"New" brominated flame retardants as emerging contaminants in the environment: sources, occurrence, pathways and measurement methods

Report of the NORMAN workshop, 23th-24th of November, 2011, Stockholm, Sweden

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Preface

New brominated flame retardants was the theme of a NORMAN workshop organised by IVL Swedish Environmental Research Institute in collaboration with Norwegian Institute for Air Research, Stockholm University, and Umeå University. The workshop was held at Spårvagnshallarna in Stockholm, Sweden the 23-24 November, 2011. More than 50 persons participated in the workshop, representing scientists, stakeholders and representatives from the industry.

This report summarises the results and discussions held at the workshop. It gives an overview of the present key issues of this field.

The workshop was followed by an expert meeting with leading European environmental experts. The main objective of this expert meeting was to discuss and evaluate the future requirements with regard to new emerging flame retardants. The expert meeting was held at IVL Swedish Environmental Research Institute in Stockholm 24-25, November, 2011. The output of the expert meeting will be a position paper where present knowledge will be summarized into a number of key issues and suggestions, which will be communicated to other researchers and policy makers.

Presentations were given by the following scientists. The texts, figures and tables in this report are taken from or based on the content of the presentations.

Åke Bergman, Stockholm University, SU

Martin Schlabach, Norwegian Institute for Air Research, NILU

Anna Rotander, Örebro University

Ethel Eljarrat, Institute of Environmental Assessment and Water Research (IDAEA) and Spanish Council of Scientific Research (CSIC)

Patrik L. Andersson, Umeå University, UmU

Peter Haglund, Umeå University, UmU

Martin Scheringer, Swiss Federal Institute of Technology, ETHZ,

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1 Introduction

Brominated flame retardants (BFRs) are used to reduce the flammability of many products, including furniture, building materials and electronics. The flame retardants polybrominated biphenyl ethers (PBDEs), e.g. pentaBDE, has previously been used in high volumes but due to their ubiquitous environmental presence and potential toxicities these chemicals have been banned in Europe.

The phase out of PBDEs has led to an increasing number of alternative flame retardant chemicals which have been introduced to comply with consumer product fire safety standards. The "new" substances include both brominated and chlorinated compounds. Examples of potential replacement include such as bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromdiphenylethane (DBDPE). Given that these alternate flame retardants share properties similar to those of the PBDE mixtures (*e.g.* aromatic moieties, high bromination, and low aqueous solubility) and that most are used as additive flame retardants, as opposed to reactive flame retardants (FRs), an environmental fate similar to the PBDEs may be expected.

Recent Nordic screening studies have identified a widespread occurrence of “new” alternative BFRs in the Nordic environment. Several of the new compounds have been found in different samples from organisms and the environment both near/close to known sources and in remote areas e.g. in the Arctic.

A number of knowledge gaps for emerging BFRs, concerning analytical aspects, environmental issues and human exposure have been identified in recent scientific papers and review articles.

With the overall aim to summarise present knowledge and to identify future research needs the NORMAN Network arranged the workshop on “new” brominated flame retardants. The workshop gathered some of the lead researchers in the field to present results from their research and to give their view on current knowledge thus providing an up to date summary on the use, occurrence and risks of the “new” brominated flame retardants.

The following topics were addressed:

- Occurrence and distribution of emerging FRs in the environment. Where do we find them and in which concentrations?
- Emissions sources and important pathways of FRs.
- Use, fate and transformation products.
- Potential ecotoxicology and human effects.
- Which effects are of concern? What is today’s knowledge and what do we need to know for reliable risk assessment?
- Measurement methods.
- The need for development and harmonization of methods.
- Do we need to include new FRs in monitoring programs?

The terminology in the field of FRs is sometimes not so straight forward. In the present report we have chosen to categorize the flame retardants into established, new and emerging flame retardants. A categorisation of the FR was also given by Dr Åke Bergman (see *2.1).*

The workshop program is given in the Appendix 1. and the presentations can be found at NORMANs web site http://www.norman-network.net

2 Meeting findings: Summary of presentations and general remarks

2.1 Improving the navigation among the brominated flame retardants by Åke Bergman, Stockholm University

This presentation gave information on the on-going EFSA work (European Food Safety Authority) on brominated flame retardants (BFRs). EFSA has published scientific opinions on a number of BFRs; including polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD).

Currently the working group under EFSA is also developing a common nomenclature for the BFRs. A suggestion given in the presentation was to categorise the substances into four categories (Table 1). The nomenclature itself is developed so that the name gives information on the structure of the compound.

Table 1: Categorisation of the brominated flame retardants (BFR)

Established BFRs:	There are extensive data sets describing each one of the chemical, or chemical groups, as BFRs (i.e. incl. data on their chemistry, fate, exposure, ecotoxicity and toxicity)
Novel BFRs:	BFRs only reported to occur in material, goods/articles or in products. No data available on environmental occurrence or presence in biota.
Emerging BFRs:	BFRs reported to occur in the abiotic environment or in biota, incl. humans, but for which the data sets are limited and/or incomplete
Potential BFRs:	Chemicals that are proposed (patented) for applications as BFRs

For the established BFRs the EFSA recommendations are now complete and the working group is evaluating the emerging BFRs.

There are currently around 20 BFRs in use, worldwide. For these substances there are many important data gaps, in particularly for the emerging BFRs. For example, data on production, use and ecotoxicology are missing.

Finally the presentation concluded that improving the navigation among BFRs will require:

- Agreement on which they are and how to group them
- Production, use and/or consumption data
- Use of common abbreviations
- Prioritisation of data generation and reporting

The audience agreed to the need for a common nomenclature but in the discussions it became clear that the abbreviations must not be too long or complicated, otherwise they will not be used and alternative abbreviations will continue to be used in the literature.

Furthermore Dr. Bergman called for research data presented in a way that can be used in an assessment process such as the EFSA assessment.

2.2 Occurrence and distribution of emerging flame retardants in the environment

2.2.1 "New" Brominated Flame Retardants (BFR) in the Nordic and Arctic Environments by Martin Schlabach, NILU – Norwegian Institute for Air Research

Screening studies of established and emerging BFRs have recently been performed in the Nordic environment and in the Arctic in a number projects. The overall aim of these screening studies was to investigate the occurrence of flame retardants in environmental and emission samples (for references, see below). Results from these studies were presented, and a summary of which substances that were most frequently found in the different studies is given in Table 2. Explanations of abbreviations and CAS-numbers for the substances are given in Appendix2.

Table 2: Substances that were most frequently found in recent screening studies (See Appendix for explanations of the abbreviations)

Phenolic BFRs	BFR esters & ethers	Others flame retardants
24DBP	DPTE	DP
246TBP	BTBPE	HBB
		(TBA)
		BEHTBP
		EHTeBB

In the Nordic screening (S*creening project financed by the Nordic Council of Ministers through the Nordic Chemicals Group*) the occurrence of emerging BFRs were studied in both environmental samples (air, moss, needles, sediment and different aquatic biota) and in emission samples (sludge, wastewater). Several of the studied emerging BFRs and Dechlorane plus were found frequently in all matrices studied indicating a widespread distribution in the Nordic environment. The most frequently found substances were 1,2-Bis (2,4,6-tribromophenoxy) ethane (BTBPE), 2,4,6-Tribromoanisole (TBA), Dechlorane Plus (DP), Pentabromotoluene (PBT) and Decabromodiphenylethane (DBDPE), with a detection frequency of more than 50% in all matrices studied. Many of the emerging BFRs were found at similar concentrations as PBDEs. Table 3 contains a summary of concentration ranges for the FRs in biota, sediment and sludge. Geographic differences were also seen in occurrence among substances .The most frequently found substances in the Norwegian screening studies were BTBPE, Tetrabromobisphenol-A (TBBPA) and DPBPE, but in the Arctic screening study, 2,4,6-Tribromophenol (246TBP), Bis (2-ethylhexyl) tetrabromophthalate (BEHTBP) and 2-Ethylhexyl- 2,3,4,5-tetrabromobenzoate (EHTeBB) were the most frequently found FRs. The detection frequencies of the different compounds were not directly comparable between the different studies, which makes definite conclusions difficult to make.

Table 3: Summary of concentrations ranges for the FRs in biota sediment and sludge as found in the screening studies presented (See Appendix for explanations of the abbreviations)

Matrix	Biota (ng/g f.w.)	Sediment (ng/g d.w.)	Sludge (ng/g d.w.)
Phenolic BFRs			
24DBP	<0.02-6.4	<0.03-2.9	<0.04-40
246TBP	<0.03-86	<0.03-7.8	<0.01-100
BFR esters & ethers			
BTBPE	<0.0052-0.2	<0.0081-1.7	<0.075-3.9
TBA	0.013-14	0.0009-0.66	0.00034-2
BEHTBP	<0.026-0.46	<0.013-3.3	<0.13-42
EHTeBB	<0.006-0.18	<0.0082-0.21	<0.25-2.6
Other BFRs			
DP syn+anti	0.002-0.083	0.0084-3.4	0.051-34
HBB	0.0058-0.072	<0.022-0.19	<0.14-0.72
PBT	0.0015-0.021	<0.011-2.7	<0.027-5.2
PBEB	<0.00034-0.0044	<0.0098-0.046	<0.00095-0.13
DBDPE	<0.082-0.12	<0.00001-2.4	<2.5-160
TBECH, sum	0.0032-1.6	0.010-350	0.018-9.0
Reference compounds			
pentaBDE	0.062-36	0.096-13	0.18-76

The following was concluded:

- The selection procedure based on monitoring and fate modelling is working – the selected substances were also found in the environment
- Waste reclamation sites are important point sources
- The presence of these substances in background air samples indicate potential for long range atmospheric transport
- The widespread occurrence in biota indicate potential for bioaccumulation and thus negative effects on higher organisms cannot be excluded
- Real effect data are scarce, which make the eco toxicological relevance of these results unclear
- Finally, broader monitoring and more effect studies are recommended

Data in this presentation were taken from following screening studies:

Environmental screening of selected “new” brominated flame retardants and selected polyfluorinated compounds 2009”. KLIF, Oslo TA-2625/2010

Screening of decabromodiphenyl ethane (dbdpe) in lake sediment, marine sediment and peregrine falcon (Falco peregrinus) eggs. Ricklund, N., A. et al. (2009). ITM, Stockholm

New brominated flame retardants in Arctic biota. Sagerup et al. KLIF, Oslo TA-2630/2010

Results from the Swedish National Screening Programme 2009: Subreport 2. Dechlorane Plus. Kaj et al. IVL report B1950

Arctic mammal screening on new brominated flame retardants, Bert van Bavel, Örebro University

Brominated Flame Retardants (BFR) in the Nordic Environment. Remberger et al. Tema Norden report 2011:528

2.2.2 BFRs in marine mammals from Arctic and North Atlantic regions, 1986-2009 by Anna Rotander, MTM Research Centre, School of Science and Technology, Örebro University

An overview of results from studies of BFRs in marine mammals from Arctic and from north Atlantic regions from the period 1986-2009 was given in this presentation. In addition to the brominated compounds, which are in focus here, chlorinated and fluorinated compounds were measured in this study. The samples were taken from specimen banks and originally collected by local hunters.

The study included species of pooled blubber samples from pilot whale (*Globicephala melas*), ringed seal (*Phoca hisida*), minke whale (*Balaenoptera acutorstrata*), fin whale (*Balaenoptera physalus*), harbour porpoise (*Phocoena phocoena*), hooded seal (*Cystophora cristata*) and white-sided dolphin (*Lagenorhynchus acutis*), covering a time period of more than 20 years (1986-2009). Some of these are migratory species and thus their feeding behaviour will affect the results.

For one of the substance groups studied, PBDEs, an increase in the levels in fat could be seen since the mid-80s. After the end of the 90s levels seem to level out/decrease. Furthermore an increased relative exposure to higher brominated BDEs was indicated in some species. There were however large data variations for some pools/species.

In most whale species the highest levels found were for MeO-PBDE. Only weak correlations between PBDEs and MeO-PBDEs were found, which may be due to natural formation of MeO-PBDEs. However, metabolisation cannot be ruled out.

A screening of a number of new BFRs, including allyl 2,4,6-tribromophenyl ether (ATE), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), pentabromotoluene (PBT), hexabromobenzene (HBB), 2-ethyl-1-hexyl 2,3,4,5-tetrabromobenzoate (EHTBB), hexachlorocyclopentenyl-dibromocyclooctane (HCDBCO), 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE), and bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP), and decabromodiphenyl ethane (DBDPE) was performed in selected samples of pilot whale, ringed seal and minke whale. Of these new BFRs only HBB was found in whale samples (1-10 ng/g), while concentrations of the other BFRs were below the limit of detection (LOD). However many peaks were present in the chromatogram that were not in the standard, indicating that there were many unknown brominated organic compounds in the samples.

Results from other studies were also presented; Tomy et al. found BTBPE in a few Canadian Belugas (0.1-2.5 ng/g lw) and ringed seals (<0.01-0.29 ng/g lw) and β-TBECH in Beluga blubber (1.1-9.3 ng/g) but did not find DBDPE in ringed seals.

In summary: Both PBDEs, their metabolites and new BFRs are detected in marine mammals from remote areas. Many unknown brominated organic compounds occurred in the samples

A need for further method development for determination "new" BFRs was identified as well as a need for Inter-laboratory comparisons.

2.2.3 Chlorinated Flame Retardants (Dechloranes): Analysis, Occurrence and Behaviour by Ethel Eljarrat, Institute of Environmental Assessment and Water Research (IDAEA) and Spanish Council of Scientific Research (CSIC)

The last presentation on the topic occurrence and distribution of emerging flame retardants in the environment was on the chlorinated flame retardants dechloranes, with a focus on dechlorane plus (DP).

Dechlorane plus (DP) was developed as a flame retardant to replace Mirex which was banned in the 1970s. It is now a potential replacement for the restricted Deca-BDE. DP was identified in the environment in 2006 and after that research has been performed on the occurrence and behaviour of this substance. This presentation gave an overview of previous and current studies, which showed that DP is present in numerous environmental matrices (air, dust, soil and sediment), wildlife and humans.

In background samples (samples not taken close to production plants), the concentrations were lower compared to those of PBDEs. In the recent SCARCE project (Assessing and predicting effects on water quantity and quality in Iberian rivers caused by global change), measuring contaminants in sediments from rivers in Spain, DP was detected in all samples. More data are needed about the concentration levels in background areas

The detection of DP in sediment cores suggested environmental persistence of this compound, the detection of DP in samples from Greenland to Antarctica implies that DP is subjected to long-range atmospheric transport and detection of DP in wildlife with elevated concentration levels in higher trophic level organisms indicates that DP is potentially bioaccumulative. Biota to sediment accumulation factors are lower than for PCBs but in the same order of magnitude as for BDE209.

The isomers of DP, syn- and anti-DP, have been demonstrated to have different behaviour, which means that the isomers need to be assessed individually with regards to the impact of DP on the environment and on human exposure. High persistent retention in the brain compared to the liver was observed for anti-DP, suggesting that this isomer can across the blood-brain barrier of fish, and may cause adverse effects to the nervous system in the exposed biota. Further research is needed on the neurotoxicity of anti-DP. In sediment samples on the other hand the approximately same isomeric ratio as in the technical mixture was found. In other studies a decreasing level of anti-DP fraction (f-anti) estimated as the concentration of the anti-DP divided by the total DP, was found with increasing trophic level; an indication that syn-DP is more bioaccumulative.

For DP there were slightly higher detection limits compared to the PBDEs and expected concentrations are lower than those of PBDEs. There was thus a need to enhance the sensitivity of the methods which was achieved with the use of tandem MS. Signal to noise ratios decreased significantly and tandem MS enhanced sensitivity between 4-130 times (depending on matrix). Furthermore it was recommended to avoid the use of HRMS as this is an expensive technique that is not available in all laboratories and to use methane as chemical ionization moderating gas.

Other Dechloranes, such as Dec602, Dec603 and Dec604, have also been studied recently. Their widespread occurrence, generally at lower concentration levels than DP, demonstrates the need for further research studies.

Some DP related compounds, such as DPMA (DP monoadduct), have also been investigated. Careful examination of technical DP mixtures revealed the presence of DPMA as impurities. Moreover, studies on lake trout suggested a greater bioaccumulation of DPMA due to its smaller molecular size. More studies are needed on the analytical procedure of DPMA as well as on the occurrence and behaviour of this compound. In the analytical work there was low recovery of DPMA in air and biotic samples due to acid treatment.

In summary:

- Dechloranes are frequently present in the environment and in humans. More data is however needed about the concentration levels especially in background areas.
- Toxicity data for DP are rarely reported. Most of the toxicity data were provided by DP manufacturers.
- More acute and chronic toxicity data, including also those from academic communities, are needed for a better environmental and human risk assessment.
- Several future research needs were identified

2.3 Emissions, sources important pathways and fate of flame retardants

2.3.1 Fate studies of selected BFRs by Patrik L. Andersson, UmU, Umeå University

This presentation showed results from several studies on the environmental fate for a structurally varied set of BFRs. These were selected based on a thorough chemical characterization combined with multivariate statistics to represent more than 60 organic BFRs. The studied compounds included both legacy (established) BFRs represented by polybrominated diphenylethers and tetrabromobisphenol-A and emerging BFRs, such as 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), hexabromobenzene (HBB), and tetrabromobisphenol A 2,3-dibromopropylether (TBBPA DBPE).

There was a large variation in degradation rates among different substances (sludge and soil mixed) but most of the substances have longer half lives in anaerobic environments. A comparison of the persistence (P- values) showed that most of the legacy BFRs are very persistent. Of the “new” BFRs however it was shown that TBECH is not persistent, HBB is a border-line case but TBBPA is persistent in anaerobic conditions.

Most degradation experiments were made in room temperature. A study conducted under real environmental conditions at a temperature of 8 °C showed that the half-lives could be rather long. Furthermore, it was also found that the typical laboratory soil overestimates the biota to soil accumulation factors for earthworms. Also aging of the soil had an effect on the bioaccumulation.

Uptake of BFRs in zebra fish through feed was also studied. In this study TBECH was taken up effectively but also eliminated effectively; with a half-life of only one day. TBECH was taken up in similar levels as BDE183 but with much shorter half-life. Furthermore, TBECH was found to be transferred from zebra fish to the eggs (lipid normalised data) but no significant increase in concentrations was seen. Also degradation and transformation products were found in the eggs, e.g. debromination of BDE 183 and/or BDE 209, and HBB.

Results from a recent screening of emerging BFRs in Norway were also presented. HBB, BTBPE and DBDPE were frequently found in sediments close to landfills and a metal recycling station while the detection frequencies of these substances were low in the biological samples. BDE209 was found in many different samples and most frequently in highest levels.

The concluding remarks of this presentation were that:

- The legacy BFRs are most abundant in the environment
- New BFRs are emerging
- There are great analytical challenges in this field
- The substances show large variation in fate
- The toxicity of the new BFRs is largely unknown

Finally a question was raised; "which are the most critical and which are the next generation BFRs?"

2.3.2 Polybrominated dibenzofurans: Potential PBDE transformation products of concern by Peter Haglund, UmU, Umeå University

This presentation included the following topics:

- Transformation of BFRs to PBDFs
- Occurrence of PBDFs in flame-retarded goods
- Formation of PBDFs in accidental fires
- Levels of PBDFs in environmental compartments
- Human exposure

The PBDFs can be formed via different mechanisms; either from incomplete combustion of BFRs via formation of bromophenols and bromobenzenes or via incomplete combustion where the bromine (HBr, Br_2, Br) is incorporated into PBDF structures via de novo synthesis (Figure 1). These substances may be present in products as impurities from production or as transformation products that are formed during processing at high temperatures. Also UV light may act to form transformation products. In addition they may also be formed in (accidental) fires.

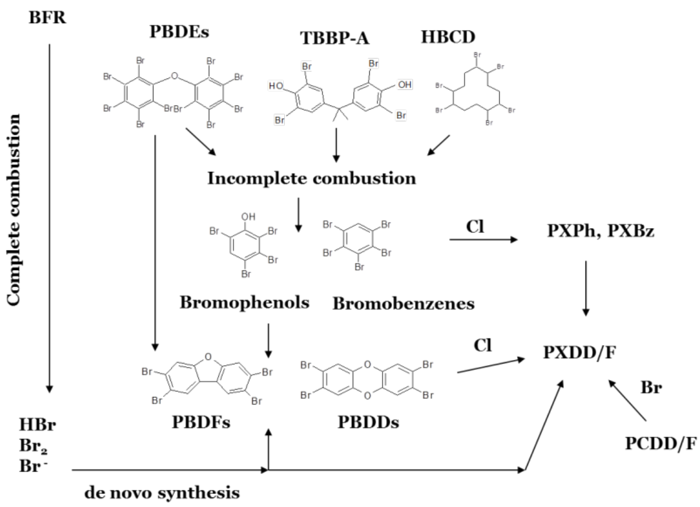


Figure 1: Pyrolysis and combustion of BFRs.

In a simulated TV fire (CRT TV) 1.8% PBDE (61 g), 0.00019% (0.0065 g) TBBPA and 0.059% (2 g) PBDD/F were found in the TV cabinet. The ash contained 370 ng/g of PBDEs and 740 ng/g of PBDD/Fs. Of the brominated dioxins/furans that were studied (PBDD/Fs, PBCDD/Fs, PCDD/Fs) the PBDD/Fs were found in the highest levels in the ash. In the TV cabinet the PBDF congener found in the highest concentration was the heptabrominated dibenzofurans (HpBDFs), whereas in the ashes the congener found in the highest levels was the pentabrominated dibenzofurans (PeBDFs). Also in soil samples, from the vicinity of an e-waste recycling facility where there had been a fire, the PeBDFs were found in the highest levels, followed by the tetrabrominated dibenzofurans (TBDFs). The congener patterns found after the fires were more diverse than the pattern before the fires.

Dr. Haglund also presented results from a city dump in Peru where e-waste is combusted under less controlled conditions. In the ashes from a cable burn site PBDEs were found in concentrations of 11 000 ng/g and PBDD/Fs at 310 ng/g. Sediments and free-range hens eggs from the dump site contained increased levels of these compounds, in comparison with samples taken upstream (sediments) and 50 km away from the site (eggs). In these studies the PBDF-emissions were often higher than the PCDD/F-emissions. Further, it was identified that high temperatures/ long residence times lead to less halogenated and potentially more toxic congeners.

In a recent Swedish screening PBDD/Fs were measured in a number of different matrices in the Swedish environment. The congener found to be dominant in both air, sludge and breast milk was octabrominated dibenzofuran (OBDF). In this screening study it was found that levels in air very much reflect the pattern of pyrolyzed or incinerated plastics.

Higher concentrations of PBDD/Fs were found in sewage sludge compared to storm water sludge indicating that atmospheric deposition is not the only pathway of these substances.

The presentation was concluded in the following points:

- PBDEs are easily transformed to PBDFs
- Uncontrolled fires lead to significant emissions of PBDEs and PBDFs
- The PBDF-emissions are often higher than the PCDD/F-emissions
- High temperatures/ long residence times leads to less halogenated and potentially more toxic congeners
- BFRs are present everywhere in society, and high levels of transformation products were detected in urban air, storm water and storm water sludge.
- PBDF concentrations in sewage sludge were significantly higher than the levels in storm water sludge, which indicates technosphere sources
- Human milk contains high PBDF amounts; which may lead to a significant exposure of infants. The toxicity of the PBDFs may have to be investigated further

The presentation was followed by a discussion of whether dioxins and furans may be formed during processing and moulding of plastics.

2.3.3 Long-range transport of various BFRs, in particular the non-PBDEs in comparison to PBDEs by Martin Scheringer, ETHZ, Swiss Federal Institute of Technology, Zurich

The general main point in this presentation was that many non-PBDE BFRs have properties similar to those of PBDE which makes them effective as flame retardants (intended) but they have also POP and PBT properties (unintended). The key question raised was: "What level of detail do we need to reach in our research into non-PBDE BFRs before there is a sufficient basis for a decision on a regulation/ban of these substances?"

A screening modelling exercise in which the properties of a number of new BFRs were compared to those of PBDEs was described. The results from this PBT modelling were that many non-PBDE BFRs have properties similar to those of the PBDEs, e.g. have long-range transport potential.

The overall persistence (Pov) and long-range transport potential (LRTP) were modelled using the OECD Tool described in a journal paper by Wegmann et al., *Environmental Modelling & Software* **24** (2009), 228–237.

Recent field measurement data on emerging FRs; HBB, DPTE and DP, in air and water in global transects showed that these substances were present in all samples from the Arctic to the Antarctic. Other non-PBDEs were present in some samples. Thus, the modeling results were backed up by field data.

A large number of new products containing bromine are put onto the market and the following question was raised in the presentation; "Are we on the wrong track"? A conclusion of this presentation was that the current scheme of substitution needs to be replaced.

Information about the San Antonio Statement on Brominated and Chlorinated Flame Retardants published by di Gangi et al in Environmental Health Perspectives 118 (2010), A516–A518 was also given.

2.4 Potential ecotoxicology and human effects

2.4.1 Indoor environment and human exposure of BFRs by Line Smastuen Haug, Norwegian Institute of Public Health

For traditional POPs the diet has been identified as the main exposure pathway while the same relationship has not been found for the PBDEs, for which house dust and indoor air seems to be important additional exposure pathways. Results from a study of PBDE exposure in the indoor environment were presented. The characterisation of different human exposure pathways of BFRs was done by comparing estimates of exposure from diet, indoor air and house dust with biomarkers of exposure.

X-Ray fluorescence (XRF) measurements were made to identify bromine containing articles in the homes of the persons included in the study. Variations in bromine burden were found for the studied persons, although the amount of electronic equipment in the homes was similar. The bromine content in the articles varied largely, both between similar articles but also within the articles.

For the banned pentaBDE congener BDE 47 the main intake route was identified to be via the diet but for HBCDD, which is still in use, the dust intake was of higher importance for the adults. It has also been found that hand washing significantly reduces exposure (*Watkins et al. Environ Health Perspect.119 (2011),1247-52)*

The messages from this presentation were:

- Knowledge on the importance of different exposure pathways is important for selecting appropriate actions to minimise exposure.
- The indoor environment can be an important exposure pathway for several POPs (PBDEs and HBCDD and especially for those that are:
  - used in large quantities indoors
  - not yet banned or restricted
- The relative importance of each exposure pathway might vary a lot between individuals
  - Variability in concentrations in delivering media
  - Variability in the exposure factors

2.4.2 What do we know about the effects of new BFRs? by Cynthia de Wit, SU, Stockholm University

Previous studies have shown that polybrominated diphenyl ethers (PBDEs) cause effects in laboratory studies. Associations with BDEs in the PentaBDE technical product with effects have also been seen in humans. These include effects on the thyroid system, neurobehavioral effects, immune effects and disturbances of both male and female reproductive systems. Hexabromocyclododecane has shown similar types of effects in laboratory studies but no human studies have been carried out as yet. Polybrominated dibenzo-p-dioxins and furans have similar effects and potencies as their chlorinated derivatives.

Data on the effects of the new BFRs are scarce but some studies have shown that:

- The phenolic compounds may be thyroid disruptors; HBB may be related to HCB
- TBBPA has been shown to have thyroid effects and thus its derivatives may have similar effects
- TBECH is a strong androgen agonist and may have reproductive effects, and also effects on the thyroid
- PBT has shown some Ah-receptor activity (in vitro)
- TBP has shown thyroid effects
- HxBBz has shown liver effects
- TBPA may have Ah-receptor activity
- Brominated tris (TDBPP) has shown to be a mutagen and is also a suspected carcinogen. It has been found in children’s urine (after wearing pyjamas)
- HCDBCO, BTBPE, DBDPE; have shown CYP (enzyme) effects and thyroid effects (in vitro)

The main conclusion from the presentation was that not much is known about the effects of ”new” BFRs. Similar effect as seen for the PBDEs and HBCDD can be suspected also for new BFRs, i.e. effects of the thyroid system, neurobehavioral effects and effects on reproduction, some may also have dioxin-like activity. Large knowledge gaps need to be filled.

2.5 Measurements and methods

2.5.1 Old", "New" and "Novel" Flame Retardants in the Environment Analytical Methods and Levels by Sicco Brandsma, IVM, Institute for Environmental Studies

Analytical methods that are available and levels that have been found in the environment for three groups of FRs were presented and discussed; starting with the "old" well known studies flame retardants like PBDEs, HBCD and TBBP-A followed by the "new"" brominated alternatives like DBDPE, BTBPE, TBB, TBPH and pentabromotoluene (PBT) and the other classes of alternatives such as organophosphorous flame retardants (PFRs).

Analytical methods described in the literature for different matrices were presented. For the new BFRs (BTBPE, DBDPE, TBB, TBPH and PBT) suitable extraction and clean-up methods and instrumentation were listed. A number of critical parameters for chemical analysis of the new BFRs were identified:

- Sulphuric acid treatment can only be used for DBDPE
- Non-destructive clean-up methods needed for BTBPE, TBB and TBPH
- TBA reagents may cause debromination of DBDPE
- DBDPE, TBB and TBPH undergo photodegradation
- Difficulties encountered in the analysis of DecaBDE are also expected for DBDPE
- DBDPE is poorly soluble in organic solvent, has higher boiling point than DecaBDE, is thermally degrades to mainly bromotoluenes and it has blank problems

The following were concluded:

- GC-ECNI-MS is a sensitive method to measure BDBPE, DBDPE, TBB and TBPH
- The new BFRs can be analysed in the same run as PBDEs
- The GC column need to be < 15 meter to avoid degradation of DBDPE
- Use of non-destructive clean-up methods is needed (no acids)
- LC-MS/MS in APPI/APCI mode good alternative

The new brominated flame retardants and PBDEs were measured in sediment and in suspended particle matter (SPM) from the Western Scheldt. PBCCH, pTBX and TBoCT were found in both sediment and SPM and the concentrations of these FRs ranged from 0.05 to 0.30 µg/kg dry weight (Lopez el al 2011).

Furthermore results of the occurrence of PFRs in Western Scheldt were presented. For these substances the highest concentrations were found in sediments and SPM. For tricresyl phosphate (TCP), 2-ethylhexyl diphenyl phosphate (EHDP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and triphenyl phosphate (TPP) no food web accumulation could be observed but tris(chloro 2-propyl) phosphate (TCPP), tris(2-butoxyethyl) phosphate (TBEP), tris-iso-butyl phosphate (TiBP), tris(2-ethylhexyl) phosphate (TEHP) and Trts(2-chloroethyl) phosphate (TCEP) are found higher in the food web. Concentrations were in the same range or higher than the PBDEs observed in the same samples.

Information was also given of the European research project ENFIRO (Life Cycle and Risk Assessment of Environmental Compatible Flame Retardants Prototypical case study in which ”Novel” alternatives (BFRs only reported in material goods/articles products) are studied. In this project the substitution options for some BFRs are studied

Lopez, P., Brandsma, S.H., Leonards, P.E.G. & Boer, J. de (2011). Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediments and suspended particulate matter. *Analytical and Bioanalytical Chemistry, 400*(8), 871-883.

3 Summary of the findings and main conclusions from the workshop

The workshop summarised scientific results and gave an overview of the present knowledge and key issues in the field of “new” and emerging flame retardants, with a focus on the brominated substances.

A widespread occurrence of these “new” alternative flame retardants in different parts of the environment was identified. However, there is a general lack of environment data in all matrices. Most data presented at the workshop were from different screening studies and research projects thus a need for broader environmental monitoring was identified.

The need for a better understanding of emissions, important pathways and how these new chemicals will affect our environment and our health was identified. More effect studies were pointed out as especially important.

Banned brominated flame retardants have been replaced by other related substances; some of these substances may have equally harmful effects as those they have replaced. A key question raised at the workshop was: What level of detail do we need to reach in our research into non-PBDE BFRs before there is a sufficient basis for a decision on a regulation/ban of these substances?

Summary of main conclusions based on the presentations:

- There is a need for a common set of abbreviations for the BFR compounds. These should reflect the structure of the compound but cannot be too long.
- Several of the “new” BFRs have been found in the Nordic environment and in Arctic areas in the same concentration levels as PBDEs.
- The presence of BFRs in background air samples indicates potential for long range atmospheric transport and the widespread occurrence in biota indicate potential for bioaccumulation.
- A large number of “new” BFRs have been identified in different biota samples but there are also many unknown bromine substances.
- Dechlorane plus, also a possible substitute for BDEs, was frequently found in environmental matrices. More research is needed on fate and effects of this compound as for the other dechloranes, such as Dec602, Dec603 and Dec604.
- Several “new” BFRs meet the criteria for persistence (P) (or potentially meet the P criteria), which has been shown both experimentally and by modelling exercises.

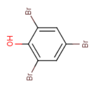
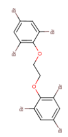
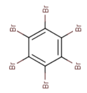
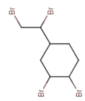
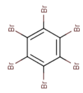
- The results from a PBT modelling exercise of BFRs showed that many non-PBDE BFRs have properties similar to those of the PBDEs, e.g. long-range transport potential.
- PBDD/Fs are present in plastic articles and are formed during fires - Uncontrolled fires lead to significant emissions of PBDEs and PBDFs.
- Indoor environment, air and dust, is an important pathway for the exposure of many POPs such as PBDEs – studies on the “new” BFRs are needed.
- There are great analytical challenges in the field of FRs. Analytical methods have improved during recent years but further improvements are still needed.
- The toxicity of the new BFRs is largely unknown. Real data are scarce on effects, which make the ecotoxicological relevance of results unclear. Large knowledge gaps need to be filled.

Appendix 1

23-24 of November
2011 Stockholm
Sweden

Norman Workshop

"New" brominated flame retardants as emerging contaminants in the environment

Organised by

Norman
IVL Swedish Environmental Research Institute
Norwegian Institute for Air Research
Stockholm University
Umeå University


IVL Swedish Environmental Research Institute

UMEÅ UNIVERSITET

Stockholms universitet

NILU

About the workshop

Because flame retardants such as polybrominated diphenyl ethers (PBDEs) are being phased out, an increasing number of alternative flame retardant chemicals have been introduced to comply with consumer product fire safety standards.

Recent studies have identified a widespread occurrence of some “new” brominated flame retardants (BFRs) in the environment. Several of the substances are persistent and may undergo long range atmospheric transport.

The workshop will bring together scientists and stakeholders working in the field. Present knowledge will be summarised and the need for new knowledge, monitoring and future research will be identified.

Following topics will be addressed:

Occurrence and distribution of emerging flame retardants (FR) in the environment.
Where do we find them and in which concentrations?

Emissions sources and important pathways of FR.
Use, fate and transformation products will be discussed.

Potential ecotoxicology and human effects.
Which effects are of concern? What is today’s knowledge and what do we need to know for reliable risk assessment?

Measurement methods.
The need for development and harmonization of methods will be addressed. Do we need to include new FRs in monitoring programs?

How big is the problem with emerging FRs?
Which message will we give to policy makers?

The workshop will be followed by a meeting with invited experts. The main objective of this expert meeting is to discuss and evaluate the future requirements with regard to new emerging brominated flame retardants.

The outcome from the expert meeting will be a position paper.

Programme

23 November Spårvagnshallarna		
12:20	Registration	
13.00	Welcome and Chair	**Åke Iverfeldt** IVL Swedish Environmental Research Institute
13:15	Presentation of the NORMAN network	**Valeria Dulio** INERIS, Institut National de l'Environnement Industriel et des Risques
13:30	Background to the workshop	**Eva Brorström-Lundén** IVL Swedish Environmental Research Institute
13:45	Improving the navigation among BFRs	**Åke Bergman** SU, Stockholm University
14:15	"New" Brominated Flame Retardants (BFR) in the Nordic and Arctic Environments	**Martin Schlabach** NILU – Norwegian Institute for Air Research
14:45	Coffee	
15:15	BFRs in marine mammals from Arctic and North Atlantic regions, 1986-2009	**Anna Rotander** and **Bert van Bavel** ORU, Örebro University
15:45	Chlorinated Flame Retardants (Dechloranes): analysis, occurrence and behaviour.	**Ethel Eljarrat** CSIC
16:15	Occurrence and use of brominated flame retardants and the fate of their toxic transformers: a challenge for policy makers	**Stefan Posner** SWEREA
16:45	Fate studies of selected BFRs	**Patrik L. Andersson** UmU, Umeå University
17:15	Polybrominated dibenzofurans: potential PBDE transformation products of concern	**Peter Haglund** UmU, Umeå University
17:45	Closing remarks	**Eva Brorström-Lundén** IVL Swedish Environmental Research Institute
19:00	Dinner, Spårvagnshallarnas festvåning, Tegnérgatan 2 C	

Programme

24 November Spårvagnshallarna		
08:30	Welcome and chair	**Valeria Dulio** INERIS, Institut National de l'Environnement Industriel et des Risques
08:35	Long-range transport of various BFRs, in particular the non-PBDEs in comparison to PBDEs	**Martin Scheringer** ETHZ, Swiss Federal Institute of Technology, Zurich
09:00	Indoor environment and human exposure of BFRs	**Line Smastuen Haug** Norwegian Institute of Public Health
09:30	What do we know about the effects of new BFRs?	**Cynthia de Wit** SU, Stockholm University
10:00	Coffe	
10:30	"Old", "new" and "novel" flame retardants in the environment - analytical methods and levels	**Sicco Brandsma.** IVM, Intitute for Environmental Studies
11:00	Conclusions from workshop/debate	**Eva Brorström-Lundén** IVL Swedish Environmental Research Institute
12:00	End of workshop	

Organisational matters

Registration and registration fees

To register use the attached registration form and send it to: **sandra.delamotte@ivl.se**
If you do not have a registration form please send an e-mail to sandra.delamotte@ivl.se

Registration fees for participation will be 100 € for Norman members and 150 € for non-Norman members. The fee covers the costs of all refreshments offered during the coffee breaks and dinner on the 23rd of November.

Final registration date: November 18th.

Accommodations

Special rates are available at the following hotels:

1. Elite Hotel Stockholm Plaza, Birger Jarlsgatan 29, +46 8 566 220 00
2. Crystal Plaza, Birger Jarlsgatan 35, +46 8 406 88 00
3. Elite Eden Park Hotel, Sturegatan 22, +46 8 555 627 00
4. Elite Hotel Arcadia, Körsbärsvägen 1, +46 8 566 215 00
5. Mornington Hotel, Nybrogatan 45, +46 8 507 330 00

Please mention IVL Swedish Environmental Research Institute when you make your reservation in order to obtain the discount.

Venue

Spårvagnshallarna
Birger Jarlsgatan 57, 113 56 Stockholm, Sweden +46-8 15 22 44

Directions to Spårvagnshallarna: http://www.sparvagnshallarna.com/karta.asp/id/71
Konferens Spårvagnshallarna is one of the most modern conference sites in Stockholm, situated in the heart of the city, with Stockholm's splendid variety of shopping and entertainment right next door.

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Working language

The official language of the workshop is English.

Appendix 2

List of compound names, abbreviations and CAS-numbers

Compound name	Abbreviation	CAS #
Phenolic BFRs		
2,4-Dibromophenol	24DBP	615-58-7
2,4,6-Tribromophenol	246TBP	118-79-6
Pentabromophenol	PBP	608-71-9
Tetrabromobisphenol-A	TBBPA	79-94-7
BFR ethers and esters		
2,4,6-Tribromophenyl allyl ether	ATE	3278-89-5
2,3-Dibromopropyl- 2,4,6- tribromophenyl ether	DPTE	35109-60-5
1,2-Bis (2,4,6-tribromophenoxy) ethane	BTBPE	37853-59-1
2-Bromoallyl-2,4,6-tribromophenyl ether	BATE	-
2,4,6-Tribromoanisol	TBA	607-99-8
Bis (2-ethylhexyl) tetrabromophthalate	BEHTBP	26040-51-7
2-Ethylhexyl- 2,3,4,5-tetrabromobenzoate	EHTeBB	183658-27-7
Other flame retardants		
Dechlorane Plus	DP	13560-89-9
Hexabromobenzene	HBB	87-82-1
Pentabromotoluene	PBT	87-83-2
Pentabromoethylbenzene	PBEB	85-22-3
Decabromodiphenylethane	DBDPE	84852-53-9
1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	TBECH	3322-93-8
2,4,4'-Tribromobiphenyl ether	BDE-28	41318-75-6
2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	5436-43-1
2',3,4,6'-Tetrabromodiphenyl ether/ 2,2',4,5'-Tetrabromodiphenyl ether	BDE-71/49	189084-62-6/243982-82-3
2,3,4,4'-Tetrabromodiphenyl ether	BDE-66	189084-61-5
3,3',4,4'-Tetrabromodiphenyl ether	BDE-77	40088-47-9
2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	60348-60-6
2,2',4,4',6-Pentabromodiphenyl ether	BDE-100	189084-66-0
2,2',3,4,4'-Pentabromodiphenyl ether	BDE-85	182346-21-0
2,3',4,4',6-Pentabromodiphenyl ether	BDE-119	189084-66-0
2,2',4,4',5,5'-Hexabromobiphenyl ether	BDB 153	68631-49-2
2,2',3,4,4',5'-Hexabromodiphenyl ether	BDE-138	182677-30-1
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	207122-15-4
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE-183	207122-16-5
2,2',3,3',4,4',5,6'-Octabromodiphenyl ether	BDE-196	446255-38-5
2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether	BDE-206	63387-28-0
2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether	BDE-209	1163-19-5