

# Danger: Dust



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# DANGER: DUST



## WILL REACH PROTECT THE PUBLIC FROM THE PBDES, PHTHALATES AND NONYLPHENOLS CURRENTLY FOUND IN DUST AND RAINWATER IN THE CZECH REPUBLIC?

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The exposure of people – and particularly children - in the Czech republic to elevated levels of chlorinated dioxins, furans and PCBs confirmed in 2004 gave cause for concern about human exposure levels to anthropogenic chemicals<sup>1</sup>. This study reports on the risks of exposures to a wider range of man made chemicals from dust in buildings. Many of these chemicals are similar to PCBs and dioxins and they are, or are likely to be, hazardous to health. The results are considered in the context of the new regulatory system for chemicals currently being established in the European Union.

### Introduction

On 27 February 2001 the European Commission issued a White Paper on a Strategy for a future Chemicals Policy. This was in many ways a ground breaking and inspiring document which promised fundamental changes in the way that chemicals were regulated and controlled. The Commission wrote: "We have decided on a step-by-step approach to phase out and substitute the most dangerous substances - the ones that

cause cancer, accumulate in our bodies and in our environment and affect our ability to reproduce. This decision is crucial for future generations"<sup>2</sup>.

The White Paper evolved and resulted in the release on 29th Oct 2003 of the Commission's proposal for the Registration, Evaluation and Authorisation of Chemicals (REACH). Sustained attacks and intensive lobbying by some industrial interests have sadly undermined and weakened the worthy ambitions of the Commission and the proposals have gradually been diluted and compromised.

Nonetheless the European Parliament first reading was finalised on the 17th of November 2005 and the Council reached a political agreement on the 13th of December 2005<sup>3</sup>. A common position was then reached by the Council on 12th June 2006<sup>4</sup>.

The REACH regulations should now enter into force in 2007. When it does come into force an 'acid test' will be how effectively the new regulations protect the public from exposure to dangerous chemicals.

This report considers three such classes of chemicals for which the current regulatory systems are completely inadequate and to which the public are being exposed in their homes and offices – and of which thousands of tonnes every year have been added to consumer products in spite of hardly any data being available on the human or ecotoxicity of the products or their metabolites. It is hoped that the REACH legislation will result in such exposure being purely a historical artefact.

Two key benefits of REACH should be the much greater rapidity of decision-making than under existing EU rules, and the availability of data on substitutes for substances found to pose unacceptable risks. It is certainly vital to speed up the process – the risks associated with the chemicals considered in this report have been known for at least 30 years and effective regulatory action has been slow to take effect and has completely failed to eliminate the chemicals from the environment. Given the scale of assessments required for REACH it is difficult to be optimistic that progress will happen quickly enough to avoid a repeat of the terrible human and environmental consequences that arose from the mistakes of the past.

In the future enterprises that manufacture or import more than one tonne of a chemical substance per year will be required to register it in a central database. Furthermore REACH will give greater responsibility to industry to manage the risks from chemicals and to provide users in the supply chain with safety information on the substances.

Substances “of very high concern” will be evaluated as a priority by the European Chemicals Agency – this should include chemicals linked with causing cancer, genetic mutations or reproductive problems and which tend to build up in the human body and the environment<sup>1</sup>.

The European chemicals agency will still be able to authorise chemicals of very high concern in cases where their replacement proves too difficult, too costly or when there are no alternatives. The EU Council of Ministers agreed in December 2005<sup>3</sup> that the agency would be able to allow the temporary use of these chemicals but the conditions are outlined in the authorisation provisions Common Position as ensuring “the good functioning of the internal market while assuring that the risks from substances of very high concern are properly controlled. Authorisations for the placing on the market and use should be granted by the Commission only if the risks arising from their use are adequately controlled, where this is possible, or the use can be justified for socio-economic reasons and no suitable alternatives are available, which are economically and technically viable.”

Unfortunately this leaves grave concerns that the groups of chemicals considered in this study may remain in production and use for longer than necessary. They are:

- Polybrominated diphenyl ethers (PBDEs) are halo-organic molecules used as additive flame-retardants in a variety of plastics, textiles, surface coatings, foams and man made fibres.
- Phthalates are a group of chemicals mainly used to soften and increase the flexibility of plastic and polyvinylchloride (PVC). They are thus used in hundreds of consumer products.
- Nonylphenols are used as dispersing agents in paper and pulp production, emulsifying agents in paints and pesticides, spermicides, industrial cleaners and the manufacture of plastics together with many other uses.

Although the nonylphenols and phthalates are important pollutants this report has focused particularly on the PBDEs. The levels which have been found here and in other studies are of particular concern given the mounting evidence that the toxicity of these chemicals actually increase after release into the environment. Already they have been shown to be persistent in living organisms and to biomagnify up the food chain. A wide range of biota is contaminated with PBDEs including vegetables, farm animals, fish, aquatic mammals and birds. They have also been found in human adipose tissue, human hair, blood plasma and breast milk.

It had been thought that the main exposure pathway was from food but it is of particular concern that recent research indicates that dust from homes and offices can be a significant source of exposure to these compounds, and probably the other chemicals considered in this review.

This study reports the results of the detailed analysis of four dust and four rain samples from the Czech Republic. These samples were all analysed for PBDEs, phthalates and nonyl-phenols. The report also briefly reviews the science of these chemicals, and particularly PBDEs, in the context of these sample results and makes recommendations for future regulatory action and sampling programmes.

These recommendations include the inclusion of all the chemicals considered here that are not already subject to bans to be included on the “candidate list” of substances that are considered to meet the

“substances of very high concern” criteria. It is expected that this “candidate list” will be published by the end of 2008 on the basis of substances nominated by Member States and may contain up to 1500 chemicals. The inclusion of chemicals on that list should, it is hoped, provide a powerful incentive for users to move to safer alternatives and to phase out those chemicals as rapidly as possible. That incentive may be the most powerful and protective element of REACH in practice.

In 2003 The Royal Commission on Environmental Pollution in the United Kingdom concluded a review of Chemicals in Products saying: “At the very least, we recommend that where synthetic chemicals are found in elevated concentrations in biological fluids such as breast milk and tissues of humans, marine mammals or top predators, regulatory steps be taken to remove them from the market immediately”. Dust can provide a significant part of the human intake for some chemicals and urgent steps need to be taken to avoid a repeat of the levels of contamination - and human harm - that we have seen with pollutants like PCBs.

### Results of the Czech Sampling Programme

As part of this project samples of both dust and rainwater were collected and analysed. The details of the sampling and analytical procedures are outlined in Annex 2.

### The Dust Samples

Four dust samples were taken the locations indicated in the table below:

Reference	Location
4250	Prague - Prague office of Dr. Martina Bursík, chairman of the Green Party, Sněmovní 7
4251	Ústí nad Labem - office of the head of the Regional Authority, Jiří Šulc
4252	Hydrometeorological observatory ČHMU on the top of mountain Churáňov
4253	Ostrava - Regional Authority building in Moravia-Silesian Region



The results confirm that the office dusts contain a wide range of brominated flame-retardants together with significant levels of phthalates and nonylphenols.

**Polybrominated diphenyl ethers(PBDEs)**

The table below compares the levels of PBDEs found with similar recent studies around the world

Congener	Penta					Octa			Deca	Total	Reference
	28	47	100	99	85	154	153	183	209	Σ PBDEs	
Finland	0.1	9.9	3.5	8.8	1.8	0.8	3.8	ND	100.0	128.7	5
Denmark	3.0	66.0	11.0	ND	1.9	1.8	23.0	11.0	260.0	377.7	5
UKa	4.1	223.0	33.0	287.0	12.2	16.8	33.8	19.2	9,820.0	10,449.1	5
USAb	20.7	1,220.0	274.0	1,700.0	83.4	156.0	181.0	30.7	2,090.0	5,755.8	6
USAc	ND	1,857.0	911.0	2,352.0	100.0	136.0	243.0	60.4	8,286.0	13,965.4	7
Italy	2.8	89.0	15.0	59.0	3.3	5.4	21.0	ND	6,900.0	7,095.5	8
Netherlands	ND	97.0	30.0	130.0	7.4	11.0	48.0	ND	800.0	1,123.4	8
Sweden	1.0	78.0	19.0	68.0	31.0	5.0	9.8	ND	700.0	883.9	8
Austria	3.0	64.0	23.0	72.0	5.4	9.4	18.0	ND	510.0	704.8	8
Germany	6.9	8.0	14.0	50.0	2.9	6.3	17.0	ND	1,500.0	1,677.1	8
Kuwait	0.6	10.4	1.7	8.9	1.0	1.9	1.8	5.3	202.7	233.6	9
Czech Republic:											
5083-01d		30	<20	80		<20	<20	<20	<20		10
5083-02 e		160	<20	40		<20	30	60	330		10
5083-03 e		120	<20	50		<20	40	70	440		10
4250	0.657	31.60	8.90	54.0		4.89	16.80	123.00	185		This study
4251	0.336	5.94	1.96	10.7		1.82	5.89	34.30	542		This study
4252	0.928	84.90	21.20	98.4		6.10	6.03	9.67	90.8		This study
4253	0.408	14.80	1.84	9.6		0.83	1.63	5.89	199		This study

- a Average of 100 homes.
- b Average of 17 homes.
- c Average of 10 homes.
- d House dust
- e Office dust

There are some difficulties in comparing data on, particularly, total PBDEs from studies in which different suites of BDE congeners have been determined. The usual approach is to take the sum of PBDEs 17,28,47,66,85,99,100,138,153,184, and 190. A welcome new approach with a common suite which will

allow the study of all three commercial PBDE formulations has recently been suggested in an attempt to overcome this <sup>11</sup>.

Harrad reported total PBDE in dust levels from selected studies as:

That study minimum	16.2	Harrad <sup>12</sup>
average	215.2	Harrad <sup>12</sup>
median	87.1	Harrad <sup>12</sup>
maximum	625.4	Harrad <sup>12</sup>
minimum, Ottawa	64	Wilford <sup>13</sup>
maximum, Ottawa	170,000	Wilford <sup>13</sup>
average, Ottawa	4500	Wilford <sup>13</sup>
Minimum Spain	2.9	Fabrellas <sup>14</sup>
Maximum, Spain	380.2	Fabrellas <sup>14</sup>
average, Spain	36.6	Fabrellas <sup>14</sup>
Minimum, Belgium	6.2	Fabrellas <sup>14</sup>
maximum, Belgium	384.8	Fabrellas <sup>14</sup>
average, Belgium	58.7	Fabrellas <sup>14</sup>

In this study the highest levels of PBDEs were, perhaps not surprisingly, Deca-BDE (209) followed by DBE-183, 99 and 47.

The pattern of PBDE congeners in biological samples is usually quite similar to that of the commercial PentaBDE mixture, with BDE-47, BDE-99 and BDE-100 predominating. Although there the relative concentrations varied this is broadly consistent with the levels of human breast milk contamination in the Czech republic reported by Hajslova et al.<sup>15</sup>. These results did not include Deca (BDE209) but found that the highest concentrations in breast milk were BDE 47 followed by BDE 183 and BDE 99.

The technical mixtures of Penta, Octa and, to a lesser extent, Deca, do vary to some extent and so some variation is expected in the environmental contamination levels – particularly if there may have been some degradation in the environment.

Whilst it must be said that the levels of PBDEs found in dust in the Czech republic are not particularly high compared with those reported in the United States they were generally of the same order as reported elsewhere in Europe. This does not give any reassurance that the levels can be considered safe or acceptable, however, as discussed further below.



## Phthalates

The results for the range of phthalates analysed, compared with data from the US are:

			This study				TNO/Greenpeace Czech Rep (a)			US Results (b)
			4250	4251	4252	4253	5083-01	5083-02	5083-03	Max Concs
			µg/g	µg/g	µg/g	µg/g				
131-11-3	DIMETHYL PHTHALATE	DMP	< 1.6	< 3.4	< 2.3	< 1.6	1.0	0.55	0.78	0.272
84-66-2	DIETHYL PHTHALATE	DEP	< 2.0	22	4.0	8.6	7.8	3.0	5.5	3.58
84-69-5	DIISOBUTYL PHTHALATE	DiBP	4.7	42	44	77	52	16	27	8.35
84-74-2	DI-N-BUTYL PHTHALATE	DBP	20	84	460	93	130	66	105	49.5
117-82-8	BIS(2-METHOXYETHYL) PHTHALATE	DMEP	< 34	< 68	< 42	< 32	NR	NR	NR	
146-50-9	BIS (4 METHYL 2 PENTYL) PHTHALATE		< 2.7	< 5.4	< 3.4	< 2.6	NR	NR	NR	
?	BIS (ETHOXY ETHYL) PHTHALATE		< 35	< 64	< 30	< 26	NR	NR	NR	
131-18-0	DIAMYLPHthalate (Dipentyl phthalate)		< 1.8	< 3.3	< 1.5	< 1.3	NR	NR	NR	
84-75-3	DI HEXYL PHTHALATE	DHXP	< 2.2	< 3.9	< 1.9	< 1.6	NR	NR	NR	
85-68-7	BUTYLBENZYLPHthalate	BBzP	< 2.6	< 11	< 5.6	20	41	20	299	137
117-83-9	BIS(2-BUTOXYETHYL) PHTHALATE	BEP	< 10	< 41	< 22	< 18	NR	NR	NR	
84-61-7	DI-CYCLOHEXYL PHTHALATE (DICYCLOHEXYL ESTER)	DCHP	10	< 6.9	< 3.6	< 3.0	1.3	0.21	0.76	
117-81-7	BIS(2-ETHYLHEXYL) PHTHALATE	DEHP	10	810	2400	1900	250	102	169	425
117-84-0	DI-N-OCTYLPHthalate	DOP	< 3.2	5.8	3.5	4.7	3.2	1.6	23	
84-76-4	DINONYLPHthalate	DNP	< 4.0	< 7.3	< 3.4	< 3.4				
	Sum of Phthalates		45	964	2,912	2,103				

a) Greenpeace Czech republic<sup>10</sup>

b) US Results from Costner<sup>16</sup>

Other data on dust contamination by DEHP has been reported by Becker<sup>17</sup> (all mg/kg) and Axel<sup>18</sup>:

	P50	P95	Study
Urban and rural homes N=252	515	1840	Becker <sup>17</sup>
Hamburg N=65	600	1600	Kersten and Reich in 17
Private homes N= 272	450	2000	Pohner in 17
Northern Germany N=286	740	2600	Butte and Heinzow in 17
German Env Survey N=199	416	1190	Becker 2002 in 17
Denmark Schools N=15	3,214	7,063	Axel <sup>18</sup>
Denmark Homes	858	2,595	Clausen in Axel <sup>18</sup>
Norway 1997	640		Oie Axel <sup>18</sup>

P50 = 50th percentile P95= 95th Percentile

The phthalates of most concern in relation to the dust concentrations found in this study were:

1) DEHP, which had by far the largest concentrations and the levels found were 5 or more times greater than previously reported in the Czech Republic. The results for samples 4252 and 4253 are also very high compared with levels reported by Costner and Thorpe in the US. Only the levels in schools in Denmark together with homes in Denmark and one study in Germany exceeded the highest level found in this study and then only at the 95 %ile level.

2) DBP, particularly in sample 4252, which is again significantly higher than previous results in the Czech republic and nearly ten times higher than US maximum levels.

3) DiBP, which apart from a slightly elevated concentration in sample 4253 are consistent with previous results. The levels in the Czech Republic are generally elevated compared with US levels; and

4) DEP which are higher than previous results and those from the US in sample 4251.



**Nonylphenols**

The results are presented in the table below and compared with data from the United States.

	CAS No.	This study				US Study (a)	
		4250	4251	4252	4253	5083-01	5083-02
		µg/g	µg/g	µg/g	µg/g		
T-OCTYLPHENOL	1806-26-4	99	370	70	220	3,410	394
N-OCTYLPHENOL 1-(P-HYDROXYPHENYL)OCTANE	1806-26-4	< 20	< 38	< 21	< 20		
P-N-NONYLPHENOL	104-40-5	< 49	< 92	< 50	< 48		
P-NONYLPHENOL	104-40-5	3,300	6,900	4,500	20,000	10,500	3,740
4-NONYLPHENOL MONO-ETHOXYLATE	9016-45-9	1,900	890	500	4,100	14,800	3,720
4-NONYLPHENOL DI-ETHOXYLATE	20427-84-3	1,100	780	1,800	4,400	17,900	5,850

(a) US Results from Costner <sup>16</sup>

The levels of nonylphenol found in the Ostrava regional authority building are particularly notable and are approximately twice the maximum concentrations reported in the US study by Costner.

It is significant that nonylphenol was found at reasonably high levels in all samples as when Wilson sampled dust in the US she reported<sup>19</sup> that Nonylphenol (NP) was detected in less than 11% of the samples in any medium.

**Rainwater**

Four samples of rainwater were taken from the locations in the table below:

Reference	Location
4144	Ostrava, Feroná
4254	Chlumova 17, Praha 3
4255	Ústí nad Labem, Základní škola v ulici Elišky Krásnohorské 310/76
4256	Hydrometeorologická stanice ČHMU na Churáňově

Results for PBDEs, Phthalates and nonylphenols in rainwater compared with results from the Netherlands were:

		This study				20 Netherlands		
		4144	4254	4255	4256			
		pg/l	pg/l	µpg/l	pg/l	pg/l	pg/l	
BDE28		< 13	52	37	13	11,400	570	17,100
BDE47		123	677	366	83	4,400	1,400	8,000
BDE100		< 10	80	60	22	2,100	1,300	2,900
BDE99		58	469	153	51	4,700	1,500	8,800
BDE154		21	72	56	16	1,000	1,000	1,000
BDE153		24	121	113	27	2,400	800	3,900
BDE183		49	178	129	44	5,500	2,300	9,500
BDE196		<150	<180	<2200	<110			
BDE206		<230	<270	<3,300	<170			
BDE209		990	2,900	16,000	610	ND	ND	ND
<b>Phthalates</b>		ng/l	ng/l	ng/l	ng/l	ng/l	ng/l	ng/l
Dimethyl Phthalate	DMP	<8.8	10	8.4	7.7	82	22	750
Diethyl Phthalate	DEP	620	290	240	320	434	14	4050
Diisobutyl Phthalate	DiBP	1500	510	290	570	810	77	3976
Di N Butyl Phthalate	DBP	3600	1500	810	2600	498	139	1173
Di-Cyclohexyl Phthalate (Dicyclohexyl Ester)	DCHP	<16	96	<12	<15	38	10	196
Bis(2-Ethylhexyl)	DEHP	1,100	640	600	1,100	4,037	574	30,902
<b>Nonylphenols</b>								
T-Octylphenol		< 8.8	< 4.9	< 7.7	< 8.1	8.4	8.4	8.4
N-Octylphenol 1-(P-Hydroxyphenyl) Octane		< 23	< 13	< 20	< 21			
P-N-Nonylphenol		< 55	< 31	< 49	< 51			
P-Nonylphenol		165	< 42	< 65	< 68	97	256	42
4-Nonylphenol MonoEthoxylate		< 55	< 31	< 48	< 50	130	31	924
4-Nonylphenol Di-Ethoxylate		< 130	< 70	< 110	< 120			



Levels of contamination in rainwater are more difficult to compare with concentrations in other countries as there are few results that have been published and they are more variable depending upon the levels of rainfall prior to the sampling period.

The similarity with other POPs suggests that particle associated PBDEs are effectively removed during small precipitation episodes and that particle scavenging is an important mechanism for wet PBDE deposition<sup>21</sup>.

The more volatile (lower brominated) PBDEs dominate in the vapour phase, while BDE-209 (Deca-BDE) typically predominates on particulates<sup>22</sup>.

Whilst most of the PBDE levels appear rather low compared with the results from the Netherlands the Deca (BDE-209) levels are strikingly high – and particularly in sample 4255 at Usti nad Labem.

Similarly for most of the phthalates the results are again low compared with those from the Netherlands. However notable exceptions are the high levels of DBP which in 3 out of the four samples were higher than the Dutch levels – and more than three times greater in Ostrava. Notable also were the relatively low concentrations of DEHP in the rain compared with the levels in the dust – strongly indicating that the likely source of the high dust levels is from inside the offices – probably PVC products.

Nonylphenol levels were almost all below the limits of detection apart from one sample in Ostrava which was similar to levels reported in the Netherlands.

## Discussion about each group of the analyzed chemical compounds

### Phthalates

Phthalates are non-halogenated ester derivatives of phthalic acid which are widely used in a range of industrial and consumer applications.

Some are marketed as discreet chemical products (e.g. di(ethylhexyl) phthalate or DEHP), while others are complex isomeric mixtures comprising many individual compounds with similar chemical structures (e.g. di-iso-nonyl phthalate, DINP, and diiso-decyl phthalate, DIDP). As a result of their high volume uses in open applications, they are now among the most ubiquitous man-made chemicals found in the environment.

By far their greatest use is as plasticising (softening) additives in flexible plastics, especially PVC almost 1 million tonnes per year, primarily for use within the EU. Applications of PVC include consumer products such as flexible plastic and vinyl toys, shower curtains, wallpaper, vinyl miniblinds, food packaging, plastic wrap, building materials, and vinyl flooring.

Phthalates are also used in cosmetics and personal care products, including perfume, hair spray, soap, shampoo, nail polish, and skin moisturizers, wood finishes, detergents, adhesives, lubricants, medical tubing and fluid bags, solvents and insecticides.

All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal (amounting to thousands of tonnes per year across). As a consequence, phthalates have long been recognised as one

of the most abundant and widespread man-made environmental contaminants.

### Hazards

Phthalates are relatively persistent in the environment and can bioaccumulate. Substantial concerns also exist with regard to their toxicity to wildlife and to humans, although the precise mechanisms and levels of toxicity vary from one compound to another. In many cases, it is the metabolites of the phthalates which are responsible for the greatest toxicity<sup>23</sup>.

EU risk assessments for DEHP, DINP and DIDP concluded

that there were no significant risks to aquatic or terrestrial organisms. However, the EU's Scientific Committee on Toxicity, Ecotoxicity and the Environment has disagreed with this conclusion for the terrestrial environment, noting that there is very little evidence to justify such a conclusion. The CSTE has also highlighted concerns relating to secondary poisoning, i.e. the build up of phthalates through the food chain<sup>24</sup>.

DEHP, still the most widely used phthalate in Europe, is a known reproductive toxin, interfering with testes development in mammals, and is classified in the EU as "toxic to reproduction". Indeed, its toxicity to the developing male reproductive system has been recognised for more than 50 years<sup>25</sup>.

Observed toxicity is due mainly to the compound MEHP, formed in the body as a metabolite of DEHP, and appears to impact on many aspects of development and liver function, including hormone metabolism and immune function<sup>23</sup>.

### Control and regulation

In Europe this year three phthalate esters—including di(2-ethylhexyl) phthalate

(DEHP), the highest volume phthalate—will be permanently banned for use in toys, and another three—including diisononyl phthalate (DINP)—will be banned in toys that can be mouthed. The European Union has also banned some phthalates in cosmetics<sup>26</sup>.

Japan has a ban in place for DINP and DEHP in toys as well as a ban on DEHP in food-handling gloves. California has proposed similar bans on phthalates in toys.

Five Phthalates were listed for assessment under the EU existing substances regulations: butyl benzyl phthalate (BBP), dibutyl phthalate (DBP), diethylhexyl phthalate (DEHP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP).

The final assessments for DIDP, DINP and DBP were close to being published in 2001, and have changed little since, but became caught in a bureaucratic backlog (ENDS 318, pp 46-47). It is hoped that this is the sort of delay that REACH will help to avoid.

The European Commission published its first batch of phthalate risk assessments on 13th March 2006. It was concluded that controls are adequate for two of the three substances<sup>27</sup>.

The European Council for Plasticisers and Intermediates (ECPI) put out a statement welcoming the fact that "the most widely-used plasticisers are safe". But there is evidence that some of the compounds act as endocrine disruptors and may be responsible for reduced male fertility. While current controls on DIDP and DINP - including restrictions on their use in toys and childcare products - are thought sufficient, extra restrictions on DBP are said to be necessary to protect workers and the environment around production sites. The risk assessment for DEHP - the most important phthalate after DINP and DIDP - is also expected to recommend extra risk reduction measures<sup>28</sup>.



DEHP has been recognised as an endocrine disruptor for some time and the report has been amended to include a recent Scandinavian study which linked high levels in breast milk to suppressed testosterone levels in infant boys . An even more recent study shows reduced ano-genital distances in males born to mothers exposed to levels considerably below the current reference doses<sup>29,30</sup>.

DEHP' s use in medical products is under review, and its use in the food industry could be considerably restricted.

### Nonylphenols

Alkyphenols (APs), are non-halogenated chemicals manufactured almost exclusively to produce alkylphenoethoxylates (APEs), a group of non-ionic surfactants. The most widely used APEs are ethoxylates of nonylphenol (NPEs) and, to a lesser extent, octylphenol (OPEs).

Once released to the environment, APEs can degrade back to APs, which are persistent, bioaccumulative and toxic to aquatic life.

NPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications. Of the 77 000 tonnes used in Western Europe in 1997, the largest share (almost 30%) was used in industrial and institutional cleaning products (detergents), although uses such as emulsifiers (11%), textile finishers (10%), leather finishers (7%) and as components of pesticides and other agricultural products (6%) and water-based paints (5%) were also significant<sup>31</sup>.

Moreover, a substantial proportion (16%, or over 12 000 tonnes) was reportedly used in "other niche markets" (including

as ingredients in cosmetics, shampoos and other personal care products), or were simply "unaccounted for" .

The main hazards associated with APEs result from their partial degradation to shorter-chain ethoxylates and to the parent APs themselves (i.e. NP and OP), both of which are toxic to aquatic organisms. The EU risk assessment for nonylphenol identified significant risks through current uses of NPEs to the aquatic environment, to the soil and to higher organisms through secondary poisoning (i.e. resulting from the accumulation of NP through the food chain<sup>31</sup>).

With respect to human exposure through use in consumer products, the EU' s Scientific Committee on Toxicity, Ecotoxicity and the Environment<sup>32</sup> (CSTEE) concluded inter alia that the:- "serious lack of measured data for NP in connection with production and use of this compound and its derivatives makes the assessment of both occupational and consumer exposure uncertain" .<sup>24</sup> Adding "It will probably take a rather long time before the recommendation for further studies will result in an answer" .

### Brominated Flame Retardants

#### History

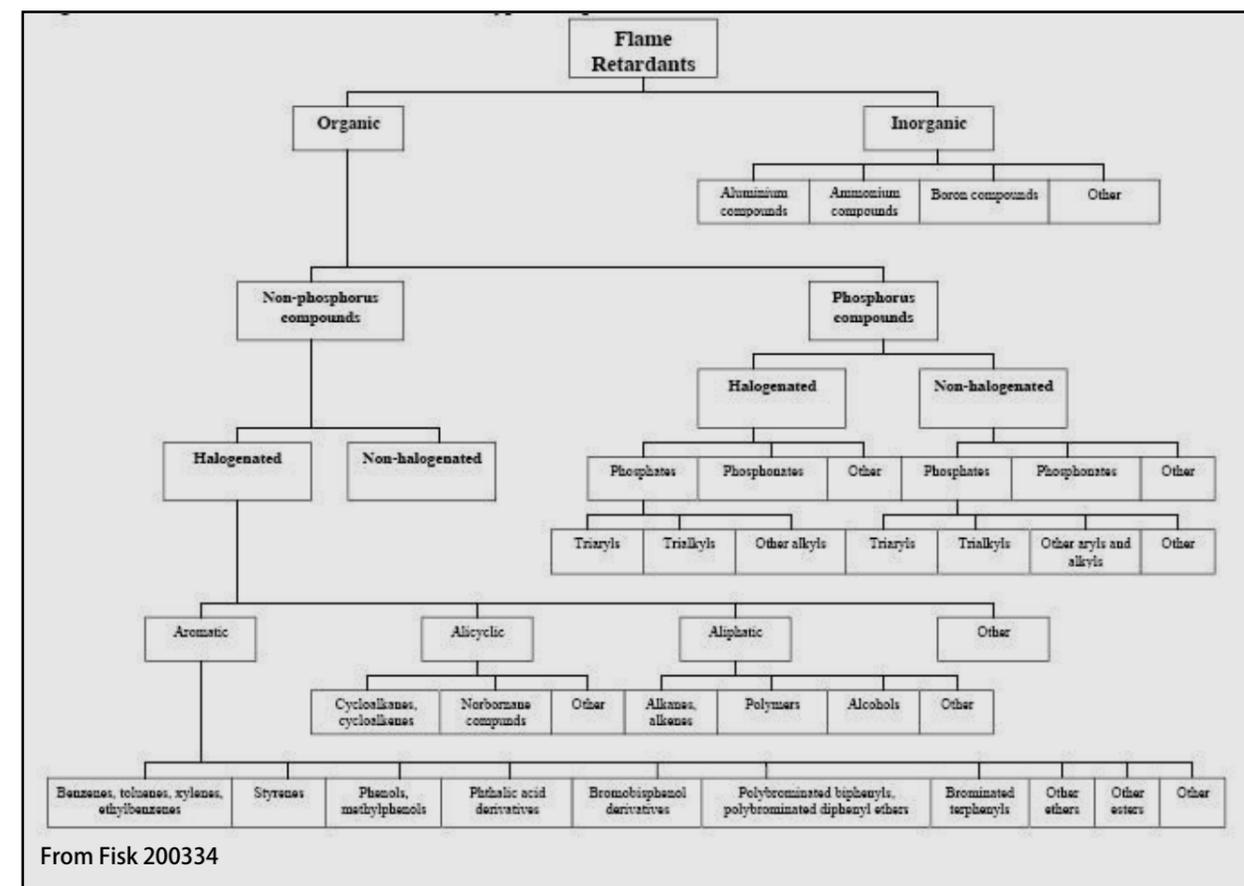
The use of flame retardant formulations dates back to at least Egyptian times:

Development	Date
Alum used to reduce the flammability of wood by the Egyptians	About 450 BC
The Romans used a mixture of alum and vinegar on wood	About 200 BC
Mixture of clay and gypsum used to reduce flammability of theatre curtains	1638
Mixture of alum, ferrous sulphate and borax used on wood and textiles by Wyld in Britain	1735
Alum used to reduce flammability of balloons	1783
Gay-Lussac reported a mixture of (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> , NH <sub>4</sub> Cl and borax to be effective on linen and hemp	1821
Perkin described a flame-retardant treatment for cotton using a mixture of sodium stannate and ammonium sulphate	1912

(Hindersinn, 1990 quoted by WHO <sup>33</sup>)

Modern chemistry has resulted in the use of more than 175 different flame retardant chemicals, divided into four major groups: inorganic, halogenated organic, organo-

phosphorus and nitrogen-based compounds and mixtures <sup>33</sup>. It is the brominated organic compounds which are the main focus of this report.



**Production and use of Brominated flame retardants and PBDEs**

PBDEs have been produced since the 1970's in increasingly larger quantities<sup>37</sup> by bromination of diphenyl ether in the presence of a Friedel-Craft catalyst (i.e., AlCl<sub>3</sub>) in a solvent such as dibromomethane<sup>37</sup>. Diphenyl ether molecules contain 10 hydrogen atoms, any of which can be exchanged with bromine, resulting in 209 possible congeners.

The commercial PBDEs mixtures are produced with three degrees of bromination (percentages vary depending upon the supplier and these values are approximate) : deca-, consisting of 97–98% decabromodiphenyl ether (DeBDE); octa-, consisting

of 10–12% hexabromodiphenyl ether (HxBDEs), 43–44% heptabromodiphenyl ether (HeptaBDE) and 31–35% octabromodiphenyl (OcBDEs); and penta-, consisting of 50–62% pentabromodiphenyl ether (PeBDEs) and 24–38% tetrabromodiphenyl ethers (TeBDEs)<sup>38</sup>.

In order to achieve the fire prevention capacity needed, up to 32% (by weight) of plastic products may be PBDEs (WHO, 1994).

Unfortunately the bromine industry has been reluctant to publish upto date information which would allow trends in the use of brominated flame-retardants to be derived. Consequently the last published data for World usage of brominated flame-retardants dates from 2001:

The usage of The selected brominated flame retardants in different areas of the world in 2001 (in tones)

	America	Europe	Asia	Rest of the world	Total	% of total world usage
TBBP-A	18 000	11 600	89 400	600	119 700	59
HBCD	2800	9500	3900	500	16 700	8
Deca-mix PBDE formulation	24 500	7600	23 000	1050	56 100	27
Octa-mix PBDE formulation	1500	610	1500	180	3790	2
Penta-mix PBDE formulation	7100	150	150	100	7500	4
Total	53 900	29 460	117 950	2430	203 790	

Law, Allchin et al. 2006<sup>11</sup>

The high levels of usage in North America are particularly notable – especially for Penta which even by 2001 had dropped to very low levels in Europe. After Tetrabromobisphenol A (TBBPA) PBDEs were the highest production group of BFRs in use at that time.

**Environmental Contamination**

Norstrom warned in a 1976 paper analysing the main flame retardants available at that time, including various PBDE formulations that “the use of brominated aromatics as flame retardants is a new potential source of environmental contamination”. They noted that the US market for brominated flame-retardants “rose from 20 million lb in 1971 to 45 million lb in 1973”. Their conclusion was “in our opinion and in the light of the PCB history and from other cases where halogenated aromatics have been released into the environment it is clear that such compounds are potential environmental hazards. Consequently their use ought to be controlled”<sup>39</sup>.

Unfortunately it took less than four years for their concerns to be vindicated and by 1980 PBDEs had been reported as being found around at least two production facilities. The first report of PBDEs in the wider environment was published in 1981 when Andersson found several PBDE isomers, mainly tetra and pentabrominated, in pike, bream, tench, sea trout and eels from Sweden<sup>40</sup>.

Because PBDEs are generally used as additives and they do not bind chemically to the products the chemicals may continuously leak to the environment<sup>41</sup>. Obvious potential sources include industries using PBDEs in their production (i.e. car producers, textile and electronic industries) and in the environment around these production sites. It is clear that some facilities are significant local sources and sediments and fish near textile industries (in River Viskan, Sweden) have, for example, shown to be heavily polluted with PBDEs<sup>42</sup>.

Leakage from readymade products (i.e. computers and electrical equipment, textiles, building material and vehicles) during usage

may also contribute to a considerable diffuse spread of PBDEs<sup>43</sup>.

It is also likely that combustion sources, particularly waste incinerators in urban areas, will also play a role in distributing PBDEs in the atmosphere<sup>44</sup>. Whilst it has been suggested that although traditionally the levels of brominated organics in waste have been low compared with chlorinated organics it is possible that during batchwise combustion including residues left after electrical and electronics recycling the levels of organic bromine will increase dramatically and may well rise to match the chlorine levels<sup>45</sup>. This raises concerns both in relation to PBDE emissions and also for the emissions of brominated dioxins.

Agrell and his co-workers suggested that treatment of waste is presently a source of ‘old’ PBDEs to the environment, whereas the BDE209 concentrations are a reflection of present use of BDE209 by society and diffuse leakage from products in use. They concluded that “emission of PBDEs to the atmosphere from waste treatment processes should be considered as important sources when assessing the transport of these substances in the environment”<sup>46</sup>. As the municipal waste incinerator in Prague is on the edge of the city, about 6 – 7 km from where the rain water sample was taken the influence on these samples is likely to be rather small. In this case it seems most likely that dust from office equipment and other flame retardants in buildings may well be the most significant source of PBDEs in large cities such as Prague. Prague has many more offices compared to Ostrava, which is an industrialized city.

However it is currently the case that no data seems to be available for emissions of PBDEs from incinerators in Prague to confirm whether they are a source of PBDEs in the urban area and it is recommended that a sampling programme should be initiated for



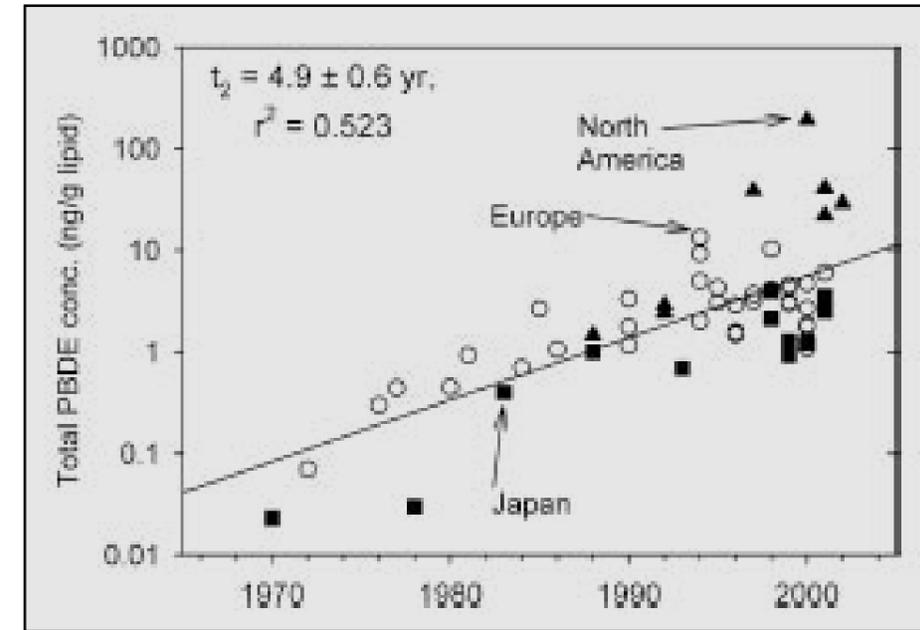
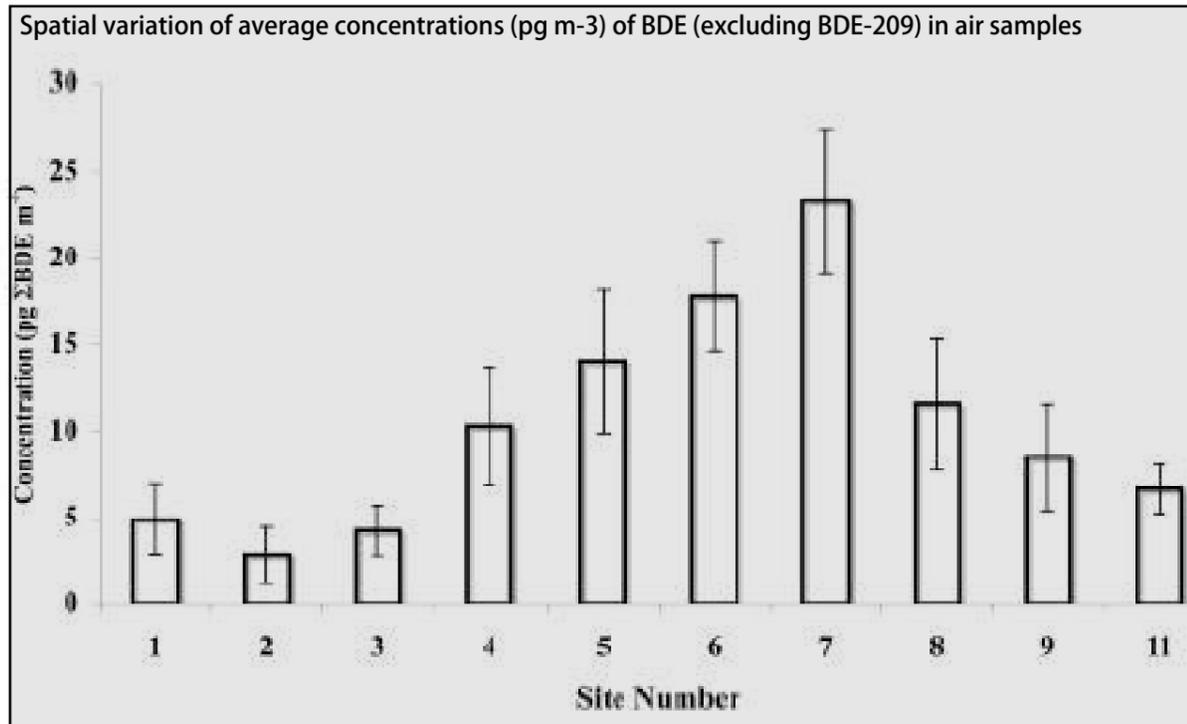
both PBDEs and brominated dioxins – if only to eliminate this established source from the need for further investigation.

Open burning of waste treated with flame-retardants may also be a significant source. Farrar and co-workers investigated ambient levels of PBDEs in November 2000 during the UK national bonfire festival held to commemorate the ‘Guy Fawkes gunpowder plot’ of 1605. Many thousands of bonfires are lit during the evening of 5th November, both as part of public displays and in people’s gardens. Unsurprisingly, concentrations of PAH increased sharply in

response to the widespread combustion, but levels of BDEs also increased at the suburban sampling location - and to a greater extent than those of the PAHs. Concentrations of BDE47 and BDE99 rose from ca. 2 pg/m<sup>3</sup> to 7.5 and 14 pg/m<sup>3</sup>, respectively, with over 95% being particle-associated. The authors hypothesized that products treated with the penta-mix PBDE formulation (notably household furnishing foams and textiles) were being burned on private bonfires. The mixture of BDEs in the air during the festival was enriched in higher brominated congeners (BDE99, BDE153 and BDE154) compared to that in background air<sup>47</sup>.

For this and other reasons air and water near sources and urban areas are enriched relative to rural levels<sup>22</sup>. Recent air sampling transects through Toronto<sup>48</sup>, Ontario<sup>49</sup> and Birmingham<sup>50</sup> demonstrates this clearly.

Harner et al. found that PBDEs were fairly uniform along the transect with air concentrations in Toronto (10–30 pg/m<sup>3</sup>) and about a factor of two greater than at rural sites. They noted that the lowest concentrations were observed during the winter and probably associated with reduced inputs from



indoor sources of PBDEs and to a preference for PBDEs to partition to the particle-phase at colder temperatures. The composition of PBDEs in the air samples did not differ across the transect or for the different seasons.

Butt sampled window films and found that in Ontario indoor films concentrations of PBDEs were 1.5-20 times greater than outdoor films. This was consistent with indoor sources of PBDEs and enhanced degradation in outdoor films. Mean calculated air concentrations were 4.8 pg/m<sup>3</sup> for outdoor and 42.1 pg/m<sup>3</sup> for indoor urban sites, indicating that urban indoor air is a source of PBDEs to urban outdoor air and the outdoor regional environment.

In Birmingham concentrations clearly decrease with increasing distance from the city centre, supporting the existence of an urban ‘pulse’, indicating the West Midlands conurbation to be a major source of PBDEs to the wider environment.

#### Human Exposure to PBDEs

The environmental concentrations and human body burdens of PBDEs, particularly

BDE-209 seem to be increasing, and several trends, including in humans, indicate that this increase may be rapid<sup>41,51</sup>.

Total PBDE concentrations in human blood, milk, and tissue (in ng/g lipid) shown as a function of the year in which the samples were taken;<sup>51</sup>

Whilst it has been assumed that food was likely to be the major exposure pathway to PBDEs recent evidence suggests that dust could be a significant exposure pathway for some individuals, particularly children<sup>12,13,52-54</sup>.

It can be seen that recently published estimates indicate that upto about 70% of a toddler’s intake of PBDEs (and probably other similar chemicals in dust) can be taken from dust. For average adults the percentage is much smaller at only around 1% but even for adults the 95%ile level of the high dust ingestion scenario would result in 37.1% of the intake being from dust.

Very recently published correspondence in Atmospheric Environment<sup>55</sup> highlights the special dangers of the realisation that much



	adult				toddler (6-24 months)			
	intake (ng d <sup>-1</sup> )							
	5th per- centile	median	average	95th per- centile	5th per- centile	median	average	95th per- centile
air	0.18	0.82	2.1	8.8	0.03	0.16	0.4	1.7
food	90.5	90.5	90.5	90.5	51.6	51.6	51.6	51.6
dust (mean)	0.07	0.36	0.9	2.4	0.98	4.8	11.8	32.3
dust (high)	1.78	8.71	21.5	58.7	3.56	17.4	43.1	117.3
Σ (mean dust ingestion)	90.8	91.7	93.5	101.7	52.6	56.6	63.8	85.6
Σ (high dust ingestion)	92.5	100.0	114.1	158	55.2	69.2	95.1	170.6
% contribution								
mean dust ingestion scenario								
air	0.2	0.9	2.3	8.7	0.1	0.3	0.6	2.0
food	99.7	98.7	96.8	88.9	98.0	91.2	80.8	60.3
dust	0.1	0.4	1.0	2.4	1.9	8.5	18.6	37.7
high dust ingestion scenario								
air	0.2	0.8	1.9	5.6	0.1	0.2	0.4	1.0
dust	97.9	90.5	79.3	57.3	93.5	74.6	54.3	30.2
food	1.9	8.7	18.9	37.1	6.5	25.2	45.3	68.8

Summary of Estimates of Exposure (ng day<sup>-1</sup>) of UK Adults and Toddlers to <sup>a</sup>BDE via Dust Ingestion, Inhalation, and Diet, and Relative Significance (%) of Each Pathway<sup>12</sup>

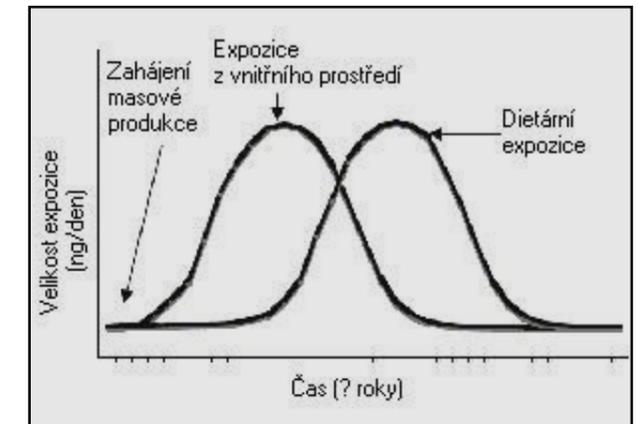
of the current exposure may be through house dust. The authors wrote "Our fear is that the current elevated indoor burden of PBDEs represents a 'time bomb'. Specifically, this indoor reservoir is slowly 'bleeding' these chemicals into the outdoor environment, whence, due to regional and long-range atmospheric transport and their persistence, they will be incorporated into and magnified by terrestrial and aquatic food chains. Over time, we hypothesize that our main exposure route will shift from indoor air and dust, to our diet.

For PCBs our current position on this graph is towards the right where diet dominates, whereas for PBDEs, we are towards the left where indoor exposures dominate. The actual magnitude of future exposures from indoors versus diet depends on factors such as the amount of PBDEs yet to be released into the outdoor environment and the efficiency with which these are incorporated into human foodstuffs".

Estimates in the literature show that ingestion of dust can lead to almost 100-fold

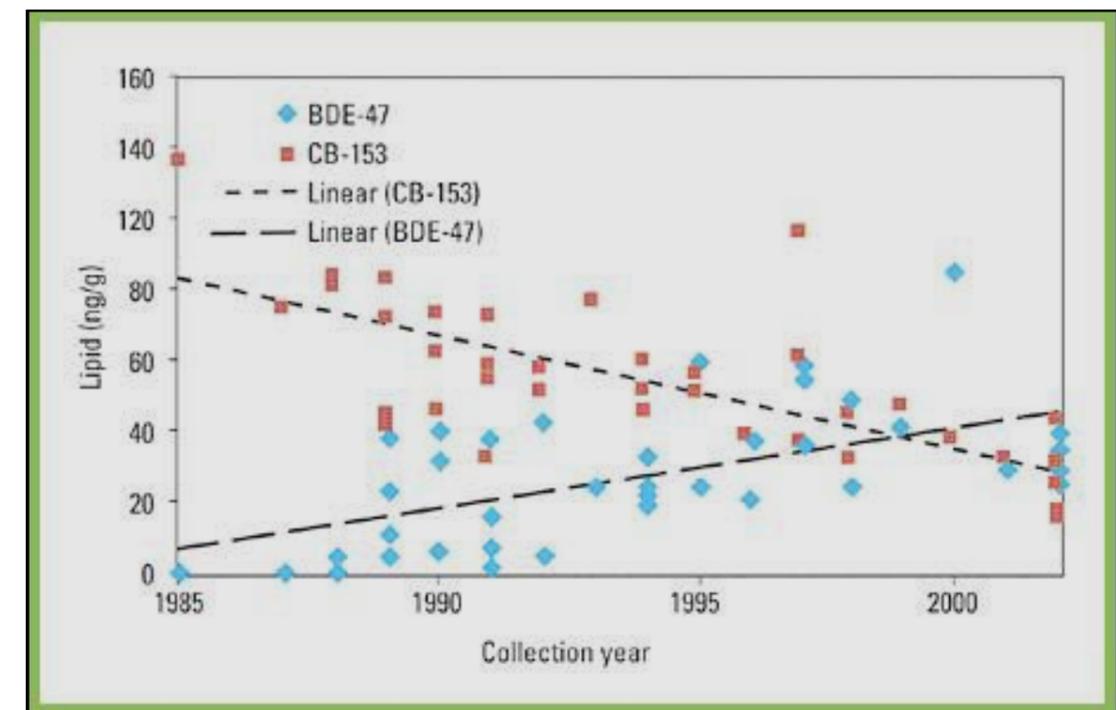
higher exposure than "average" for a toddler with a high dust intake rate living in a home in which PBDE concentrations are elevated<sup>52</sup>. In the United States, where the PBDE concentrations are higher than in Europe a recent study of ingestion of house dust has reported BDE-209 levels in these children were comparable to levels found in occupationally-exposed workers in Sweden<sup>56</sup> and an order of magnitude higher than BDE-209 levels in their parents. The authors suggested that these concentrations may be high enough to cause harm<sup>57</sup>.

It seems, therefore, that exposure to PBDEs and subsequent body burdens, may be following a similar pattern to PCBs. Unlike with PCBs, however, we are exposed to much higher levels of PBDEs in our homes and offices. Already Betts reports that more than half of the people in recent US studies had higher amounts of PBDEs than PCBs in their fat and that the PBDE concentrations in the people with the highest overall levels were more than 100 times higher than their PCB concentrations<sup>59</sup>.



In the Czech Republic Hajslova et al. have recognized, as discussed above, that while for many other halogenated POPs dietary intake is dominant, in the case of PBDEs dermal and/or inhalation exposures might be of great importance<sup>15</sup>.

Kannan's findings are similar to what other researchers have seen in North Americans: People's PBDE levels—unlike those of other POPs like PCBs—do not correlate with their



This slide was created for ES&T 58 by Andreas Sjödin of the U.S. Centers for Disease Control and shows that the levels of the most bioaccumulative polybrominated diphenyl ether (PBDE) congener, BDE-47, in U.S. human blood samples are now higher, on average, than the levels of the most bioaccumulative PCB congener, CB-153.



age. This points to other sources besides diet, says Petreas, who is also studying PBDE levels in people. "We all find these extremes. . . 5–10% of the people are way higher than anyone else, and 1% is very high," she says<sup>59</sup>

Similarly Hajslova et al. concluded that "absence of the mathematical relationship between the PBDEs content and age of the donors indicates that individual habits rather than a general exposure determine the body burden by PBDEs"<sup>15</sup>. Consequently a wide range of exposure levels is found even with the limited data from the Czech republic.

Hajslova confirmed that "individual PBDE patterns shows large inter-individual differences. He noted that "these findings are rather different from other environmental contaminants (e.g. PCBs), where those patterns exhibit only small variation through the general population"<sup>60</sup>. In these circumstances there is clearly a vital need for education about the risks associated with exposure to these chemicals and advice about how to minimise adverse impacts.

After confirming that several PBDEs accumulate in human body Hajslova wrote "The contamination of human milk with PBDEs is of great concern since these compounds may be transferred to an infant in this way". Assuming that an infant weighing 5 kg consumes 700 ml breast milk per day it was calculated that the average daily intake of PBDEs via milk was estimated to be approximately 32 ng. Of course for those mothers who are more heavily contaminated the dose to the baby is higher. In the worst case it could be expected that the baby would receive 5 to 10 times higher doses of PBDEs. The authors confirmed that "due to lack of comprehensive toxicological the health risk for infants can not be assessed at present". This is clearly an unacceptable situation. Parents should not be forced to unwillingly dose their baby children with unwanted chemical

contaminants – particularly where there is no guarantee that the levels are not causing harm.

It is, in any case, suggested that the current concentrations of certain PBDE isomers may be high enough to cause adverse effects in some wildlife. There is also concern that levels could cause adverse effects in sensitive human populations such as young children, indigenous peoples, and fish consumers<sup>41</sup>.

On a more optimistic note some researchers claim that penta-BDE burdens in Europe may have peaked following the banning of that mixture<sup>22</sup>. However the absence of temporal data sets in the Czech Republic does not allow any conclusions to be reached for this country. It is also not yet clear how all the congeners metabolise in the environment and biota and what the consequences may be for environmental levels in the future.

### Health Risks

The global production of chemicals increased from 1 million tonnes in 1930 to 400 million tonnes by 2000<sup>2</sup>. By 1981 there were 100,106 different chemical substances available on the market and more than 3000 "new" chemicals have since been added<sup>61</sup>. Currently more than 30,000 of these substances are marketed at volumes of over a tonne per year<sup>2</sup>. Yet very few of these chemicals have been fully tested. The current EU process to restrict the marketing and use of substances has been very slow. It started in 1976 and restricts the marketing or use of only about 100 substances, including the use of some of them in articles, as well as the marketing to the general public of about 900 substances classified as carcinogenic, mutagenic or toxic to reproduction. Since 1993, only 141 high-volume chemicals have been identified for risk assessment and possible

recommendations for risk reduction, of which only twenty seven have completed the process<sup>61</sup>.

The situation in the United States is no better. The US Agency for Toxic Substances and Disease Registry (ATSDR), for example, has only 275 toxicological profiles which have been published or are under development as "finals" or "drafts for public comment".

Non-occupational exposure of the general human population to a range of man-made lipophilic organic chemicals, such as those classed as 'persistent organic pollutants' (POPs), and similar chemicals, has been of increasing concern over the last several decades. This concern is based on the realisation that chemicals with these properties can have serious effects in wildlife and humans, and moreover, that once such effects become apparent, ongoing exposure cannot be prevented in the short term. Concern is also linked to the increasing realisation that many chemicals have been inadequately tested for their safety and the increasing sophistication of toxicology. Moreover, there is mounting evidence that environmentally relevant concentrations of some chemicals may have measurable toxic (e.g. endocrine effects) and genotoxic effects in humans and other animals<sup>62</sup>.

When the UK Environment Agency reviewed the brominated flame retardants that may be on the market they found<sup>34</sup> that at least 75 had been in recent regular use and that upto 116 may be in use. Of these 116 compounds there was no production and use data for nearly 50%; some mammalian toxicity data was available for only 47 compounds and ecotoxicity data for less than 25%. Practically all the production data and use data was classed as confidential in any case.

Other researches have confirmed there is still rather little known about the toxicology

of PBDEs – and especially congener specific data<sup>63</sup>. Our knowledge about the sources and environmental behaviour is still more limited. Taken together with the paucity of good information about the toxicity makes risk and health impact assessment rather difficult<sup>41</sup>.

Despite the limited data the chemical structures and hence major physical properties of common BFRs resemble persistent organic pollutants (POPs), such as PCBs and PBBs. These similarities suggest possible toxicological commonalities as well, e.g., impacts on endocrine function<sup>22</sup>. There is uncertainty about the toxicological parallels as differences between these chemicals with respect to degree of halogenation, molecular sizes and topological considerations may result in significantly different potencies and fates.

The industry does not share these concerns. In spite of the lack of testing and the inadequacy of the data on health risks the trade association claims "it has been scientifically proven"<sup>3</sup> that there is no risk to human health. This must be considered a gross simplification and the most optimistic conclusion that can realistically be drawn is that the evidence is still incomplete about the thresholds, if any, at which adverse health effects occur.

USEPA and others<sup>8</sup> have conducted reviews of the covering some of the toxicology of the main PBDEs being considered in this report. In general, the findings are that most PBDEs are of low toxicity. They are generally not considered to be acutely toxic, irritating, skin sensitizing, mutagenic, or carcinogenic. USEPA has determined that, at low doses, PeDBE induces liver enzymes in laboratory animals. Although the relevance of liver enzyme induction to clinical human health effects has not been established, in the interest of health protectiveness, USEPA has determined that this is an adverse effect.



USEPA has developed a reference dose of 2  $\mu\text{g}/\text{kg}\text{-day}$  for PeBDE and a reference dose of 10  $\mu\text{g}/\text{kg}\text{-day}$  for DBDE based on liver enlargement in laboratory animals. ATSDR has developed acute and intermediate maximum risk levels of 0.03  $\text{mg}/\text{kg}\text{-day}$  and 0.007  $\text{mg}/\text{kg}\text{-day}$  based on hepatic and thyroid effects, respectively<sup>9</sup>. Recent evidence suggests that PBDEs may be porphyrinogenic, immunotoxic, teratogenic, and neurotoxic. Neurotoxicity has been found at low doses (0.8  $\text{mg}/\text{kg}$ ) in behavioural tests in laboratory animals, however, the significance of this to humans is currently unknown<sup>10</sup>.

### Hidden Dangers – Polybrominated Dibenzo Dioxins and Furans (PBDD/DFs)

For technical and financial reasons the dust samples tested for this report were not analysed for Polybrominated Dibenzo Dioxins and Furans (PBDD/DFs).

Whilst we are not aware of any data on the levels of PBDD/DFs in the Czech Republic we strongly suspect that the dust samples also contain high levels of these contaminants and that they may be responsible for a significant part of the risk to human health.

The World Health Organisation (WHO) warned in 1998 that “PBDDs/PBDFs have been found as contaminants in brominated organic chemicals (e.g. bromophenols) and, in particular, in flame retardants, such as polybrominated diphenyl ethers (PBDEs), decabromobiphenyl (decaBB or DBB), 1,2-bis(tribromophenoxy)ethane, tetrabromobiphenyl A (TBBPA), and others”<sup>64</sup>.

Other work has confirmed that contamination of PBDEs with PBDD/PBDFs continues and significant levels of PBDDs/DFs were recently detected in waste television cabinets and other flame-retarded plastics<sup>65</sup>. PBDDs/

DFs and monobromo-polychlorodibenzo-dioxins and -furans (MoBPCDDs/DFs) were found in various other environmental media along with BFRs<sup>65</sup>.

Commercial PBDE mixtures tested by Hanari and his co-workers<sup>66</sup> contained both Poly brominated biphenyls (PBBs) and PBDFs, as impurities, at concentrations in the range of several tens to several thousands of nanograms per gram. Concentrations of total PBDFs were generally greater than those of total PBBs and unlike a slightly earlier study by Sanders<sup>67</sup> PBDDs were not detected at levels above the limit of detection. Hanari reported that the profiles of PBB and PBDF congeners varied with the degree of bromination of the commercial PBDE mixtures (i.e., more highly brominated mixtures of PBDEs contained heavily brominated homologues of PBBs and PBDFs).

Sanders suggested that PBDFs and PBDDs, may be responsible for most, if not all, dioxin-like properties previously observed for PBDEs<sup>67</sup>. This would be consistent with the work of Peters who reported this year finding that highly purified environmentally relevant PBDEs from which possible dioxin like contaminants had been removed acted as antagonists to TCDD induced EROD activity<sup>68</sup>. It seems particularly anomalous, therefore, that most of the testing of PBDE congeners (such as in the FIRE project) has been done after having stripped the brominated dioxins and furans from the chemicals. This will not give the environmentally relevant impacts – in the real world the chemicals will be applied and released together with the associated PBDFs. If congeners are ‘cleaned’ in this way then it is obviously vital that this is made very clear in the results so that the impression is not given that the toxicity data reflects the technical mixtures when that is not the case.

On the basis of the production/usage of commercial PBDE mixtures in 2001, Hanari calculated that the potential global annual emissions of PBBs and PBDFs were 40 and 2300 kg, respectively. The content in the PBDEs used in Europe in 2001 was calculated to be 315 kg – mainly as a contaminant of Deca-BDE.

PBDD/DFs can also be formed during extrusion of plastics containing PBDEs<sup>69</sup>, during the degradation process<sup>70</sup> or during incineration (as above), in domestic fire<sup>71</sup>, or pyrolysis<sup>72</sup> of PBDEs.

This is potentially very serious as the research carried out to date suggests that PBDDs/DFs and mixed PXDDs/DFs have similar – and possibly greater - toxicity to their chlorinated homologs<sup>73,74</sup>.

In addition, the fact that PBDDs/DFs were detected in Japanese human adipose tissue<sup>75</sup> confirms human exposure to these compounds. In spite of their dioxin-like toxic potency and many potential sources, the information available on environmental levels and human exposure regarding to PBDDs/DFs is quite limited<sup>76</sup>.

We do know, however, that the results presented by Benko<sup>1</sup> for exposure to breast feeding infants in the Czech Republic of chlorinated dioxins, furans and PCBs showed that the calculated median daily intake of the total TEQ for breast-fed infants already exceeds by about two orders of magnitude a tolerable daily intake (TDI) of 1–4  $\text{pg}/\text{kg}\text{ b.w.}$  recommended by the WHO.

Bencko wrote “the health consequences of this potential temporary elevation of infant exposure via breastfeeding are uncertain. Therefore, it is important to implement all possible measures to prevent PCDD/PCDF/PCB contamination of the environment and to continue monitoring of such compounds

in human body fluids, namely in blood samples”.

The WHO review of the TEF scheme has just concluded<sup>77</sup> that whilst there is no reason the inclusion of PBDEs in the TEF/TEQ concept that based on mechanistic considerations “PBDDs, PBDFs, PXCDDs, PXCDFs, PCNs, PBNs and PBBs undoubtedly belong in the TEF concept”. The problem, however, is that there is a distinct lack of human exposure data. The WHO proposal, therefore, is that preliminary exposure assessments should be done in the near future to indicate if these compounds are relevant for humans with respect to TEQ dietary intake. That is rather too late when we are currently exposed and have to assess the possible impacts and this is tacitly acknowledged by the WHO review which says “if the presence of PBDDs and PBDFs in human food as well as in people is more extensively demonstrated there will be a clear need for assigning TEFs to these compounds. ...In addition, it was concluded that among all compounds proposed in this paragraph for development of WHO TEFs, the PBDDs and PBDFs should be given high priority”.

In 2001 the UK Committee on Toxicity (COT) set a TDI of 2  $\text{pg}\text{ WHO-TEQ}/\text{kg}\text{ bw}/\text{day}$  to protect against the most sensitive effect of dioxins (considered to be impaired development of the foetal male reproductive system, caused by foetal exposure in utero and correlated with the maternal body burden of dioxins)<sup>78</sup>. This year, in the absence of any WHO guideline they considered the implications of brominated dioxins and how these should be assessed in the light of some of the first total diet exposure data based on the 2003 UK Total Diet Study.

On the basis of the available data COT advised that “TEFs developed for the chlorinated dioxins could be used as an indication of the dioxin-like activity of the PBDDs, PBDFs and dioxin-like PBBs. The TEQs for the bro-

<sup>3</sup> [http://www.bsef.com/env\\_health/](http://www.bsef.com/env_health/) (accessed 11th June 2006)



minated contaminants could be combined with the TEQs for the chlorinated dioxins to provide an indication of the total intake of chemicals with dioxin-like properties as this would be more protective of public health than to view the chemicals separately". The Committee highlighted that there are still uncertainties and that this was tentative advice but it is probably the most realistic approach currently available.

When the TEFs are calculated as proposed by COT then the UK total diet study results<sup>79</sup> show dietary intakes for adults of brominated dioxins/furans of 0.4 pg/kg bw day through to 0.8 ng/kg bw day with the largest contribution coming from milk.

For children 1.5 to 2.5 years this rises to upto 3.0 pg/kg for high-level consumers. To these intakes must be added the dust intakes as discussed above and, in many cases, the body burden accumulated from breast feeding – and although children are unlikely to spend very much time in offices pregnant mothers are likely to increase their own body burdens from exposure to contaminated dusts. In these circumstances it is certainly possible for young children to significantly exceed the WHO TDI taking into account both chlorinated and brominated dioxins.

Hanari warns "the measurable concentrations of PBDFs in commercial PBDE mixtures, the ongoing use of PBDE-containing products and the continued use of deca-BDE together suggest that human and environmental exposures to PBDFs are likely to increase in the future. Further studies are needed to monitor the distribution and trends of PBDFs in the environment".

WHO went further and concluded their review of PBDD/DFs by counselling that "Owing to the accumulating and toxic potential of some PBDDs/PBDFs, every effort should be made to prevent exposure of humans to,

and pollution of the environment by, these compounds".

### Regulatory Controls:

One recommendation that the World Health Organisation made to reduce the exposure to PBDDs and similar compounds was "Brominated flame retardants should not be used where suitable replacements are available, and future efforts should encourage the development of further substitutes"<sup>64</sup>.

The implementation of the WHO advice has been with mixed enthusiasm. On the one hand the UK Department for Trade and Industry published a report in 1999 claiming that "flame retardants have also become entrenched in the chemical paranoia or chemophobia that characterises many people's response to synthetic chemicals, particularly those associated with halogen and phosphorus containing substances and others with exotic-sounding chemical names"<sup>80</sup>. It is not clear whether this criticism was aimed at WHO. On the other hand organizations like the Swedish Chemicals Inspectorate formed a commission, produced a report on 'Phase-out of PBDEs and PBBs'<sup>81</sup> and made plans to implement a ban.

Some progress has been made to implement the WHO advice - Penta and Octa are now banned in the EU following the amendments to Marketing and Use of Dangerous Substances Directive 76/769/EEC in 2003 by Directive 2003/11/EC<sup>82</sup>. The Directive specifies that both octa BDE and penta BDE may not be placed on the market or used as a substance or as a constituent of substances or of preparations in concentrations higher than 0.1% by mass; and articles may not be placed on the market if they, or flame retarded parts thereof contain this substance in concentrations higher than 0.1 % by mass.

The current debate is now mainly about the future of Deca-BDE for which there are already proposed bans in several countries and US states:

- Switzerland has issued a ban on electrical products containing more than 0.1% Deca-BDE that becomes effective in July, 2007.
- Norway has notified the World Trade Organization of its intent to ban Deca-BDE.
- Eight U.S. states have banned Penta- and Octa-BDE by May 2006. Each of those states has indicated ongoing concern about the risks posed by Deca-BDE and its breakdown products. At least one state has introduced legislation which would ban the sale of Deca-BDE containing products as soon as a safer alternative is identified.<sup>83</sup>

Pure Deca-BDE is in principle exempt from the European Union (EU)'s Restriction of certain Hazardous Substances in electrical and electronic equipment (RoHS) directive which bans a number of other hazardous substances in electrical and electronic equipment, including lead, mercury, and several PBDEs. This follows a Commission decision on 15th October 2005.

That directive took effect on 1st July 2006 but at the last minute the Commission clarified that the exception does not allow the use of the technical mixtures of Deca as these also include a significant level (c 3%) of nona contamination (see above) which would result in about 0.3% nona in products thus exceeding the threshold for contaminants of 0.1%<sup>84</sup>.

The Danish government and some members of the European Parliament have in any case objected to the EC's move to exempt even pure deca-BDE. Connie Hedegaard, Danish minister of the environment, said "It is unacceptable to exempt deca-BDE from the general ban when there are alternatives to it." Industry groups such as the Bromine Science & Environmental Forum, which is

composed of manufacturers of brominated flame retardants, and the American Plastics Council support the commission's decision to allow the use of deca-BDE to continue in Europe<sup>85</sup> and are currently trying to reverse the clarification provided by the Commission.

The Danish government announced on 3rd January 2006 that it would file a legal suit against the European Commission for allowing the continued use of Deca-BDE in plastics used to make electronic devices.<sup>85</sup> The European Parliament also initiated legal proceedings on this matter.

In March 2005, the Scientific Committee on Health and Environmental Risks (SCHER), a committee of physicians and professors who serve an advisory role to the European Commission, reviewed the risk assessment for Deca-BDE completed by the U.K. in May 2004. At that time ENDS had reported "EU Member States have taken the highly unusual step of signing off a risk assessment of the widely used flame retardant deca-BDE despite mounting evidence of environmental contamination"<sup>86</sup>. The SCHER disagreed with the recommendation that risk reduction measures on Deca-BDE are not currently necessary. The May 2004 Risk Assessment itself discussed the need for further study of Deca-BDE, particularly the debromination of Deca-BDE to lower PBDE congeners which it cites as of "high concern" and noted that, "many of these substances [lower PBDE congeners] are considered to be persistent, bioaccumulative, and toxic (PBT) or very persistent and very bioaccumulative (vPvB)."

One of the key questions that is currently being addressed is whether Deca breaks down in the environment into the more toxic and hazardous lower brominated congeners. The research is indicating that it probably does<sup>87</sup> although most of the work to date has been based in laboratories using accelerated degradation techniques and, for exam-



## DANGER: DUST

ple, artificial sources of ultra-violet light to speed photolysis <sup>70</sup>.

### Future Stockholm Convention Persistent Organic Pollutants (POPs)?

There is little doubt that the evidence supports all PBDEs – and the brominated dioxins and furans contaminating them - being listed as POPs and added to the Stockholm Convention:

“Based on the accumulating evidence of their presence in the Arctic and indications of long-range transport for several BFRs, we conclude that Penta-, Octa- and DecaBDE, PBBs and HBCD have characteristics that qualify them as POPs according to the Stockholm Convention. There are indications that TBBPA may also behave as a POP but there are too few data as yet to reach firm conclusions and more research is needed to fill these data gaps.” <sup>88</sup>

### Conclusion

In conclusion, we agree with Harrad and Diamond when they wrote “we must continue to learn from our experience with PCBs when managing ‘new’ POPs such as PBDEs ..... Currently, we can reduce our exposure to PBDEs by minimizing their accumulation in the indoor environment; however, it will be much more difficult to reduce exposure once they are in the food supply. We urge concerted action to not only ban current manufacture and use of PBDEs, but to find ways of reducing the existing indoor reservoir of these compounds and managing the end-of-life of PBDE-containing products” . <sup>55</sup>

An ongoing programme of dust sampling should be carried out in the Czech Republic to establish the sources of the pollutants that

are reported in this review. They should also help to show the magnitude of the contamination by these pollutants. This sampling programme should be extended to include homes, schools and other public buildings such as hospitals. Action can then be taken to protect workers, schoolchildren and families.

REACH should help to reduce the delays which have been inherent in the regulation of these chemicals to date. Furthermore it should ensure that the mistakes of the past where large volume chemicals have been released onto the market with little or no toxicity information are not repeated.

Each of the brominated flame retardants, phthalates and nonylphenol which have been found in the dusts in this review should be added to the candidate list of substances of very high concern.

It is vital that any future toxicity testing reflects the real world contamination associated with a chemical. The testing of PBDE congeners having stripped the brominated dioxins and furans from the chemicals will not, for example, give the environmentally relevant impacts – in the real world the chemicals will be applied and released together with the associated contaminants.

Finally other actions are urgently necessary in relation to brominated dioxins. The WHO review<sup>77</sup> of Dioxin TEFs confirmed that “at present it is unclear to what extent the ongoing use of brominated flame retardants, especially polybrominated diphenylethers (PBDEs), could lead to an increase in human and environmental exposure to PBDDs and PBDFs. Therefore it is recommended by the expert panel to perform a more thorough exposure analysis for humans”. Environmental monitoring should be increased to establish the scale of this problem in the Czech Republic and this work needs to be carried out as a matter of urgency.



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## Appendix 1

## Dust Sampling Results:

	4144	4254	4255	4256
	pg/l	pg/l	pg/l	pg/l
PBDE28	< 13	52	37	13
PBDE47	123	677	366	83
PBDE100	< 10	80	60	22
PBDE99	58	469	153	51
PBDE154	21	72	56	16
PBDE153	24	121	113	27
PBDE183	49	178	129	44
PBDE196	<150	<180	<2200	<110
PBDE206	<230	<270	<3,300	<170
PBDE209	990	2,900	16,000	610
TriBDE	<13	52	37	13
TetraBDE	123	677	366	83
PentaBDE	58	549	213	73
HexaBDE	45	193	169	43
HeptaBDE	49	178	129	44
OctaBDE	<300	<350	<4300	<220
NonaBDE	<450	<540	<6600	<340
DecaBDE	990	2,900	16,000	610
Sum of PBDE	1,265	4,549	16,914	866

		4250	4251	4252	4253	CAS
		µg/g	µg/g	µg/g	µg/g	
DIMETHYL PHTHALATE	DMP	< 1.6	< 3.4	< 2.3	< 1.6	131-11-3
DIETHYL PHTHALATE	DEP	< 2.0	22	4.0	8.6	84-66-2
DIISOBUTYL PHTHALATE	DiBP	4.7	42	44	77	84-69-5
DI N BUTYL PHTHALATE	DBP	20	84	460	93	84-74-2
BIS(2-METHOXYETHYL) PHTHALATE	DMEP	< 34	< 68	< 42	< 32	117-82-8
BIS (4 METHYL 2 PENTYL) PHTHALATE		< 2.7	< 5.4	< 3.4	< 2.6	146-50-9
BIS (ETHOXY ETHYL) PHTHALATE		< 35	< 64	< 30	< 26	?
DIAMYLPHTHALATE (Dipentyl phthalate)		< 1.8	< 3.3	< 1.5	< 1.3	131-18-0
DI HEXYL PHTHALATE	DHXP	< 2.2	< 3.9	< 1.9	< 1.6	84-75-3
BUTYLBENZYLPHTHALATE	BBzP	< 2.6	< 11	< 5.6	20	85-68-7
BIS(2-BUTYOXYETHYL)PHTHALATE	BEP	< 10	< 41	< 22	< 18	117-83-9
DI-CYCLOHEXYL PHTHALATE (DICYCLOHEXYL ESTER)	DCHP	10	< 6.9	< 3.6	< 3.0	84-61-7
BIS(2-ETHYLHEXYL)PHTHALATE	DEHP	10	810	2400	1900	117-81-7
DI-N-OCTYLPHTHALATE	DOP	< 3.2	5.8	3.5	4.7	117-84-0
DINONYLPHTHALATE	DNP	< 4.0	< 7.3	< 3.4	< 3.4	84-76-4V
Sum of Phthalates		45	964	2,912	2,103	
		4250	4251	4252	4253	
		ng/g	ng/g	ng/g	ng/g	
T-OCTYLPHENOL		99	370	70	220	1806-26-4
N-OCTYLPHENOL 1-(P-HYDROXYPHENYL)OCTANE		< 20	< 38	< 21	< 20	1806-26-4
P-N-NONYLPHENOL		< 49	< 92	< 50	< 48	104-40-5
P-NONYLPHENOL		3,300	6,900	4,500	20,000	104-40-5
4-NONYLPHENOL MONO-ETHOXYLATE		1,900	890	500	4,100	9016-45-9
4-NONYLPHENOL DI-ETHOXYLATE		1,100	780	1,800	4,400	20427-84-3



**Rainwater Results**

	4144	4254	4255	4256
	pg/l	pg/l	pg/l	pg/l
PBDE28	< 13	52	37	13
PBDE47	123	677	366	83
PBDE100	< 10	80	60	22
PBDE99	58	469	153	51
PBDE154	21	72	56	16
PBDE153	24	121	113	27
PBDE183	49	178	129	44
PBDE196	<150	<180	<2200	<110
PBDE206	<230	<270	<3,300	<170
PBDE209	990	2,900	16,000	610
TriBDE	<13	52	37	13
TetraBDE	123	677	366	83
PentaBDE	58	549	213	73
HexaBDE	45	193	169	43
HeptaBDE	49	178	129	44
OctaBDE	<300	<350	<4300	<220
NonaBDE	<450	<540	<6600	<340
DecaBDE	990	2,900	16,000	610
Sum of PBDE	1,265	4,549	16,914	866
	4144	4254	4255	4256
	ng/l	ng/l	ng/l	ng/l
t-octylphenol	< 8.8	< 4.9	< 7.7	< 8.1
n-octylphenol	< 23	< 13	< 20	< 21
p-n-nonylphenol	< 55	< 31	< 49	< 51
p-nonylphenol	165	< 42	< 65	< 68
4-nonylphenol mono-ethoxylate	< 55	< 31	< 48	< 50
4-nonylphenol diethoxylate	< 130	< 70	< 110	< 120

## Appendix 2: Sampling procedure and used analytical methods.

### Dust sampling

All dust samples were taken by vacuum cleaner AEG Vampyr 1700 Watt. The same kind of vacuum cleaner was used also in other European countries with the purpose of taking dust samples for their analyses for presence of chemical substances, and, according to statement of Greenpeace Czech Republic, this vacuum cleaner was tested for content of the analysed substances (phthalates and brominated flame retardants). In the case of each locality, a new dust bag was used. After finishing the sampling, the bag was securely sealed and stored until handing over to the laboratory. In all cases, dust was collected from the whole room, i.e., not only from the floor, but also from chair upholstery, window sills, surface of office equipment, etc.

### Rainwater sampling (wet deposition)

All rainwater samples were collected into glass vessels within the period of three days. After finishing the sampling, the vessels were sealed and handed over to the laboratory. The sampling vessels were placed in wooden protective casings, and rainwater was collected by means of glass funnels leading to the vessels. All pieces of sampling equipment were located in uncovered areas where nothing prevented free access of rainfall. Simultaneously, the vessels were located in safe places where a danger of unauthorized manipulation did not exist. For the Arnika Association, the sampling vessels, as well as casings, had been prepared by the National Reference Laboratory for POPs which subsequently analysed the taken samples.

### Analytical evaluation

The collected samples had been handed over to the National Reference Laboratory for Persistent Organic Pollutants (POPs) which subsequently tested them for presence of 31 kinds of chemical substances from the groups of polybrominated diphenyl ethers, phthalates and alkylphenols.

From the samples, the target analytes were isolated by means of extraction with non-polar solvents (hexane, toluene). Subsequently, the extracts were gently concentrated, and the interfering substances were removed by means of column chromatography.

Analytical determination of all target analytes was carried out by means of capillary gas chromatography in combination with mass spectrometry (HRGC/MS), using a spectrometer of the ion trap type. In the case of PBDEs and alkylphenols, the spectrometer operated in the MS/MS mode (designated also as tandem mass spectrometry, HRGC/MS/MS). In the case of phthalates, MS1 mode was used. Isotope-labelled inner standards (C13) were used for quantification of PBDEs and alkylphenols.



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