..Salmon Freshw. Perch Human milk	1-6 ng/m3 0.4-730 ng/m3 19-58 ng/m3 9 ng/m3 570 ng/g 33-170 ng/L 54-117- 270-1400 ng/L -1300 µg/kg 60 ng/g lw 190ng/g lw 23 ng/g lw 320 ng/g lw 45 ng/g lw	Saito et al 2007 Marklund et al 2005 Carlsson et al 1997 Carlsson et al 2000 Stapleton et al 2009 Martinez-C. et al 2007 Bacaloni et al 2007 Martinez-C. et al 2007 Martinez-C. et al 2007 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010
Tributyl phosphate, TBP	126-73-8	Flame retardant Plasticizer Lubricant	Air Indoor Indoor Indoor Indoor Dust Water River River River Effluent Effluent Rain Roof Groundwat. Sedim. River Marine Herring ……..Perch ……..Salmon Freshw. Perch Human milk	1-37 ng/m3 1-120 ng/m3 21-99 ng/m3 27 ng/m3 - ~ 380 ng/L 20-110 ng/L 70-1040 ng/L -810 ng/L 622 ng/L 910 ng/L 670-900 ng/L -1120 ng/L -50 µg/kg 3.4 ng/g lw 20ng/g lw 1.6 ng/g lw 81 ng/g lw 12 ng/g lw	Saito et al 2007 Marklund et al 2005 Carlsson et al 1997 Carlsson et al 2000 Andresen et al 2004 Martinez-C. et al 2007 Fries&Puttmann 2003 Martinez-C. et al 2007 Fries&Puttmann 2003 Fries&Puttmann 2003 Fries&Puttmann 2003 Fries&Puttmann 2003 Martinez-C. et al 2007 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010 Marklund-S et al 2010

Polyfluorinated compounds

Six specific polyfluorinated compounds (PFC) are on the case-study list (see Table 1). Four perflourocarboxylates/acids (PFCA) and two perfluoroalkyl sulfonates (PFAS), the latter two substituting PFOS. This was the only substance group where the literature search resulted in references concerning occurrence both in abiotic environments, in high trophic level animals (birds fish, seals) and in humans. See tables 5, 6, and 7.

Table 5. Scientific references found for the selected PFCs in abiotic environments

Name	CAS no	Use	Occurrence found	Conc. levels	Ref
Perfluorobutric acid, PFBA	375-22-4	surfactant	Tap water (n=13)	max 25 ng/L	Mak et al 2009
Perfluorhexanoic acid, PFHxA	307-24-4		River water (n=17) Surface River water (n=15) WWTP, effluent (n=9) Tap water (n=13)	max 5.3 ng/L max 5.0 ng/L 3.7-57.4 ng/L max 19 ng/L	So et al 2007 Ahrens et al 2009 Mak et al 2009
Perfluoroheptanoic acid, PFHpA	375-85-9		River water (n=17) Surface River water (n=15) WWTP, effluent (n=9) Tap water (n=13)	max 5 ng/L max 2.4 ng/L 1.6-15.7 ng/L max 6 ng/L	So et al 2007 Ahrens et al 2009 Mak et l 2009
Perfluordecanoic acid, PFDA	335-76-2		River water (n=17) WWTP, influent -"- , effluent -"- , sludge Surface River water (n=15) WWTP, effluent (n=9) Tap water	max 3.8 ng/L <1.6 ng/L <1.6-3.6 ng/L 1.2-32 µg/kg max 0.7 ng/L 0.9-34.5 ng/L < 0.5 ng/L	So et al 2007 Bossi et al 2008 Ahrens et al 2009 Mak et al 2009
Perfluorobutane sulfonate, PFBS	29420-49-3		River water (n=17) Surface River water (n=15) WWTP, effluent (n=9) Tap water (n=13)	max 3.4 ng/L max 3.4 ng/L max 25.9 ng/L max 16 ng/L	So et al 2007 Ahrens et al 2009 Mak et al 2009
Perfluorohexane sulfonate, PFHxS	3871-99-6		River water (n=17) WWTP, influent -"- , effluent -"- , sludge Surface River water (n=15) WWTP, effluent (n=9) Tap water (n=12) -"- extreme value (India)	<0.4 ng/L <0.2-32.8 ng/L <0.2-2.7 ng/L 0.4-10.7 µg/kg max 1.3 ng/L max 6.3 ng/L <1 ng/L 81 ng/L	So et al 2007 Bossi et al 2008 Ahrens et al 2009 Mak et al 2009

Table 6. Scientific references found for the selected PFCs in wildlife.

Name	CAS no	Use	Occurrence found	Conc. levels (ng/g ww)	Ref
Perfluorobutric acid, PFBA	375-22-4				
Perfluorhexanoic acid, PFHxA	307-24-4		Arctic cod, Several species	0.6-5.4 <LOD (0.3)	Haukås et al 2007 Powley et al 2008
Perfluoroheptanoic acid, PFHpA	375-85-9		Ringed seal Baikal seal, liver serum Fur seal pup, muscle -"- liver Gentoo penguin egg Adélie penguin, egg	<1.6 <0.6 (♂,♀) <0.3-8.2 (♂,) <0.3-2.0 (♀) 0.5±0.3 1.0±1.9 <0.5 2.5±5.5	Butt et al 2007 Isibashi et al 2008 Schiavone et al 2009
Perfluordecanoic acid, PFDA	335-76-2		Harbor seal, kidney, liver, muscle, spleen Ringed seal, liver Baikal seal, liver serum Arctic cod Ringed seal, blubber -"- blood -"- liver Bearded seal, liver Guillemots, egg Fur seal pup, liver Gentoo penguin, egg Adélie penguin, egg	nd-46 , 1.8-14 nd-15, 6.1-22, respectively 0.1-10 <0.6-26(♂,) 1.1-35 (♀) <0.3-3.1(♂,) <0.3-1.4 (♀) 0.3-0.5 <0.2 0.4-1.1 2.0-3.3 0.4 nd-110 0.6±0.5 0.1±0.2 1.3±2.9	van de Vijver et al 2005 Butt et al 2007 Isibashi et al 2008 Powley et al 2008 Löfstrand et al 2008 Schiavone et al 2009
Perfluorobutane sulfonate, PFBS	29420-49-3		Harbor seal, spleen	1.7-3.3	van de Vijver et al 2005
Perfluorohexane sulfonate, PFHxS	3871-99-6		Baikal seal, liver serum	<0.6 (♂,♀) <0.1-0.6 (♂,) <0.1-0.3 (♀)	Isibashi et al 2008

Table 7. Scientific references found for the selected PFCs in human tissues

Name	CAS no	Use	Occurrence found	Conc. levels	Ref
Perfluorobutric acid, PFBA	375-22-4				
Perfluorhexanoic acid, PFHxA	307-24-4		Human whole blood	4-65 pg/mL	Falandysz et al 2006
Perfluoroheptanoic acid, PFHpA	375-85-9		Human whole blood	17-470 pg/mL	Falandysz et al 2006
Perfluordecanoic acid, PFDA	335-76-2		Human whole blood Human milk (China, n=19)	90-510 pg/mL 15 ng/L	Falandysz et al 2006 So et al 2007
Perfluorobutane sulfonate, PFBS	29420-49-3		Human whole blood	<2 ng/mL	Falandysz et al 2006
Perfluorohexane sulfonate, PFHxS	3871-99-6		Human whole blood Human whole blood, ♂+♀ Human milk (China, n=19) Human milk (n=12) Human milk (n=51) Human milk (n=23) Human milk (n=10)	170-1000 pg/mL 1.4-4.0 ng/mL 100 ng/L 16-51 ng/L -25 ng/L <12-64 ng/L 20-110 ng/L	Falandysz et al 2006 Kärrman et al 2006 So et al 2007 Kärrman et al 2007 Nakata et al 2007 Tao et al 2008 Kärrman et al 2010

Phthalate esters

Only one phthalate ester, Di-isononyl phthalate (DINP) (28553-12-0), is on the list (Table 1). DINP is a complex branched phthalate (C-9), with a large number of isomers. It is a widely used plasticiser in flexible PVC plastic (e.g. toys). According to Kavlock et al (2002), and based on very limited monitoring data for DINP in air, drinking- surface- and ground water, only trace concentrations of DINP have been reported in the matrices mentioned above.

The literature search showed very few references concerning occurrence in the environment. Björklund et al (2009) studied DINP in urban runoff. In a study of 8 DPEs (including DINP), MacIntosh et al (2004) reports that the tested compounds did not biomagnified in a marine aquatic food web. Silva et al (2006a and b) described the use of urine metabolites of DIMP as biomarkers of exposure in rats and humans. No reference were found on accumulation in vertebrates or human tissues. Bouma et al (2002) studied migration of phthalates from PVC toys into saliva (in vitro) and found that the studied compounds complied with the SCTEE guidance values. A method for monitoring emissions of hydrolysis products from phthalates is presented by Westberg et al (2009).

Table 8. References found for di-isononylphthalate (DINP) in the abiotic environment

Name	CAS no	Use	Occurrence found	Conc. levels	Ref
Di-isononylphthalat, DINP	4979-32-2	Plastiziser	Water Runoff Sedim.	0.3-90 µg/L ~200 µg/g dw	Björklund et al 2009 Björklund et al 2009

Concluding remarks

The most obvious result from the present survey is the lack of data for all but the PFCs and some data on OPCs and PEs. On one hand, these are compounds that have been attracting some interest over the recent years, on the other it is intriguingly few studies in relation to their industrial importance.

Far more data are required to allow exposure assessments in humans and wildlife, making even hazard assessments difficult.

References

Ahrens, L., Felizeter, s., Sturm, R., Xie, Z., Ebinghaus, R. 2009, Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany. *Marine Pollut Bull* 58, 1326–1333

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

Bacaloni, A., Cavaliere, C., Foglia, P., Nazzari, M., Samperi, R., Laganà, A. 2007, Liquid chromatography/tandem mass spectrometry determination of organophosphorus flame retardants and plasticizers in drinking and surface waters. *Rapid Commun Mass Spectrom* 21, 1123–1130

Björklund, K, Palm-Cousins, A., Strömvall, A-M., Malmqvist, P-A. Phthalates and nonylphenols in urban runoff: Occurrence, distribution and area emission factors. *Sci Tot Environ* 2009, 407, 4665–4672

Bossi, R., Strand, J., Sortkjaer, O., Larsen, M.M. 2008, Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. *Environ Intern* 34, 443–450

Bouma, K. and Schakel, D.J. 2002, Migration of phthalates from PVC toys into saliva stimulant by dynamic extraction. *Food Additives and Contaminants* 19, 602-610

Butt, C., Muir, D.G., Stirling, I., Kwan, M., Mabury, S., 2007, Rapid response of arctic ringed seals to changes in perfluoroalkyl production. *Environ Sci Technol* 41, 42-49

Calafat, A.M., Wong, L-Y., Kuklenyik, Z., Reidy, J.A., Needham, L.L. 2007, Polyfluoroalkyl Chemicals in the U.S. Population: Data from the National Health and Nutrition Examination Survey (NHANES) 2003–2004 and Comparisons with NHANES 1999–2000. *Environ Health Persp* 115, 1596-1602

Carlsson, H., Nilsson, U., Becker, G., Östman, C. 1997, Organophosphate ester flame retardants and plasticizers in the inddor environment: Analytical methodology and occurence. *Environ Sci Technol* 31, 2931-2936

Carlsson, H., Nilsson, U., Östman, C. 2000, Video display units: An emission source of the contact allergenic flame retardant triphenyl phosphate in the indoor environment. *Environ Sci Technol* 34, 3885-3889

Falndysz, J., Tanuyasu, S., Gulkowka, A., Yamashita, N., Schulte-Oehlmann, U. 2006, Is Fish a Major Source of Fluorinated Surfactants and Repellents in Humans Living on the Baltic Coast? *Environ. Sci. Technol.* 40, 748-751

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

Kavlock, R., Boekelheide, Chapin, K.R., Cunningham, M., Faustman, E. et al. 2002, NTP Center for the Evaluation of Risks to Human Reproduction: phthalates expert panel report on the reproductive and developmental toxicity of di-isononyl phthalate. *Repr Toxicol* 16, 679–708

Fukuoka, M., Satoh, M., Tanaka, A. 1995, Metabolism of 2-thiobenzothiazoles in the rat; Urinary, faecal and biliary metabolites of 2-benzothiazyl sulfenamides. *Arch Toxicol* 70, 1-9

Haukås, M., Berger, U., Hop, H., Gulliksen, B., Gabrielsen, G.W. 2007, Bioaccumulation of per- and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web. *Environ Pollut* 148, 360e371

Isibashi, H., Iwata, H., Kim, E-Y., Tao, L., Kannan, K., Amano, M., Miazaki, N., Tanabe, S., Batoev, V.B., Petrov, E. 2008, Contamination and effects of perfluorochemicals in baikal seal (*Pusa sibirica*). 1. Residue level, tissue distribution, and temporal trend. *Environ. Sci. Technol. 42,* 2295–2301.

Jonsson, O.B.,, Dyremark, E., Nilsson, U.L. 2001, Development of a microporous membrane liquid–liquid extractor for organophosphate esters in human blood plasma: identification of triphenyl phosphate and octyl diphenyl phosphate in donor plasma. *J Chromatogr B* 755, 157–164

Khoroshko, L.O., Petrova, V.N., Viktorovskii, I.V., Lahtiperä, M., Sinkkonen, S., Paasivirta, J. 2005,
A wood preservative metabolite in river water. *Environ Sci & Pollut Res* 12 (1) 8–9

Kloepfler, A., Jekel, M., Reemtsa, T. 2005, Occurrence, sources, and fate of benzothiazoles in municipal wastewater treatment plants. *Environ Sci Technol* 39, 3792-3798

Kumata, H., Sanada, Y., Takada, H., Ueno, T. 2000, Historical trends of N-cyklohexyl-2-benzothiazoleamine, 2-(4-morpholinyl)benzothiazole, and other anthropogenic contaminants in the urban reservoir sediment core. *Environ Sci Technol* 34, 246–253

Kärrman, A., van Bavel, B., Järnberg, U., Hardell, L., Lindström, G. 2006, Perfluorinated chemicals in relation to other persistent organic pollutants in human blood. *Chemosphere* 64, 2582-1591

Kärrman, A., Domingo, J.L., Llebaria, X., Nadal, M., Bigas, E., Lindström, G. 2010, Biomonitoring perfluorinated compounds in Catalonia, Spain: concentrations and trends in human liver and milk samples. *Environ Sci Pollut Res* 17, 750–758

Löfstrand, K. Jörundsdóttir, H., Gregg, T., Svavarson, J., Weihe, P., Nygård, T., Bergman, Å. 2008, Spatial trends of polyfluorinated compounds in guillemot ((Uria aalge<9 rggs from North-western Europe. Chemosphere 72, 1475-1480.

Mak, Y.L., Taniyasu, S., Yeung, L.W.Y., Lu, G., Jin, L., Yang, Y., Lam, P.K.S., Kannan, K., Yamashita, N. 2009, Perfluorinated Compounds in TapWater from China and Several Other Countries. *Environ. Sci. Technol.* 43, 4824–4829

Manninen, A., Seppo, A.S.,Vartiainen, M., Liesivuori, J., Turunen, T., Pasanen, M. 1996, Determination of urinary 2-mercaptobenzothiazole (2-MBT), the main metabolite of 2-(thiocyanomethylthio)benzothiazole (TCMTB) in humans and rats. *Arch Toxicol* 70, 579-584

Marklund, A., Andersson, B., Haglund, P. 2005, Organophosphorus flame retardands and plasticizers in air from various indoor environments. *J Environ Monit* 7, 814-819

Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S, Gans, O. 2007, Determination of selected organophosphate esters in the aquatic environment of Austria. *Sci Tot Environ* 388, 290–299

Nakata, H., Murata, S., Filatreau, J. Occurrence and concentrations of benzotriazole UV Stabilizers in marine organisms and sediments from the Ariake Sea, Japan. *Environ. Sci. Technol.* 2009, *43,* 6920–6926.

Powly, C.R., George, S.W., Rusell, M.H., Hoke, R.A., Buck, R.C. 2008, Polyfluorinated chemicals in a spatially and temporally integrated food web in the Western Arctic. *Chemosphere* 70, 664–672

Reddy, C.M., Quinn, J.G., King, J.W. 2000, Free and bound benzotriazoles in marine and freshwater sediments. *Environ. Sci. Technol.* 34, 973-979

Reemtsma, T., Fiehn, O., Kalnowski, G., Jekel, M. 1995, Microbial transformations and biological effects of fungicide-derived benzothiazoles determined in Industrial wastewater. *Environ. Sci. Technol.* 29, 478–485

Saito, I., Onuki, A., Seto, H. 2007, Indoor organophosphate and polybrominated flame retardants in Tokyo. *Indoor Air* 17: 28–36

Schiavone, A., Corsoloni, S., Kannan, K., Trivelpiece, L.T.W., Torres Jr, D., Focardi, S. 2009, Perfluorinated contaminants in fur seal pups and penguin eggs from South Shetland, Antarctica. *Sci Tot Environ* 407, 3899–3904

Schindler, B.K., Förster, K., Angerer, J. 2009, Determination of human urinary organophosphate flame retardant metabolites. *J Chromatogr B*, 877, 375–381

Silva, M.J., Kato, K,, Wolf, C., Samandar, E., Silva, S.S., Gray, E.L., Needham, L.L,, Calafat. A,M. 2006, Urinary biomarkers of di-isononyl phthalate in rats. *Toxicology* 223 101–112

Silva, M.J., Reidy, J.A., Preau, J.L., Needham, L.L., Calafat, A.M. 2006, Oxidative metabolites of diisononyl pthalate as biomarkers for human exposure assessment. *Environ Health Perspect* 2006, 114,8 , 2006

Staaf, T., Östman, C., 2006, Organophosphate triesters in indoor environments. *J Environ Monitor* 2005, 7(9), 883-887

Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., et al. 2009, Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environ Sci Technol.* 2009, 43, 7490-7495-947

So, M.K., Miyake, Y., Yeung, W:Y:, Ho, Y.M., Taniyasu, S., Rostkowski, P., Yamashita, N., Zhou, B.S., Shi, X.J., Wang, J.X., Giesy, J.P., Yu, H., Lam P.K.S. 2007, Perfluorinated compounds in the Pearl River and Yangtze River of China. *Chemosphere* 68, 2085–2095

van Leerdam,, J.A., Hogenboom, A.C., van der Kooia, M.M.E., de Voogta, P. 2009, Determination of polar 1H-benzotriazoles and benzothiazoles in water by solid-phase extraction and liquid chromatography LTQ FT Orbitrap mass Spectrometry. *Int J Mass Spectrom* 282, 99–107

Tao, L., Kannan, K., Aldous, K.M., Mauer, M.P., Eadon, G.A. 2008, Biomonitoring of perfluorochemicals in plasma of New York State personnel responding to the World Trade Center disaster, *Environ Sci Technol* 42, 3472-3478

Weiss, S. and Reemtsma, T. 2005, Determination of Benzotriazole Corrosion Inhibitors from Aqueous Environmental Samples by Liquid Chromatography-Electrospray Ionization-Tandem Mass Spectrometry.
Anal Chem 77, 7415-7420

Westberg, Å., Momcilovic, D., Björk, F., Karlsson, S. 2009, Quality assessment of building products by the micro-scale headspace vial (MHV) method and HS-SPME for monitoring the emission of hydrolysis products from phthalates. *Polymer Degradation and Stability* 94*,* 914–920

van de Vijver, K. I., Hoff, P., Das, K., Brasseur, S., van Dongen, W., Esmans, E., Reijnders, P., Bludt, R., de Coen, W. 2005, Tissue distribution of perfluorinated chemicals in harbor seals (*Phoca vitulina*) from the Dutch Wadden Sea. *Environ. Sci. Technol.* 39, 6978-6984