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RISK ASSESSMENT OF POLYBROMINATED BIPHENYLS AND POLYBROMINATED DIPHENYL ETHERS

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CONTENTS

SUMMARY

In the present report a risk assessment of polybrominated flame retardants carried out by the Dutch ministry of Housing, Spatial Planning and the Environment in 1990 is evaluated in the view of new information. The report focusses on the following aspects:

1. possible formation of polybromodibenzodioxins, polybromodibenzofurans and their chlorinated analogs (PBDD/F and PCDD/F, respectively) due to combustion of plastics containing brominated flame retardants in a municipal waste incinerator (MWI),
2. degradation of decabromodiphenylether (DeBDE), commercially the most important brominated flame retardant at the moment, in the environment,
3. environmental risk assessment of commercial pentabromodiphenylether (PeBDE) with a special emphasis on the possible risks due to secondary poisoning.

On these aspects the following is concluded:

ad 1: One can expect an increase in PBDD/F and PCDD/F formation in MWI as a consequence of the growing use of brominated flame retardants in plastics. However, it is not possible to draw strict conclusions from this supposition. First of all, it is not evident that the use of brominated flame retardants will increase. Then, since the products of incineration in a MWI form a complex function of process conditions, no calculations input/yield can be done.

ad 2: Although information is very scarce DeBDE can be classified as a persistant chemical. Photodegradation in water has been shown but will probably not be an important route since most of the DeBDE ends up in the sediment where the sunlight intensity is low. Biodegradation, aerobic as well as anaerobic, has not been studied. Both routes may occur but it can be expected that the rates will be very low.

ad 3: Biomagnification of commercial PeBDE does occur in significant quantities. Based on actual levels in fish and sediment the Maximum Permissible Concentration, taking into account secondary poisoning of predators via consumption of fish, is not exceeded. The Negligible Concentration is exceeded by at least a factor 10, however.

SAMENVATTING

In dit rapport wordt een herevaluatie uitgevoerd van een risicobeoordeling van gebromeerde brandvertragers die is opgesteld in 1990 door het ministerie van VROM. De volgende aspecten komen aan de orde:

1. de mogelijke vorming van polybroomdioxinen, polybroomdibenzofuranen en de gechloreerde analogen (PBDD/F en PCDD/F) door de verbranding in een afvalverbrandingsinstallatie (AVI) van plastics die gebromeerde brandvertragers bevatten.
2. afbraak in het milieu van decabroomdifenyl ether (DeBDE), op dit moment de commercieel meest gebruikte brandvertrager.
3. risicobeoordeling voor het milieu van commercieel pentabroomdifenyl ether (PeBDE) waarbij de nadruk ligt op mogelijke risico's via doorvergiftiging.

Ten aanzien van deze 3 aspecten wordt het volgende geconcludeerd:

ad 1: Een verhoging van de vorming van PBDD/F en PCDD/F in AVI's kan verwacht worden door de toename van het gebruik van gebromeerde brandvertagers. Op grond van deze veronderstelling kunnen echter geen kwantitatieve conclusies getrokken worden. Ten eerste is het niet duidelijk of het gebruik van gebromeerde brandvertragers zal toenemen. Daarnaast is de vorming van verbrandingsprodukten een complexe functie van de proces condities in een AVI waardoor het uitvoeren van input/produktie berekeningen niet mogelijk is.

ad 2: Ondanks het gebrek aan informatie moet DeBDE beschouwd worden als een persistente verbinding. Fotodegradatie in water is aangetoond. Dit zal echter waarschijnlijk geen belangrijke route zijn aangezien DeBDE zich voornamelijk zal bevinden in het sediment waar de zonlicht intensiteit laag is. Zowel over aerobe als anaerobe degradatie zijn nauwelijks gegevens beschikbaar. Beide routes kunnen optreden, maar de afbraaksnelheden zullen waarschijnlijk erg laag zijn.

ad 3: Biomagnificatie van commercieel PeBDE treedt op. Op basis van actuele concentraties in vis en sediment wordt het Maximaal Toelaatbaar Risiconiveau, waarbij doorvergiftiging van predatoren door consumptie van vis is meegenomen, niet overschreden. Het Verwaarloosbaar Risiconiveau echter wordt minimaal met een factor 10 overschreden.

INTRODUCTION

Polybrominated biphenyls and polybrominated diphenylethers are used as flame retardants in polymeric materials. Several years ago discussions started on the possible risks of these compounds in the Netherlands [1]. The Dutch ministry of Housing, Spatial Planning and the Environment prepared an evaluation document in which a risk assessment was carried out for man and environment. Based on this document the ministry decided to ban the use of polybrominated flame retardants in plastic resins and products [2]. Legislation for a ban was prepared and a draft-proposal was published in February 1993 [3].

Since the 1990 risk assessment much new information has become available on polybrominated flame retardants. Therefore the Dutch 'Project Team Flame Retardants' and the ministry of Housing, Spatial Planning and the Environment decided that a re-evaluation of the risks of these compounds is necessary. The National Institute for Public Health and Environmental Protection was asked to summarize and evaluate the information which has recently become available, and subsequently re-evaluate the risk assessment of 1990.

Because it was not possible to cover all aspects it was decided that the evaluation will focus on several main issues. The Dutch 'Project Team Flame Retardants', the ministry of Housing, Spatial Planning and the Environment and the National Institute for Public Health and Environmental Protection agreed that these issues are the following:

1. possible formation of polybromodibenzodioxins, polybromodibenzofurans and their chlorinated analogs due to combustion of plastics containing brominated flame retardants in a waste incinerator meeting the Dutch emission standards,
2. degradation of decabromodiphenylether, commercially the most important brominated flame retardant at the moment, in the environment,
3. environmental risk assessment of commercial pentabromodiphenylether with a special emphasis on the possible risks due to secondary poisoning.

The present report contains the results of the re-evaluation. Issue 1, 2, and 3 are discussed in Chapter 1, 2, and 3, respectively.

References

1. Stichting Natuur en Milieu (1988). Flame retardants.
2. Ministerie VROM (1990). Evaluatierapport organobroom-brandvertragers: polybroombifenyl- en polybroombifenyloxide-verbindingen (in Dutch).
3. Ontwerp besluit broomhoudende bifenylen en difenyloxiden Wet Milieugevaarlijke Stoffen (1992). Staatsblad, 272 (in Dutch).

CHAPTER 1. INCINERATION OF PRODUCTS CONTAINING POLYBROMINATED BIPHENYLS AND POLYBROMINATED DIPHENYLETHERS AS FLAME RETARDANTS

1.1. Thermal experiments on pyrolysis/incineration of brominated flame retardants (including PBBs and PBDEs)

1.1.1. Pyrolytic experiments

Recent publications show that brominated and mixed-halogenated dioxins and furans can be formed after thermal decomposition of some brominated flame retardants: polybrominated biphenyls (PBBs) and polybrominated diphenylethers (PBDEs). These thermal reactions may be of environmental concern because a significant portion of materials containing brominated flame retardants (plastic, carpets, textiles) is incinerated, with potential release of these compounds or their thermal products into the environment. Brominated compounds are expected to behave in thermal reactions in a similar manner as their chlorinated analogs.

The consumption of brominated flame retardants is estimated at approximately 2500 tonnes/year (1990) [1]. About 40% of this amount will be incinerated in MWIs. Taking into consideration the lifetime of durable consumption goods (computers, TV sets) one might respect an increase of brominated flame retardants in municipal solid waste during the coming years. The question is, whether an increase of brominated flame retardants in the input of MWIs would lead to an increase of brominated/chlorinated aromatic micropollutants as PCDD/F en PBDD/F in the environment.

According to many papers, laboratory pyrolytic tests could be a good method to study formation of halogenated dibenzodioxins and dibenzofurans during a thermal decomposition of brominated flame retardants [1-8]. However, laboratory pyrolysis of flame retardants or plastic mixtures cannot be compared to a real combustion of these chemicals in a MWI in such a way that a quantitative prediction of emissions according to the input can be given. Nevertheless, they can be useful for studying the mechanism of thermal reactions, later discussed in paragraph 1.2.

Different pyrolytic tests with brominated flame retardants were carried out. The optimum temperature for the formation of polybrominated dibenzofurans (PBDFs) and dibenzodioxins (PBDDs) during the pyrolysis of different polymers containing brominated organic flame retardants lies between 600 and 800 °C.

PBDFs were found almost in all samples (flue gas and flue ash). Both the degree of bromination and the concentration of PBDFs varied greatly. PBDDs were formed in only a few samples and related to PBDFs in very low concentrations. The largest yields (in percentage range) of PBDFs were measured in the pyrolysis products of polymers containing brominated diphenyl ethers (PBDEs). Pyrolysis conditions of PBDE seem to have less influence on reaction mechanism and products than the type of a polymer matrix [6]. In case of the pure decabromodiphenyl ether there is a surplus of bromine radicals but no substituents for them like hydrogen. The formation of hexabromobenzene, which is very stable, as the main product and lower quantities of PBDD/F can thus be explained. When decabromodiphenylether is constrained in a polymer matrix, it can react only with itself by a ring closure to form dibenzofuran. Polystyrene, and especially polyethylene increase the yield of brominated dibenzofuran formation (all degrees of bromination). The influence of a high impact polystyrene polymer matrix on the formation of PBDFs results both in lowering the optimum formation temperature to 350-400 °C [7,8] and an increase of the total yield PBDFs with a factor 7 [7].

Not every brominated flame retardant gives PBDD/F as the products of pyrolysis: there are no traces of PBDF/D in the pyrolisate of tetrabromophtalic anhydride [5]. A comparative study of oxydative and pyrolytic (in nitrogen) gas-phase degradation of three brominated flame retardant materials by Striebich et al. [9] shows in air a slightly different pattern of decomposition than in nitrogen. Anyhow, none of the organic products formed at intermediate temperature survived the exposure at 800 °C at 2.0 seconds residence time. During the tests with a high temperature flow reactor, brominated products were formed at both pyrolytic and oxidative conditions, but the yields were much lower than in most pyrolysis experiments.

Though by an ideal combustion in a MWI all intermediate hazardous organic compounds must be destroyed, one can imagine the possibility of low temperature/low oxygen zones (poorly controlled incineration or starting-up conditions), thus the pyrolytic experiments also being of a general value.

1.1.2. Incineration tests

The incineration of bromine containing flame retardants (pure compounds and mixtures in a polymeric matrix) has been studied on laboratory scale in different types of ovens [8]. Different aromatic bromine compounds commercially used as flame retardants were investigated. Only brominated diphenylethers

(PBDEs) yielded significant quantities of brominated dibenzodioxins and dibenzofurans. The pure bromoether gave a maximum of PDBF-formation at 700 °C. The polymeric matrix and the additive have a great influence on the yield. The yield of dibenzofurans from a mixture increased in comparison with a pure compound while the temperature range of optimal PBDF formation was shifted from 700 °C to 400-600 °C, in the same way as in the pyrolytic experiments. It should be noticed that the combustion process in laboratory ovens of the types described in [8] cannot be identified with a process in a real MWI, also as far as temperature concerns. In our opinion, such tests are relevant for a comparative study of flame retardants rather than a prediction of emissions from a MWI.

A couple of real-scale experiments (in a MWI) have been carried out to test the incineration products after adding several brominated compounds to the waste.

In the study of Lahl, Wilken and Wiebe [10] an addition of 2 kg of printed plates containing 4.85% of a flame retardant PBDE, direct into the oven of MWI Bielefeld (oven's capacity was 14 t/h) has led within half an hour to a considerable increase (2.3 times) of PBDD/F and PCDD/F in the ESP ash. There is no concentration peak of dioxin/furan noticed in the stack gas, because during the sampling (longer than half an hour), a sharp peak is probably flattened. Though according to the authors the incineration conditions were stable during the test one cannot exclude uncertainty, because the test was never reproduced.

In Wilken's test [11] CBr_4 was used as bromine carrier. This compound is neither used as flame retardant, nor is it a precursor of dioxins/furans. The bromine content of the waste was increased almost tenfold (normally 20-90 g/t), but was still 1/10 of the usual chlorine content of the waste. The increase of the bromine input resulted in an increase of mixed-halogenated dioxins, furans and benzenes in the flue gas and ESP ash. Mainly monobromo-polychloro dioxins were found, while analogous pure brominated compounds could not be detected. The dioxin and furan contents in ESP ash show a good correlation with the bromine content of the ash. Also, an unexpected increase in chlorinated PCDD/F in the flue gas was the consequence of bromine addition.

Other incineration tests [12] show that the production of brominated aromatic micropollutants is influenced by operation conditions. These experiments show only a possibility of an increase of halogenated dioxins/furans in the ESP-ash (less certainty about the flue gas) as a result of the increase of bromine in the input. However, no quantitative correlation can be found between the input and the output (also in terms of toxicity).

1.2. A possible reaction mechanism of bromine-chlorine exchange of polybrominated and mixed dioxins/furans

Possible sources of PCDD/F in the environment are:
1) trace contaminants from industrial chemicals,
2) thermal reaction products from chlorinated aromatic precursors (Fig.1a),
3) de novo formation in combustion processes (Fig.1b).

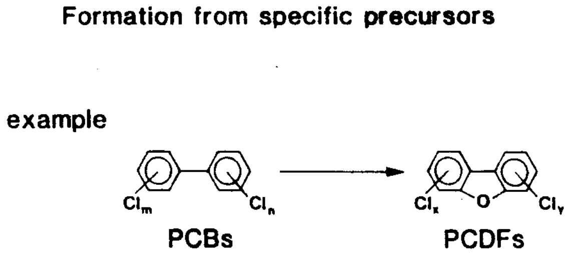

Figure 1a

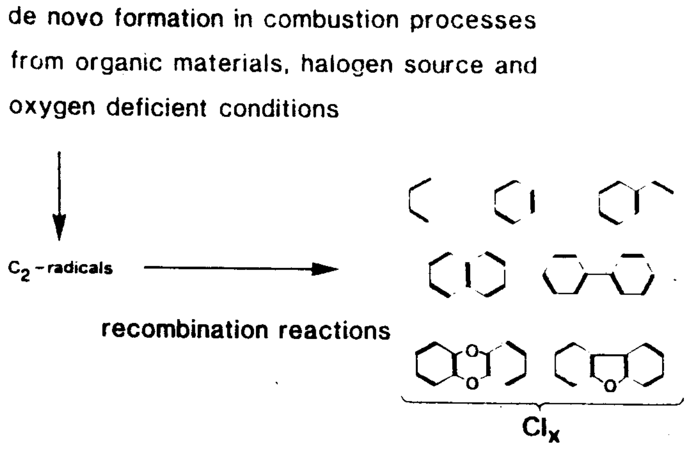

Figure 1b

In high-temperature experiments (mostly 500-800 °C), chlorinated PCDD/Fs are formed from suitable precursors (chlorophenols, PCBs, PCDPEs and chlorobenzenes) by oxidation, cyclisation and condensation reactions.

The same reactions also occur with the brominated compounds (Fig. 2).

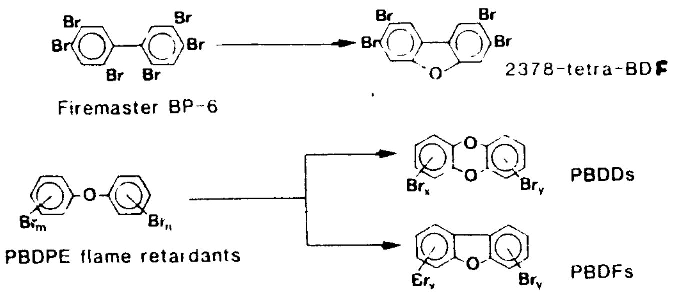

Figure 2

Mixed halogenated compounds are expected to be products of combustion processes if bromine and chlorine sources are both present. Depending on the Br/Cl ratio and the number of halogens entering a specific compound, various mixed halogenated products are expected (Fig. 3).

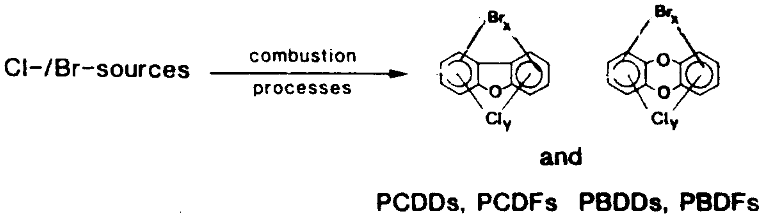

Figure 3

Because of structural considerations PBDDs and PBDFs seem to behave in a manner similar to the chloro analogs [13,14]. In many situations (e.g. municipal waste incineration), bromine is present in the range of a few percent relative to the amount of chlorine, but this can be different in other situations (incineration of hazardous or industrial waste).

A chlorine-bromine exchange tends to take place during thermal reactions with mixed Cl/Br sources, which leads to a relative increase in mixed halogenated- and/or fully chlorinated compounds [15,16,17]. During pyrolysis experiments of 1,2,3,4,-T_4BrDD with PVC and to lesser extent with NaCl and HCl, bromine has been always substituted with chlorine. The degree of exchange increases with the temperature: at 900 °C 34.7% of fully chlorinated dioxin was formed against only 6.2% at 800 °C. One can assume that the reaction mechanism is a nucleophilic aromatic substitution rather than a radical reaction [15].

The assumption of a nucleophilic addition-elimination mechanism is supported by Zier et al. [16] with a kinetic model for this reaction being developed. An explanation for the presence of PBCDD/F in ESP-ash and the increase of PCDD/F yield from a MWI after adding brominated compounds to the waste is given. The copper-catalyzed exchange reaction of the chlorination of PBDD/F formed from brominated flame retardants takes place on the surface of ESP-ash particles. Cl/Br ratio in the ash (normally 250:1) has an influence on PCDD/F to PBDD/F ratios. Chlorinated analogs normally prevail to a considerable extent in combustion residues. Measurements on real scale support the assumed mechanism. Municipal incinerators in the USA have been extensively investigated as sources of chlorinated dioxins and furans [20]. Bromochloro compounds were found at a lower concentration compared to the chlorinated species (ca. 1-20% of these compounds from the yield of chlorinated ones).

Dellinger et al. [18] assumed a certain mechanism and kinetic modelling of a gas-phase PBDD/F formation after thermal oxydation/pyrolysis of pure and mixed brominated flame retardants. Results obtained from this kinetic model suggest that a gas-phase formation of PBDD is also significant. The maximum yields, 2.0 E-02 and 7.1E-05 g/m^3_0 for PBDD and PCDD, respectively have been reported at 800 °C, thus showing an enormous prevalence of brominated compounds.

A distribution of congener groups of both Cl-, Br- and Cl/Br dioxins/furans has been calculated on the basis of incineration data [19].

1.3. Emission data on modern municipal waste incinerators

Although there is enough evidence of extra forming of brominated, mixed and chlorinated dibenzodioxins/furans after extra input of brominated flame retardants into a MWI, the latest data on flue gas from modern incineration ovens for municipal solid waste give reassurance of the efficiency of contemporary cleaning- and decontamination installations.

Data from modern Swedish municipal waste incineration plants (MWIs) with good combustion conditions and equipped with an efficient flue-gas cleaning train do not indicate that unacceptable environmental risks can be caused by bromine in waste [20]. An enhanced input of bromine, like brominated flame retardants, should cause only an increase of HBr concentration in the flue gas (HBr is a final product of full combustion/oxydation of bromininated organic compounds). The emissions of toxic TCDD equivalents (calculated according to Eadon) were 0.1 $ng/m^3{}_0$, thus conform to the legislation.

Other flue-gas cleaning devices, such as denitrification equipment appeared to reduce dioxin and furan level in the flue gas of MWIs. Measurements at a MWI in Switzerland and a hazardous waste incinerator in Germany, both equipped with a SNCR deNOx installation in 1992 [21], have shown a reduction in chlorinated dioxin and furan formation with 50% after the deNOx. Moreover, the concentrations of total dioxin/furan species after active carbon injection into the warm flue gas and a fabric filter range from 0.125 to < 0.01 $ng/m^3{}_0$ TEQ. Analogous positive results were obtained at the ROTEB (MWI Rotterdam) during the Demonstration Program deNOx at MWIs [22]. After retrofitting of SCR deNOx followed by a two stage wet scrubber and electro-dynamic venturi (EDV) in MWI plant Spittelau (Austria, Vienna), total dioxin/furan emissions during the latest three years are below 0.1 $ng/m^3{}_0$ TEQ [23,24]. After starting up the SCR plant it was found that the same catalyst was an effective oxidant of PCDD/Fs. The same experience with SCR and the same PCDD/F emission level has been obtained at the Malmö plant in Sweden [25]. A fabric filter (preceeded by activated carbon or lime injection) has been proven to retain more than 99% PCDD/F. However, extra control facilities after the fabric filter, such as a wet scrubber with a condensation device, can be a source of extra *de novo* formed PCDD/Fs [26]. Even without a carbon/cokes filter (the so-called tertiary pollution control devices) in a MWI plant equipped with only a cyclone followed by a spray absorber (lime injection) with a fabric filter, the PCDD/F emission could be kept below 0.1 $ng/m^3{}_0$ TEQ (measurements at 22 MWI plants in Germany, 1990-1992 [27]). Thus from the point of view of PCDD/F emissions to air there is evidence enough to be quite sure of the safety of modern incineration plants. In the Netherlands some MWIs will possibly obtain a temporary permission to emit more than 0.1 $ng/m^3{}_0$ TEQ: MWI-Amsterdam West: 4 $ng/m^3{}_0$ TEQ, MWI-Rijnmond: 1-2 $ng/m^3{}_0$ TEQ, Roteb: unknown but higher than 0.1 $ng/m^3{}_0$ TEQ and Shell Chemie: 7.6 $ng/m^3{}_0$ TEQ [37/40].

It should be stated that according to the new environmental standards, ESP ash and flue gas cleaning residue should be considered as hazardous waste and landfilled with special care or decontaminated.

1.4. Possible methods for detoxification of ESP-ash

Fly ash from ESP in incineration plants has been shown to act as a reagent as well as a catalyst in formation and destruction of halogenated micropollutants. It is an efficient adsorbent and chlorinating agent for aromatic compounds. The dioxin balance in MWIs of old and new types (the latter means equipped according to "the state of the art") [28] shows that the lion's share of total PCDD/F can be found in the ESP ash of both types. In the ESPs of old-type incinerators a multiple quantity (more than factor 50) is found of PCDD/F in comparison with new ones (the dioxin/furan input is the same). Some novel methods of ESP ash detoxification have been developed. These are, for instance, destruction at high temperatures in oxidizing air [29] or thermal treatment with hot raw flue gas still containing HCl [30]. Because of the chlorine-bromine and bromine-chlorine exchange (depending on the relative concentrations and residence time) between 250 and 300 °C [31,32] it could be a good preventive measure to separate the flue ash at high temperature, before the ESP. Different studies are being carried out at the moment [33]. There are also general prescriptions concerning the exploitation of a MWI developed to prevent the formation of hazardous halogenated organic pollutants during the combustion [34,35].

1.5. Potential risks in brominated flame retardant dissemination in the environment

Since process factors and the quality of combustion have been proven to strongly influence the formation of chlorinated and brominated PDD/Fs, one must avoid uncontrolled combustion. Accidental fires in buildings can form a considerable source of pollution with brominated flame retardants or the products of their thermal degradation. Fire residues from three different accidental fires in private residences were analyzed for PBDD/F and brominated flame retardants [36]. One sample, a plastic TV case, contained 5% PBDE. The same sample contained 14,910 μg PBDD/F (155.3 μg/kg TEQ) per kg. It was found that brominated dioxins and furans were generated by defined sources containing precursor substances, and were then transported to other objects of different surface structures. Distance from the source and surface characteristics of the samples influence the contamination degree of the samples.

In addition, the so-called automotive plastic waste (fluff) containing brominated flame-retarding additives can be of potential danger to the environment because of leaching-out processes [17]. It could be noticed, that automotive plastic waste is not quite relevant for the situation in the Netherlands.

1.6. Conclusions

1. One can expect an increase in PBDD/F and PCDD/F formation in MWI plants as a consequence of the growing use of brominated flame retardants in plastics. However, it is not possible to draw strict conclusions from this supposition. First of all, it is not evident that the use of brominated flame retardants will increase. Then, since the products of incineration in a MWI form a complex function of process conditions, no calculations input/yield can be done.

2. Modern plants for municipal waste incineration equipped with at least a dry absorber and a fabric filter can meet the latest environmental standards (PCDD/F concentration in the flue gas of less than 0.1 ng/m^3_0 TEQ). A possible increase in formation of dioxins/furans can be compensated by an extra heavy (activated carbon + fabric filter) unit in the cleaning train.

3. Because of a danger of a higher degree of contamination of ESP ash with hazardous halogenated organic compounds, the novel techniques of ash decontamination and immobilization should be more broadly implemented.

1.7. List of abbreviations

ESP - electrostatic precipitator
PBBs - polybrominated biphenyls
PBDEs - polybrominated diphenyl ethers
PBDD/Fs - polybrominated dibenzodioxins/furans
PCDD/Fs - polychlorinated dibenzodioxins/furans
PBCDD/Fs - mixed (poly)bromochlorodibenzodioxins/furans
MWI - municipal waste incineration (plant)
SNCR - selective non-catalytic reduction
SCR - selective catalytic reduction
TEQ - toxic equivalents

References

1. Luijk, R., v. Laar, A. (1990) Gebromeerde Brandvertragers. Feiten en standpunten. Chemiewinkel-CMCV UvA, Amsterdam.
2. Dumler, R., Thoma, H., Lenoir, D., Hutzinger, O. (1989) PBDF and PBDD from the combustion of Bromine Containing Flame Retardant Polymers: a Survey. Chemosphere **19**, (12), 2023-2032.
3. Schwind, K.-H., Hosseinpour, J., Thoma, H. (1988) Brominated/Chlorinated Dibenzo-P-Dioxins and Dibenzofurans in Fly Ash from a Municipal Waste Incinerator. Chemosphere **17**, 1875-1884.
4. Dumler, R., Lenoir, D., Hutzinger, O.; Formation of Brominated Dibenzofurans and -Dioxins from the Combustion of the Flame Retardant Decabromodiphenyl Ether under Different Conditions. Proc. 10th Int. Symp. on Dioxins and Related Cpds. Dioxin-'90, 10-14 sept 1990, Bayreuth, p. 325.
5. Thoma, H., Rist, S., Hauschulz, G., Hutzinger, O. 1986). Polybrominated Dibenzodioxins and -Furans from the Pyrolysis of Some Flame Retardants. Chemosphere **15**, (5), 649-652.
6. Thoma, H., Hauschulz, G., Knorr, E., Hutzinger, O. (1987) Polybrominated Dibenzofurans (PBDF) and Dibenzodioxins (PBDD) From the Pyrolysis of Neat Brominated Diphenylethers, Biphenyls and Plastic Mixtures of These Compounds. Chemosphere **16**, (1), 277-285.
7. Luijk, R., Wever, H., Olie, K., Govers, H.A.J., Boon, J.J. (1991) The Influence of the Polymer Matrix on the Formation of Polybrominated Dibenzo-p-Dioxins (PBDDs) and Polybrominated Dibenzofurans (PBDFs). Chemosphere **23**, (8-10), 1173-1183.
8. Dumler, R., Thoma, H., Lenoir, D., Hutzinger, O. (1989) Thermal Formation of Polybrominated Dibenzodioxins (PBDD) and Dibenzofurans (PBDF) from Bromine Containing Flame Retardants. Chemosphere **19**, (1-6), 305-308.
9. Striebich, R.C., Rubey W.A., Tirey D.A., Dellinber, B. (1991) High-Temperature Degradation of Polybrominated Flame Retardant Materials. Chemosphere **23**, (8-10), 1197-1204.
10. Lahl, U., Wilken, M., Wiebe, A. (1991) Polybromierte Diphenylether in der Müllverbrennung. Müll und Abfall, **2**, 83-87.
11. Wilken, M., Beyer, A., Jager, J.; Generation of Brominated Dioxins and Furans in a Municipal Waste Incinerator (MWI) - Results of a Case Study. Proc. of 10th Int. Symp. on Dioxins and Related Cpds. Dioxin-'90, 10-14 sept. 1990, Bayreuth, p. 377.

12. öberg, T., Warman, K., Bergström, J. (1987) Brominated Aromatics from Combustion. Chemosphere **16**, (10-12), 2451-2465.
13. Buser, H.-R.; Brominated and Brominated/Chlorinated Dibenzodioxins and Dibenzofurans (1987) Potential Environmental Contaminants. Chemosphere **16**, (4), 713-732.
14. Buser, H.-R. (1987) Bromierte und gemischt bromiert/chlorierte Dibenzodioxine und Dibenzofurane. VDI Berichte Nr. 634.
15. Thoma, H., Hauschulz, G., Hutzinger, O. (1987) Chlorine-bromine exchange during pyrolysis of 1,2,3,4-tetrabromodibenzodioxin with various chlorine donors. Chemosphere **16**, (7), 1579-1581.
16. Zier, B., Lenoir, D., Lahaniatis, E.S., Kettrup, A. (1991) Surface Catalyzed Halogenation-Dehalogenation Reactions of Aromatic Bromine Compounds Adsorbed on Fly Ash. Chemosphere **22**, (12), 1121-1129.
17. Donnelly, J.R., Grange, A.H., Nunn, N.J. (1990) Bromo-and Bromochloro-Dibenzo-p-Dioxins and Dibenzofurans in the Environment. Chemosphere, **20**, (10-12), 1423-1430.
18. Dellinger, B., Maqsud, L., Sidhu, S.; Kinetics of Toxic Combustion By-Product Formation. Proc. 13th Int. Symp. on Chlorinated Dioxins and Related Cpds. Dioxin-'93, Vienna, sept. 1993, pp 261-264.
19. Funcke, W., Hemminghaus, H.-J.; Evaluation of PCDF/D, PBDF/D and PBCDF/D Profiles in Flue Gas of Combustion Facilities using a statistical Distribution Function. Proc. 13th Int. Symp. on Chlorinated Dioxins and Related Cpds. Dioxin-'93, Vienna, sept. 1993, pp. 345-350.
20. öberg, T., Bergström, J.; Bromine and Waste Incineration - an Environmental Risk? Proc. of 10th Int. Symp. on Dioxins and Related Cpds. Dioxin-'90, 10-14 sept 1990, Bayreuth, pp 339-342.
21. Ruegg, H., Sigg, A. (1992) Dioxin Removal in a Wet Scrubber and Dry Particulate Remover. Chemosphere **25**, (1-2), 143-148.
22. De Boer, A.(Head R&D ROTEB, MWI Rotterdam), Personal Communications, February 1994.
23. Pacher, W., Hartl, H., Wurst, F., Boos, R., Sparrer.J., Lindbauer, R.L.; MWSI Plant HBW Spittelau Vienna, Austria - Three Years' Experience: Emissions below 0.1 ng/m^3_0 TEQ SC. Proc. 13 th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'93, Sept. 1993, Vienna, vol. 12, p. 7.
24. Boos, R., Stock, M., Kuna, R.P.; Simultaneous Sampling of PCDDs and PCDFs at the MWI Spittelau/Vienna. Proc. 13 th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'93, Sept. 1993, Vienna, vol. 11, p. 151.

25. Carlsson, K.B. (1992) Dioxin Destruction in Catalysts for NOx-Reduction (SCR-DENOx). Chemosphere **25**, (1-2), 135-138.
26. Marklund, S., Fängmark, I., Rappe, C. (1992) Formation and Degradation of Chlorinated Aromatic Compounds in an Air Pollution Control Device for MSW Combustor. Chemosphere **25**, (1-2), 139-142.
27. Funcke, W., Luthardt, P., Philipp, Ch., Ledebur, H., Staberow P., Teichert, B.; PCDF/D Concentrations Below 0.1 ng/m^3_0 TEQ in the Stack Gas of a Municipal Waste Incinerator without Tertiary Flue Gas Cleaning Device. Proc. 13th Int. Symp. on Chlorinated Dioxins and Related Cpds. Dioxin-'93, Vienna, sept. 1993, vol. 12, pp 43-44.
28. Vehlow, J., Vogg, H. (1991) Thermische Zerstorung Organischer Schadstoffe. Müllverbrennung und Umwelt 5, red. Karl J. Thomé-Kozmiensky, Berlin, pp 447-467.
29. Cyrys, J., Lenoir, D., Matuschek, A., Kettrup. A.; Fly Ash of MWI as a Reagent and Catalyst for the Formation of Micropollutants: Oxidation of Particulate Carbon Monitored by Simultaneous Thermal Analysis - Mass Spectrometry of DSC. Proc. 12th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'92, Aug. 1992, Tampere, Finland, vol.9, pp 53-56.
30. Ogaki, Y., Yamaguchi, H., Okuyama, K., Hamaguchi, K., Shibuya, E.; Influence of HCl on Thermal Decomposition of PCDDs/PCDFs in Fly Ash from MSW Incinerator. Proc. 13 th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'93, Sept. 1993, Vienna, vol. 12, pp 77-80.
31. Luijk, R., Govers, H.A.J.; The Exchange of Bromine and Chlorine in 2,3,7,8- Tetrabromo-Dibenzo-p-Dioxin. Proc. 12th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'92, Aug. 1992, Tampere, Finland, vol. 8, pp 99-102.
32. Heinbuch, D., Stieglitz, L.; Formation of Brominated Compounds on Fly Ash. Proc. 12th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'92, Aug. 1992, Tampere, Finland, vol. 8, pp 257-260.
33. Gerrits, B.J., Kuipers, G.; Hoge-temperatuur stofafscheiding bij afvalverbrandigsinstallaties. TNO-report 93-430, A Concept of a Preliminary Study, 1993.
34. Jager, J., Wilken, M., Beyer, A., Rakel, H., Zeschmal-Lahl B.; Practical Concepts to Minimize the Emission of Halogenated Organic Compounds from Municipal Waste Incinerators. Proc. 12th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin- '92, Aug. 1992, Tampere, Finland, vol. 9, pp 103-106.
35. Sakai, S., Karatsu, Y., Tejima, H., Honda, T.; Reduction of Dioxin Emission on Starting up and Shutting Down of Batch Operation Type MSW

Incineration Plant. Proc. 12th Int. Symp. on Chlorinated Dioxins and Related Cpds., Dioxin-'92, Aug. 1992, Tampere, Finland, vol. 9, pp 219.

36. Zelinski, V., Lorenz, W., Bahadir, M. (1993) Brominated Flame Retardants and Resulting PBDD/F in Accidental Fire Residues from Private Residences. Chemosphere **27**, (8), 1519-1528.
37. Letter from 'Gedeputeerde Staten van Noord-Holland' to 'Burgemeester en Wethouders van de gemeente Amsterdam AVI-Amsterdam; gedogen' 22-03-1994, nr. 94-511571 (in Dutch).
38. 'Provincie Zuid-Holland Gedeputeerde Staten': 'Voornemen tot gedogen/concept-gedoogbeschikking Afvalverbrandingsinstallaties Shell Nederland Chemie BV', kenmerk: 274037/198' (in Dutch).
39. 'Provincie Zuid-Holland Gedeputeerde Staten': 'Gedoogbeschikking NV Afvalverwerking Rijnmond' 09-03-1994 (in Dutch).
40. 'Provincie Zuid-Holland Gedeputeerde Staten': 'Gedoogbeschikking Dienst Roteb van de gemeente Rotterdam' 09-03-1994 (in Dutch)

CHAPTER 2. ENVIRONMENTAL FATE OF DECABROMODIPHENYLETHER (DeBDE) IN THE AQUATIC ENVIRONMENT

2.1. Introduction

A central issue in the discussions on brominated flame retardants is the environmental fate of DeBDE in the aquatic environment. It has been stated by several authors that DeBDE will not be taken up by aquatic organisms and will probably accumulate in sediment due to its high adsorption capacity [5]. Analyses of fish, water and sediment samples support this view [5]:

- DeBDE was not detected in water samples from more than 47 locations in Japan (detection limits varied from 0.06 to 2.5 μg/l),
- DeBDE was not detected in 138 fish samples from 46 locations in 1988-1989 in Japan (detection limit: 5 μg/kg wet weight),
- in sediments very diverging results were found: from < 4 μg/kg (detection limit) to 11.6 mg/kg dry sediment (measurements in Japan and USA). However, information on the sample locations is often lacking.

In the present chapter the environmental fate of DeBDE, once released to water, is discussed. Firstly, the possible uptake of DeBDE by aquatic or sediment dwelling organisms is evaluated. Secondly, degradation of DeBDE, biotic as well as abiotic, is discussed because an important item is whether degradation of DeBDE occurs to breakdown products which can be taken up by organisms.

2.2. Uptake by aquatic organisms

If DeBDE is released to the environment it will probably not be taken up by aquatic organisms [5]. Norris et al. [7] reported minimal uptake of DeBDE and octabromodiphenyl (OBB) in rainbow trout after 48 hours exposure to waterborn DeBDE and OBB. Although the exposure period was too short to calculate a reliable concentration factor, the possibility of uptake of waterborne DeBDE and OBB were demonstrated in this study.

In a 42 day Japanese study BCFs for carp of <5 and <50 are determined for DeBDE using exposure concentrations of 60 and 6 μg/l, respectively. For the closely related decabromodipehnyl (DBB) BCFs are 0.6-5.4 and <4 for exposure concentrations of 150 and 5 μg/l [14]. Boths tests are carried out using a test design corresponding to OECD Test Guideline 305C [15]. However, details on these studies are lacking.

In Atlantic salmon exposed to waterborne OBB during 96 hours no OBB was found (detection limit of 10 μg/kg) but 42 μg/kg of an unidentified hexabromobiphenyl (HxBB) was measured [12]. Probably debromination to HxBB occurred after uptake of OBB. However, it is possible that HxBB detected orginates from HxBB impurities in OBB.

According to Opperhuizen [8] uptake from water across the fish gills is hampered if the molecular diameter is > 0.95 nm and/or molecular length > 5.3 nm. For DeBDE the molecular size is close to the gill membrane pore size of 0.95 nm: the estimated diameter of the non-planar DeBDE molecule is 0.7 nm and the lenght is approximately 1.2 nm [13]. Opperhuizen et al. [9] stated that "for all polybrominated biphenyls with 6 or more bromo atoms, except 2,2',3,3',4,4'-hexabromodiphenyl, membrane permeation must be limited".

It can be concluded from these studies that uptake of DeBDE via the water phase is possible but will be limited. However, uptake via food by fish or sediment by sediment dwelling organisms is possible. Only data for uptake via food for octabromobiphenyl are available, however. Atlantic salmon were fed contaminated food for 90 days using a concentration of 100 μg/g [12]. At equilibrium concentration in fish was 2.32 μg/g. In addition fish contained unidentified penta-, hexa- and, mainly heptabromobiphenyl. Only hexabromobiphenyl was quantified: concentration at equilibrium was 10.0 μg/g. It can be concluded that uptake of DeBDE via food will probably take place but concentration factors will be low. However, mammalian pharmacokinetic tests indicate that DeBDE is poorly adsorbed from the gastro-intestinal tract and is rapidly excreted [5]. Possibly, debromination in fish occurs.

2.3. Degradation in the aquatic environment

2.3.1. Photodegradation

2.3.1.1. Photodegradation of DeBDE

The photodegradation of DeBDE has been investigated in organic solvents and in water. In xylene DeBDE photodegraded readily to the lower brominated tri- to octabromodiphenyl ethers [5, 7]. Some studies on photodegradation of PBDEs in hexane, reviewed by Pijnenburg and Everts [11] reported similar degradation products.

In water photohydroxylation is probably the favoured route. The hydroxyl substituted degradation products will decompose rapidly via increased UV absorption [5, 7]. Further debromination of molecules on which the reaction has started prevails over the start of debromination of 'new' DeBDE molecules [10].

The photodegradation of commercial DeBDE (77.4% DeBDE, 21.8% nonabromodiphenyl ether and 0.8% ocatabromodiphenyl ether [3]) in water exposed to natural sunlight, shown in the study of Norris et al. [7] is marginal: after 98 days about 1% of the initial amount (10 g in 8 l water) of DeBDE has disappeared. GC analysis of the exposed water showed new peaks caused by compounds that are more volatile than monobromodiphenyl ether. No increase was seen of any peaks with retention times similar to the lowest brominated diphenyl ethers (mono-, di- and tribromodiphenyl ether) as well as with retention times longer than that of tetrabromodiphenyl ether and shorter than those of the highly brominated starting material. The degradation products were not determined and the experiment was performed without replicates. It can be concluded that in this study the products of the photodegradation of DeBDE in water are not the lower brominated diphenyl ethers.

In addition it must be stated that photodegradation of DeBDE will mainly take place in the upper 10 centimeters of the water, the intensity of UV-light and sunlight decreasing linear with water depth [10]. It can be concluded that in water/sediment systems in the field photodegradation may occur but is probably not an important route.

2.3.1.2. Photodegradation of PBBs and PCBs

The closely related PBBs and PCBs exhibit reactions analogous to the PBDEs on exposure to UV-light and sunlight in several laboratory studies. Reductive dehalogenation occurred readily in organic solvents and hydroxylation is the dominant process in aqueous solutions [4, 6].

A recent study on the photodegradation of decabromobiphenyl showed no degradation in aqueous suspension following UV- irradiation during 8 days. When adsorbed on silicagel degradation according to a first order reaction was shown [2]. The breakdown products were at least more polar than decabromobiphenyl, but specific analysis of the lower brominated congeners was not performed. The experiment with DeBB in aqueous suspension is considered more relevant for the field situation compared to the 'silicagel study'.

Similar to the PBDEs, the strong adsorption on sediment and the decreasing sunlight intensity below the water surface will inhibit photodegradation of PCBs and PBBS under environmental conditions. Few field observations indicated either the persistence of PBBs or a partial degradation to less brominated photoproducts [4].

The available experimental data are not sufficient to determine the rate or importance of photodegradation of PBBs and PCBs in water/sediment systems under environmental conditions.

2.3.2. Biodegradation

2.3.2.1. DeBDE

Data on the aerobic as well as anaerobic biodegradation of PBDEs are not available. Probably anaerobic degradation of DeBDE in the deeper sediment layers leads to a replacement of Br- by H-atoms. The debromination occurs stepwise, the Br-atoms next in position to the O-atom are probably the first to be replaced. So the coplanar congeners of the lower brominated diphenyl ethers are probably formed. These congeners are expected to be the most toxic based on data for PBBs and PCBs [11].

2.3.2.2. PBBs and PCBs

The aerobic biodegradation of PBBs and PCBs decreases with increasing halogenation, with half-lifes ranging from months to years. Degradation of the higher substituted forms (5 or more halogens) hardly occurs [4, 6].

Reductive dehalogenation of the higher halogenated PBBs and PCBs occurs in anaerobic sediments, resulting in products that are more readily degradable in aerobic systems. However, half-lifes are expected to be in the order of decades.

Contrary to the PBDEs the ortho positions are the last to be dehalogenated in the PBBs and PCBs [1, 10].

2.4. Conclusions

If DeBDE is released to the aquatic environment the uptake by aquatic organisms will probably be low. However, reliable information, e.g. a bioaccumulation study in fish with a sufficiently long exposure time, is lacking. Uptake via food by fish or sediment by sediment dwelling organisms may occur, but concentration factors will probably be low. Again, reliable information is lacking.

Although information is very scarce it can be concluded that DeBDE can be classified as a persistant chemical. Photodegradation in water has been shown but will probably not be an important route since most of the DeBDE ends up in the sediment where the sunlight intensity is low. Biodegradation, aerobic as well as anaerobic, has not been studied. Both routes may occur but it can be expected that the rates will be very low.

As significant amounts of DeBDE are present in the environment it is highly recommended to investigate aerobic and anaerobic degradation of DeBDE under relevant environmental conditions, i.e. in water/sediment systems.

References

1. Beurskens, K., RIVM (1994) Personal communication.
2. Centre National d'Evaluation de Photoprotection (1993) Etude de laphototransformation de l'Adine 0102 en phase pseudo dispersée sur silice dans un environnement aqueux. Université Blaise Pascals, Clermont-Ferrand.
3. Hardy, M.L., Albemarle Corporation (1994) Personal communication.
4. IPCS (1992) Environmental health criteria for polybrominated biphenyls (PBBs). Draft for task group meeting. WHO, Geneve.
5. IPCS (1993a) Environmental health criteria for brominated diphenyl ethers. Final draft for editing. WHO, Geneve.
6. IPCS (1993b) Environmental health criteria 140, polychlorinated biphenyls and terphenyls (second edition). WHO, Geneve.
7. Norris, J.M., J.W. Ehrmantraut, C.L. Gibbons, R.J. Kociba, B.A. Schwetz, J.Q. Rose, C.G. Humiston, G.L. Jewett, W.B. Crummett, P.J. Gehring, J.B. Tirsell and J.S. Brosier (1973) Toxicological and environmental factors involved in the selection of decabromodiphenyl oxide as a fire retardant chemical. Applied Polymer Symp., 22, 195-219.
8. Opperhuizen, A. (1990) Bioconcentration and biomagnification: is a distinction necessary? In: Nagel, R. and R. Loskill (eds). Bioaccumulation in aquatic systems: contributions to the assessment. pp. 67-80.
9. Opperhuizen, A., E.W. v.d. Velde, F.A.P.C. Gobas, D.A.K. Liem, J.M.D. v.d. Steen (1985) Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals. Chemosphere **14**, (11/12), 1871-1896.
10. Peijnenburg, W.J.G.M., RIVM (1994) Personal communication.
11. Pijnenburg, A.M.C.M. and J.E. Everts (1991) Brandvertragers: vóórkomen en toxiciteit. Ministerie van Verkeer en Waterstaat, Rijkswaterstaat, Dienst Getijdewateren, nota GWAO-91.001.
12. Zitko, V. (1977) The accumulation of polybrominated biphenyls by fish. Bull. Environ. Contam. Toxicol. **17**, (3), 285-292.
13. Zomer, G., RIVM (1994) Personal communication.
14. Japan Chemical Industry Ecology-Toxicology & Information Center (1992) Biodegradation and bioaccumulation data of existing chemicals based on the CSLC Japan. Compiled under the supervision of Chemical Products Safety Division Basic Industries Bureau Ministry of International Trade & Industry Japan.
15. Letter from Marcia L. Hardy to Bart Brands, June 3, 1994, regarding Comments on Dutch Risk Assessment.

CHAPTER 3. ASSESSMENT OF THE RISK OF SECONDARY POISONING BY PeBDE AND TeBDE

3.1. Introduction

Commercial pentabromodiphenyl ether (PeBDE) is a mixture of 50-62% PeBDE (mainly the 2,4,5,2',4'-congener), 24-38% tetrabromodiphenyl ether (TeBDE) (mainly the 2,4,2',4'-congener) and 4-8% hexabromodiphenyl ether (HxBDE). These components are likely to be persistent and will probably bioaccumulate. Residues of PeBDE and TeBDE have been found in fish, shellfish, birds, mammals, sediment and sewage sludge samples (IPCS, 1993). This means that indirect exposure to PeBDE and TeBDE via the food chain does occur.

In the present paragraph a hazard assessment for commercial PeBDE is carried out for secondary poisoning of fish-eating birds and mammals. The method applied is based on the Uniform System for the Evaluation of Substances (USES) [12]. Two approaches are used:

1. Comparison of measured residues in fish with the Maximum Permissible Concentrations (MPCfood) and Negligible Concentrations (NCfood) for fish-eating birds and mammals.
2. Comparison of measured concentrations in sediment with MPCs and NCs in water using the equilibrium partitioning method.

In order to apply these approaches first bioaccumulation in fish, actual residues in biota, toxicity to fish-eating birds and mammals and actual sediment levels are described.

3.2. Bioaccumulation in aquatic organisms

When carp was exposed for 8 weeks to commercial PeBDE at 10 or 100 μg/l bioconcentration factors were above 10,000 [7]. As no details of this experiment are presented the value is not used for further calculations on secondary poisoning.

According to Mackay [11] bioconcentration factors (based on whole body wet weight for a fish with 5% lipid) for PeBDE and TeBDE can be estimated by:

$$BCF = 0.048\ K_{ow} \qquad [l.kg^{-1}] \qquad (1)$$

The log K_{ow} values of PeBDE are 6.64-6.97 (mean 6.8) and of TeBDE 5.87-6.16 (mean 6.0) as given by the IPCS [7]. This results for PeBDE in a BCF value in the range of 210,000 - 448,000 with a mean of 329,000 and for TeBDE 35,600 - 69,400 with a mean of 52,500.

3.3. Residues in biota

3.3.1 Fish and invertebrates

Data on the residues of 2,4,5,2',4'-PeBDE and 2,4,2',4'-TeBDE in fish and aquatic invertebrates in The Netherlands are obtained from the monitoring project from The Netherlands Institute for Fisheries Research (RIVO) carried out from 1983 until 1992 [2]. Similar residue levels are reported by the IPCS [7].

Residues in fish are based on edible tissue, wet weight. The highest PeBDE concentration found in fish is 32 μg/kg (yellow eel, Roer, 1988), and for TeBDE 340 μg/kg (yellow eel, Waal, 1983).

Mean concentrations in yellow eel of all locations in 1992 are 3.6 μg/kg PeBDE and 27.4 μg/kg TeBDE (measurements below detection limits are not included). Maximum concentrations in 1992 are 21 μg/kg PeBDE and 240 μg/kg TeBDE (river Roer, Vlodrop) while the lowest residues found are $<$ 0.5 μg/kg PeBDE and 1.1 μg/kg TeBDE. Residue levels are slightly declining in time for all but one location, i.e. the river Roer.

Data on yellow eel are used in further calculations because this data set is most extensive in time as well as with respect to the number of locations. Total residues in other fish species are lower. As the fat content in these species is also lower, residues based on lipid weight are comparable for all fish species. It is assumed that residues in edible tissue are equal to whole body residues, the difference is expected to be low [10].

For several marine fish the concentrations in liver or kidney are given, which cannot be used for the calculation of whole body or edible tissue concentrations due to the huge intra-species variation in weights of these organs. All samples of edible tissue of marine fish (e.g. cod, plaice, herring, sole) and invertebrates (mussel, shrimp, oyster) contained lower levels of PeBDE and TeBDE than the freshwater species.

For residue levels in marine organisms no significant trends in time could be established. Mean concentrations in edible tissue from several species in the Southern Nort Sea in 1991 and 1992 were 4.6 μg/kg PeBDE (5 samples, 4 species) and 3.7 μg/kg TeBDE (12 samples, 8 species) (measurements below detection limits are not included).

3.3.2. Fish-eating birds and mammals

In one cormorant from the Biesbosch residues were found in the liver of 4,000 μg/kg PeBDE and 25,000 μg/kg TeBDE and in the kidney of 2,000 μg/kg PeBDE and 18,000 μg/kg TeBDE wet weight [2]. The whole body content cannot be estimated from these data. Whether these levels are extreme or not is unknown because other data are not available for The Netherlands. Residues detected in other organs of birds in Sweden and Japan were lower: osprey muscle 140 μg/kg lipid PeBDE and newborn starlings 2.9-5.3 μg/kg lipid PeBDE [7].

A sample of blubber from one dolphin, caught in a fishing-net in the Atlantic Ocean west of Ireland, contained < 10 μg/kg PeBDE and 590 μg/kg TeBDE. One dolphin found alive stranded on a beach along the Southern Northsea contained 220 μg/kg PeBDE and 2,800 μg/kg TeBDE (mean of two samples) in blubber [1, 2]. Concentrations of PeBDE and TeBDE in the kidney, liver, spleen or muscle of these dolphins were 7-65 times lower than those in blubber. Levels in kidney and liver were 130-410 times lower than in the cormorant from the Biesbosch.

Exposure to a local source is very unlikely for dolphins. Therefore the residues in the dolphin samples are considered to be caused by exposure to 'background' concentrations in water and fish from the Atlantic Ocean and the Northsea, respectively. Based on the PeBDE and TeBDE residues in dolphin lipid and the mean residues in fish (see 2.1.), both from the Southern Northsea, a biomagnification factor of 485 is calculated for dolphins. It is assumed that dolphin blubber contains 75% lipid. Therefore, it can be concluded from these data that biomagnification does occur in significant quantities.

3.4. Toxicity to birds and mammals

3.4.1. PeBDE, TeBDE and HxBDE

No toxicity data are available on the effects of PeBDE, TeBDE and HxBDE as single compounds. Only data on commercial PeBDE being a mixture of 50-62% PeBDE, 24-38% TeBDE and 4-8% HxBDE in rats have been reviewed by the IPCS [7]. No data are present for birds.

When commercial PeBDE was given to rats during 28 days at 100 or 1000 mg/kg diet, no changes were observed in behaviour, appearance, food consumption and body weight gain. Some other effects were observed at both dose levels (e.g. increased relative liver weights, liver lesions) [7].

Commercial PeBDE was given in the diet of rats for 90 days at levels of 0, 2, 10 and 100 mg/kg bw day [7]; no increased mortality or clinical effects were observed. Decrease in body weight occurred at the highest dose, so the NOAEL for growth is 10 mg/kg bw day. Several compound-related effects occurred in the 10 and 100 mg/kg bw day groups (e.g. increase of relative liver weight, decrease of thyroxine levels, hepatocytomegaly and thyroid hyperplasia; at 100 mg/kg bw day increased liver and urine porphyrin levels). At the lowest dose, 2 mg/kg bw day, the effects observed after 24 weeks recovery were liver cell degeneration and necrosis in females, but not in males. Total bromine concentrations in all tissues were still increased, especially in the highest dose group. Data on chronic exposure are not available.

The liver effects observed at the lowest dose are considered as serious effects, but their relevance on population level is unknown. For environmental effect assessment principally only those parameters are taken into account that exclusively affect species on the level of population [14]. In general these are effects on mortality, growth and reproduction. Therefore the NOAEL of 10 mg/kg bw day for growth is used in the calculations.

3.4.2. Polybrominated biphenyls (PBBs)

As the (semi)chronic toxicity data on PeBDE and TeBDE are limited to only one 90-study in rats, a summary is given of the semi(chronic) toxicity data on the structurally related Firemaster (ca. 75% hexa- and heptabrominated biphenyl) in Appendix 1. These data are obtained from the IPCS review on PBBs [6].

Although results are often reported incompletely, e.g. no information on exposure time, it can be concluded that a huge variation in the susceptibility of species is observed, the rat being probably the least sensitive. The higher susceptibility of the mink, a predatory mammal, is obvious. On the other hand it should be realized that the PBBs studied contained coplanar congeners, which are more toxic than the ortho-substituted congeners. These non-ortho-substituted congeners show probably a dioxin-like toxicity pattern [6] and the same high interspecies variability in responses as dioxins [17]. PeBDE and TeBDE are ortho-substituted with bromine and cannot form a coplanar structure. So it is possible that the interspecies variability for PeBDE and TeBDE is not as high as for Firemaster.

3.5. Environmental levels

No data are available on the levels of PeBDE and TeBDE in water (IPCS, 1993).

In sediment PeBDE levels of 12-33 μg/kg and TeBDE levels of 11-36 μg/kg sediment dry weight were found in 1992 in The Netherlands, measured at 3-4 locations [2]. Comparable levels were reported in Japan and Sweden [7].

3.6. Calculations on secondary poisoning

In the RIVO-DLO report [2] residues of both PeBDE and TeBDE were presented and several publications of other authors reported residues of "total PBDEs". In view of the use of commercial PeBDE, being a mixture of tetra-, penta-, and hexa-BDE, it is justified to use the summed residues of PeBDE and TeBDE in the calculations on secondary poisoning. No measurements of HxBDE are available in The Netherlands. However, HxBDE has been found in the environment in Japan up to 14 μg/kg wet weight in fish and 77 μg/kg dry weight in sediment [7]. The HxBDE residues that are probably present in sediments and biota in The Netherlands are not included in this hazard assessment. Due to the lack of data on the toxicity of pure PeBDE and TeBDE a similar toxicity to mammals of PeBDE and TeBDE is assumed.

Only for mammals a hazard assessment could be made, because data on the toxicity of PeBDE and TeBDE for birds are lacking.

3.6.1. Calculation of the Hazard Quotient for fish-eating mammals based on residues in fish

The methods according to USES [12] and Romijn et al. [13] are applied. The assessment is based on the summed concentrations of PeBDE and TeBDE in fish and the assumption is made that the diets of fish-eating mammals consist of 100% fish. The hazard is calculated as:

$$Hazard\ Quotient_{aquat\ pred} = \frac{C_{fish}}{NECfood_{pred}} \qquad (2)$$

where:

C_{fish}: concentration in fish, in µg/kg edible tissue, wet weight,

$NECfood_{pred}$: No Effect Concentration for a predator, in µg/kg food.

The Maximum Permissible Concentration (MPC) and the Negligible Concentration (NC) are the most important risk limits used in environmental policy in The Netherlands [4]. The NC is defined as MPC/100. Until now MPCs and NCs have only been set for water, sediment, soil and air. Analogous to these quality objectives MPCs and NCs can be set for levels in organisms. In the present paragraph MPCs and NCs are derived for fish-eating mammals expressed as contents in their food: $MPCfood_{pred}$ and $NCfood_{pred}$. So the $NECfood_{pred}$ is set equal to the $MPCfood_{pred}$ or the $NCfood_{pred}$.

The $MPCfood_{pred}$ is based on the NOAEL (see 3.) Corrections have to be made for the extrapolation from a NOAEL for laboratory rats to a predicted NEC for fish-eating mammals in a field situation. Therefore the following factors are applied [8, 13]:

- the caloric content of laboratory food vs. food in the field: 0.38,
- the metabolic rate of laboratory animals vs. animals in the field: 0.4,
- the extrapolation from (several) species tested in the laboratory to the ecosystem (intra- and interspecies variation): 0.01. Romijn et al. (1993) use a factor of 0.1 on the lowest NOAEL available. As only one NOAEL for a single species (rat) is available and because of the high inter-species variation for the closely related PBBs (other species are probably more than 10 times more sensitive than rats) an extra factor 0.1 is applied.

This results in: NEC_{pred} = 0.00152 * NOAEL = 15.2 µg/kg bw day. Using a BW/DFI (Body Weight/Daily Food Intake) of 20 for rats the $NECfood_{pred}$ is equal to 304 µg/kg food.

A worst-case and average situation in 1992 are evaluated. In the worst-case situation the sum of the maximum concentrations of PeBDE and TeBDE in eel was 261 μg/kg edible tissue, in the average situation the sum of the mean residues of PeBDE and TeBDE was 31 μg/kg edible tissue (see 2.1). In table 1 a summary is given of these data and the corresponding hazard quotients.

Table 1. Hazard Quotients for fish eating mammals.

Concentration in fish in μg/kg		$NECfood_{pred}$ in μg/kg		HQ based on MPC		HQ based on NC	
mean	max.	MPC	NC	mean	max.	mean	max.
31	261	304	3	0.1	0.9	10	90

3.6.2. Calculation of the Hazard Quotient for aquatic organisms

The hazard for aquatic organisms is calculated as:

$$Hazard\ Quotient_{aqua} = \frac{PEC_{water}}{NEC_{water}} \qquad (3)$$

where:

PEC_{water}: Predicted Environmental Concentraton in water, in ng/l,

NEC_{water}: No Effect Concentration in water taking into account secondary poisoning, in ng/l.

3.6.2.1. Calculation of PEC_{water}

As no measured concentrations in water are available actual concentrations in sediments can be used to derive the PEC_{water} by applying the equilibrium partitioning method [5]:

$$K_p = \frac{C_{sediment}}{C_{water}} \quad (4)$$

where:

K_p: equilibrium partition coefficient, in l/kg,
$C_{sediment}$: equilibrium concentration in sediment, in µg/kg dry weight,
C_{water}: equilibrium concentration in water, in µg/l.

As experimental data on the K_p are lacking the estimation method as applied in USES [12], according to Karickhoff [9] is used:

$$K_p = 0.411 \times Foc_{sediment} \times K_{ow} \quad (5)$$

where:

K_p: equilibrium partition coefficient, in l/kg,
$Foc_{sediment}$: fraction organic carbon; a measured F_{oc} of 0.036 [2] was used,
K_{ow}: K_{ow} values calculated from the mean log K_{ow} of PeBDE of 6.8 and TeBDE of 6.0 (see 1.).

PEC_{water} values for PeBDE and TeBDE are calculated from mean and maximum sediment concentrations sampled in 1992 [2]. Mean sediment concentrations were 19 µg/kg PeBDE and 21 µg/kg TeBDE, the highest concentrations were 33 µg/kg PeBDE and 36 µg/kg TeBDE. PEC_{water} values are presented in table 2.

When calculated from residue levels in eel, sampled at the same locations as the sediment measurements, the PEC_{water} is for PeBDE about 40 times and for TeBDE about 4 times lower. The BCF in eel, containing about 20% fat, was estimated as 0.2 * K_{ow}.

3.6.2.2. Calculation of NEC_{water}

As no data are available on direct effects on aquatic organisms the NEC_{water} is based on indirect effects only. The NEC_{water} is set equal to the MPC_{water} or NC_{water}. The NC_{water} is equal to $MPC_{water}/100$.

The calculation of the MPC_{water} is performed as described by Romijn et al. (1993).

$$MPC_{water} = \frac{NECfood_{pred}}{BCF_{fish}} \tag{6}$$

where:

MPC_{water}: Maximum Permissible Concentration in water, in μg/l,

$NECfood_{pred}$: as no data are available for pure PeBDE and TeBDE a NOAEL of 304 μg/kg food for both compounds is assumed (see 5.1.),

BCF_{fish}: mean calculated BCF values: 329,000 for PeBDE and 52,500 for TeBDE (see 1.).

Hazard Quotients are calculated for the mean and maximal predicted water concentrations, and based on MPC and NC values. An overview of the data is given in table 2.

Table 2. Hazard Quotients for aquatic organisms.

	MPC	NC	PEC in ng/l		HQ based		HQ based	
	in ng/l	in ng/l	mean	max.	on MPC		on NC	
					mean	max.	mean	max.
PeBDE	0.92	0.0092	0.2	0.35	0.22	0.38	22	38
TeBDE	5.8	0.058	1.4	2.4	0.24	0.41	24	41

3.7. Discussion and conclusions

The behaviour of the individual congeners of commercial PeBDE, when released in the environment, is unknown. No data on degradation or transformation of the individual congeners are available. Measurements from De Boer and Dao [2] indicate that the main congeners of the technical mixture are also the main congeners detected in sediments and biota.

Although commercial PeBDE contains two times as much PeBDE than TeBDE the residues of both compounds in sediment are equal and TeBDE residues in fish are even 10 times higher than PeBDE residues. Several explanations are possible: other releases for TeBDE to the environment, stronger adsorption to sediment of PeBDE compared to TeBDE. Metabolism of PeBDE to TeBDE in fish might also be an explanation. Debromination of octa- and hexabromobiphenyl in fish has been shown by Zitko [15] but debromination of tetra- and lower brominated biphenyls does not occur [16].

With respect to the possible risk of commercial PeBDE due to secondary poisoning the following can be concluded:

- Biomagnification of PeBDE and TeBDE does occur in significant quantities.
- The results of the two approaches using either actual levels in fish or measured concentrations in sediment are in good agreement. Based on an average situation the PEC is 4-10 times lower than the MPC. The NC is always exceeded: a factor 10-24. Based on maximum measured residues in fish and sediment the MPC is close to the PEC.

Both approaches that are used include uncertainties and assumptions that can lead to an overestimation as well as an underestimation. An attempt has to be done to estimate the influence of these assumptions and uncertainties, however. The calculated hazard may in fact be lower because:

- levels in yellow eel have been used while levels in other fish are lower. On the other hand it must be stated that the energy content of these fish, which have a lower fat content, is lower so a fish-eating bird or mammal will consume more,
- measurements in fish lower than the detection limit are not included in the calculation of the mean.

The calculated hazard may in fact be higher because:

- fish-eating mammals are also exposed to HxBDE. In the calculations HxBDE is included in the NEC but not in the PEC. However, no quantitative data are available on HxBDE in sediment, fish and fish-eating mammals in The Netherlands,
- for mammals only data for rats are available. A factor 0.1 for interspecies variation is applied in this hazard assessment. This means that the risk will increase if other species are > 10 times more sensitive than the rat. Based on the toxicity data for PBBs this seems not unlikely,

- the relevance on population level of the liver effects at the dose 5 times lower than the NOAEL (growth) for rats as used in the calculations, is unkown.

The calculated hazard may be influenced in both directions because:

- no toxicity data for aquatic organisms, sediment dwelling organisms and birds are available. Only if these species are more sensitive than mammals, this will lead to a higher risk,
- no reliable study on bioaccumulation in fish is available,
- K_p values as well as the BCF are based on QSARs using log Kow. Kow values used are reported by IPCS [7]. The reliability of these values could not be assessed because no details are given. However, it is known that Kow values for highly lipophilic chemicals are difficult to measure. Values obtained by the shake-flask procedure, the classical method for measuring Kow until now, often show a high variance. This is due to contamination of the aqueous phase as a result of the formation of emulsions during shaking [3].
- actual water concentrations are not available. Calculation with the equilibrium partitioning method introduces extra uncertainty mainly due to the use of a log Kow based partition coefficient between water and sediment. When calculated from levels in fish the application of the log Kow based BCF brings about an important uncertainty.

Based on all considerations given above it seems reasonable to assume that there may be an uncertainty of a factor 10 in the HQs calculated in the paragraphs 5.1 and 5.2. The direct comparison of residues in fish with a dietary study with mammals seems the most reliable. Although biomagnification of PeBDE and TeBDE does occur, the PEC is always lower than the MPC. The NC is exceeded by at least a factor 10, however.

References

1. De Boer, J., RIVO (1994) Personal communication.
2. De Boer, J. and Q.T. Dao (1993) Overview of bromodiphenylether data in aquatic biota and sediments. Netherlands Institute for Fisheries Research-DLO, RIVO report C020/93.
3. De Bruijn, J.H.M., F. Busser, W. Seinen and J. Hermens (1989) Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the 'slow-stirring' method. Environ. Toxicol. Chem. **8**, 499-512.
4. DGM, VROM (1988-1989) Premises for risk management. Risk limits in the context of environmental policy. Annex to the Dutch National Environmental Policy Plan "Kiezen of Verliezen".
5. Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Schwartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas and P.R. Paquin (1991). Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem. **10**, 1541-1583.
6. IPCS (1992) Environmental health criteria for polybrominated biphenyls (PBBs). Draft for task group meeting. WHO, Geneve.
7. IPCS (1993) Environmental health criteria for brominated diphenyl ethers. Final draft for editing. WHO, Geneve.
8. Jongbloed, R.H., B.J.W.G. Mensink, J. Pijnenburg, T.P. Traas and R. Luttik (1994) A model for environmental risk-assessment and standard setting based on biomagnification. Toppredators in terrestrial ecosystems. RIVM report nr. 719101 012, in press.
9. Karickhoff, S.W. (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soil. Chemosphere **10**, 833-846.
10. Luttik, R., RIVM (1994) Personal communication.
11. Mackay, D. (1982) Correlation of bioconcentration factors. Environ. Sci. Technol. **16**, 274-276.
12. RIVM, VROM, WVC (1994) USES 1.0, Uniform System for the evaluation of substances. National Institute of Public Health and Environmental Protection (RIVM), Directorate-General for Environmental Protection (DGM), Ministry of Welfare, Health and Cultural Affairs (WVC), The Hague, Ministry of Housing, Physical Planning and Environment.
13. Romijn, C.F.A.M., R. Luttik, D. v.d. Meent, W. Slooff and J.H. Canton (1993). Presentation of a general algorithm to include effect assessment on

secondary poisoning in the derivation of environmental quality criteria. Part 1. Aquatic food chains. Ecotox. Environ. Saf. **26**, 61-85.

14. Slooff, W. (1992). RIVM guidance document. Ecotoxicological effect assessment: deriving Maximum Tolerable Concentrations (MTC) from single-species toxicity data. RIVM report No. 719102 018.
15. Zitko, V. (1977) The accumulation of polybrominated biphenyls by fish. Bull. Environ. Contam. Toxicol. **17**, 285-292.
16. Zitko, V. and O. Hutzinger (1976) Uptake of chloro- and bromobiphenyls, hexachloro- and hexabromobenzene by fish. Bull. Environ. Contam. Toxicol. **16**, 665-673.
17. Liem, A.K.D., Berg, R. van de, Bremmer, H.J., Hesse, J.M. and Slooff, W. (eds) (1993) Integrated criteria document dioxins. RIVM report No. 710401 032.

APPENDIX 1. SUMMARY OF THE TOXICITY OF FIREMASTER TO MAMMALS AND BIRDS

compound	species	exposure duration	criterion	conc mg/kg food	parameter
FM	rat		MED	500	growth
	mouse		MED	167	growth
	guinea pig		MED	100	growth
	mink		MED	6	growth
	pig		MED	20	growth
	chicken		MED	15-200	growth
	young chicken		MED	50	growth
FM BP-6	pregnant rats	d 7-18	EC	100	fetal weight
FM BP-6	pregnant mouse	d 7-18	EC	50	fetal weight
FM BP-6	chicken	8 weeks	EC	20	mort young
FM FF-1	mink	9 months start before breeding	EC	1	weight and mort young
FM FF-1	rhesus monkey	> 1 year start 7 m before breeding	EC	0.3	weight young and females
FM FF-1	chicken	5 weeks	MED	30-45	reduced egg prod and hatch; mort young
FM FF-1	jap. quail	5 weeks	EC	80	reduced egg prod

FM: Firemaster
MED: minimum effective dose
EC: effect concentration

All data from: IPCS (1992) Environmental health criteria for polybrominated biphenyls (PBBs). Draft for task group meeting. WHO, Geneve.