

# **Draft Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles**

Relevant to substances listed in Annexes A, B and C of the  
Stockholm Convention on Persistent Organic Pollutants from  
2009 to 2015

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DRAFT

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## Acknowledgements

### Author:

Roland Weber, POPs Environmental Consulting, Schwäbisch Gmünd, Germany

### Contributors:

Jun Hung, Tsinghua University, Beijing, China

Stefan Posner, Swerea IVF AB, Mölndal, Sweden

Liselott Säll, Norwegian Pollution Control Authority, Oslo, Norway

Martin Schlummer, Fraunhofer Institute, Freising, Germany

Omotayo Sindiku, Ibadan University, Ibadan, Nigeria

Takumi Takasuga, Shimadzu Techno Research, Kyoto, Japan

Xenia Trier, Technical University of Denmark, Søborg, Denmark

### Peer reviewers\*:

Christian Bogdal, ETH Zürich, Zürich, Switzerland

Jana Klánová, RECETOX, Brno, Masaryk University, Czech Republic

Jonathan Hogarth, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

Kateřina Šebková, RECETOX, Masaryk University, Brno, Czech Republic

Mihaela Claudia Păun, Ministry of Environment, Bucharest, Romania

Oladele Osibanjo, Basel Convention Coordinating Centre for Training & Technology Transfer for the African Region, University of Ibadan, Ibadan, Nigeria

Takumi Takasuga, Shimadzu Techno Research, Kyoto, Japan

Xenia Trier, Technical University of Denmark, Søborg, Denmark

\*Since the analysis is quite specific, reviewing was normally done for parts of the guidance

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## List of abbreviations and acronyms

ABS	Acrylonitrile-Butadiene-Styrene
ACN	Acetonitrile
ASR	Accelerated Solvent Extraction
BAT	Best Available Techniques
BEP	Best Environmental Practices
BFR	Brominated Flame Retardant
CEN	European Committee for Standardization
CME	Cellulose mixed ester
c-OctaBDE	Commercial Octabromodiphenyl ether
c-PentaBDE	Commercial Pentabromodiphenyl ether
COP	Conference Of Parties
CRT	Cathode Ray Tube
DART	Direct Analysis in Real Time
DecaBDE	Decabromodiphenyl ether
DIN	Deutsches Institut für Normung
ECD	Electron Capture Detector
EEE	Electrical and Electronic Equipment
EI-MS	Electron Impact Mass Spectrometry
EPED	Echelle-Plasma-Emission-Detector
EPS	Expanded Polystyrene
FPF	Flexible Polyurethane Foam
FR	Flame Retardant
GLP	Good Laboratory Practice
HBB	Hexabromobiphenyl
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HIPS	High Impact Polystyrene
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
IEC	International Electrotechnical Commission (2015) IEC
IS	Internal standard
ISO	International Organization for Standardization
JICA	Japan International Cooperation Agency
LC	Liquid chromatography
LIBS	Laser-Induced Breakdown Spectrometry
LOD	Limit of detection
LRMS	Low Resolution Mass Spectrometry
LCqMS	Liquid Chromatography Quadrupole Mass Spectrometry
MAE	Microwave-Assisted Extraction
MEKC	Micellar electrokinetic capillary chromatography
MeOH	Methanol
MTBE	Methyl Tert-Butyl Ether
NIR	Near Infrared
PAPs	Polyfluorinated Alkyl Phosphate Esters
PBB	Polybrominated Biphenyl
PBDE	Polybrominated Diphenyl Ether



PBDD/PBDF	Polybrominated Dibenzo-p-dioxins and Polybrominated Dibenzofurans
PBT	Polybutylene Terephthalate
PC	Polycarbonate
PCB	Polychlorinated Biphenyl
PCDD/PCDF	Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans
PCNs	Polychlorinated naphthalenes
PCP	Pentachlorophenol and its salts and esters
PET	Polyethylene Terephthalate
PeCB	Pentachlorobenzene
PFAS	Per- and Polyfluorinated Alkylated Substance
PFCs	Per-and Polyfluorinated Chemicals/Compounds
PFDA	Perfluorodecanoic acid; Perfluorodecanoate
PFDoA	Perfluorododecanoic acid; Perfluorododecanoate
PFHpA	Perfluoroheptanoic acid; Perfluoroheptanoate
PFHxA	Perfluorohexanoic acid; Perfluorohexanoate
PFNA	Perfluorononanoic acid; Perfluorononanoate
PFOA	Perfluorooctanoic acid; Perfluorooctanoate
PFOS	Perfluorooctane sulfonic acid; Perfluorooctane sulfonate
PFOSF	Perfluorooctane sulfonyl fluoride
PLE	Pressurised Liquid Extraction
POPs	Persistent Organic Pollutants
POP-PBDEs	Persistent Organic Pollutant Polybrominated Diphenyl Ethers (the PBDEs listed in the Convention) (tetra-, penta-, hexa-, and heptaBDE)
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PXDD/PXDF	Polybrominated-chlorinated Dibenzo-p-dioxins and Dibenzofurans
QA/QC	Quality Assurance and Quality Control
RoHS	Restriction of the use of certain Hazardous Substances in electrical and electronic equipment
SAICM	Strategic Approach for International Chemicals Management (SAICM)
SCCP	Short Chain Chlorinated Paraffin
SC	Stockholm Convention
SIM	Selected Ion Monitoring
SPE	Solid Phase Extraction
TBBPA	Tetrabromobisphenol A
THF	Tetrahydrofuran
TOF	Time of Flight
UAE	Ultrasonic-assisted extraction
WD-XRF	Wavelength dispersive XRF
WEEE	Waste Electrical and Electronic Equipment
XPS	Extruded Polystyrene
XRF	X-Ray Fluorescence
XRT	X-Ray Transmission

# 1 Background and objectives

## 1.1 Background on industrial and unintentionally released POPs

Between 2009 and 2015 fourteen additional substances were listed in the annexes to the Stockholm Convention as persistent organic pollutants (POPs). Several of these additionally listed POPs have been used or are still used in various products and articles due to exemptions (PFOS and related chemicals, PBDEs, HBCD, PCP, PCNs) and a large stock of articles in use exists (Annex 1).

A set of guidance has been developed to assist parties to meet their obligations relevant to the POPs listed between 2009 and 2015, such as the guidance for developing respective inventories<sup>1,2,3,4,5</sup> and for applying best available techniques and best environment practices BAT/BEP<sup>6,7</sup> giving also an overview of (former) uses of these substances and their relevance for the current presence of POPs in articles and products.

Among the additionally listed POPs in the Stockholm Convention, pentachlorobenzene (PeCB) and polychlorinated naphthalenes (PCNs) were listed in Annex C and can be present as unintentional by-product in a range of products and articles (see Annex 1-E and Annex 1-G).

Production of the listed polybrominated diphenyl ethers (POP-PBDEs) and PeCB is considered to have stopped for more than a decade and therefore these substances are now contained only in articles in use and in some recycling flows and related articles produced from these materials. Hexabromocyclododecane (HBCD), pentachlorophenol (PCP) and perfluorooctane sulfonic acid (PFOS) and related chemicals are still produced and therefore possibly also used in a range of new articles, products and processes where specific exemptions and acceptable purposes have been granted by the Convention (see Annex 1-A). Furthermore, PFOS might be still used by parties that have not yet ratified the amendments of the Stockholm Convention or by non-parties.

POPs used in articles and products are also included in larger re-use and recycling flows (e.g. used electrical and electronic equipment (EEE), waste electrical and electronic equipment WEEE and related plastics for recycling, second hand vehicles, polyurethane foams, synthetic carpets, certain furniture, textiles, recycled wood and paper).

POP-PBDEs are included with a time-limited exemption allowing for the recycling of wastes containing these substances and their subsequent use in articles until 2030. Therefore, a guidance for recycling and disposal of POP-PBDE has been developed<sup>4</sup>. This guidance considers the recommendations adopted by decision SC-5/5 of the Conference of the Parties to the Stockholm Convention on separation of POP-PBDEs containing materials from the recycling streams, as outlined in annex to decision POPRC-6/2. This requires to a reasonable extent monitoring of these recycling streams, including the products made from the recycled materials,

<sup>1</sup> Secretariat of the Stockholm Convention (2015a) Guidance for the inventory of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs (Draft).

<sup>2</sup> Secretariat of the Stockholm Convention (2015b) Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs (Draft).

<sup>3</sup> Secretariat of the Stockholm Convention (2017a) Guidance for the inventory of Hexabromocyclododecane (HBCD) (Draft March 2017).

<sup>4</sup> Secretariat of the Stockholm Convention (2017b) Draft guidance on preparing inventories of polychlorinated naphthalenes. UNEP/POPS/COP.8/INF/19

<sup>5</sup> Secretariat of the Stockholm Convention (2017c) Draft guidance on preparing inventories of hexachlorobutadiene UNEP/POPS/COP.8/INF/18

<sup>6</sup> Secretariat of the Stockholm Convention (2017d) Guidance on best available techniques and best environmental practices for the recycling and disposal of wastes containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants (Draft).

<sup>7</sup> Secretariat of the Stockholm Convention (2015e) Guidelines on best available techniques and best environmental practices for the production and use of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs (Draft).

for POP-PBDEs content, to ensure their environmentally sound management (Stockholm Convention 2012c)<sup>4</sup>.

In case of PFOS and related chemicals or HBCD, recycling of articles is not allowed, hence, products at the end of their life have to be managed in an environmentally sound manner. Also this may require monitoring of products potentially contaminated with HBCD or with PFOS and related chemicals.

Furthermore, for developing inventories of these additionally listed POPs, monitoring of POPs content in articles, recycling flows and wastes might be useful. The Stockholm Convention POPs inventory guidance documents include a tiered approach that all Parties to the Convention can develop inventories in the respective countries to the levels they are capable with the available resources. It is only in Tier III inventory approaches that monitoring and analysis might be needed, while Tier I and Tier II inventory methodologies include inventory approaches without sampling and analysis.

Another reason to screen and analyse POPs in articles and products is their relevance for human exposure. POPs in articles and products are closely linked to human exposure. While for legacy POPs the major exposure is with food, a major exposure for industrial POPs come from products.<sup>8,9,10,11</sup> For PBDE a major exposure stem from chemicals in consumer goods like furniture, vehicles or specific polyurethane (PUR) foam products.<sup>12,13</sup> Also toys even from recycling of PBDE containing articles can lead to relevant exposure of children. Also the recycling of PBDE containing PUR foam resulted in high blood levels in recyclers and carpet installers.<sup>14</sup> The external cost for PBDE exposure has been estimated to \$12.6 billion for Europe<sup>15</sup> and 266 billion for the US<sup>16</sup> respectively. To track POPs in articles and products to reduce human exposure is another major reason for monitoring POPs in products. Furthermore the export of industrial POPs in products and articles to developing countries is of same or higher relevance than the long range transport of POPs by air or water and needs a better assessment and control.<sup>17</sup>

## 1.2 Purpose and objective of this guidance

This document provides guidance on monitoring (sampling, screening and analysis) of the industrial and unintentional POPs in articles and products in use and in the recycling streams for POPs listed from 2009 to 2015. The guidance does not address POPs pesticides.

The document intends to assist parties in their effort to develop and improve their inventories on industrial POPs and unintentional POPs, where for some specific inventory questions a Tier III

<sup>8</sup> Ionas AC, Ulevicus J, et. al (2016) Children's exposure to polybrominated diphenyl ethers (PBDEs) through mouthing toys. *Environ Int.* 87, 101-107.

<sup>9</sup> Chen S-J, Ma Y-J, et al. (2009) Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure and Risk Assessment. *Environ Sci Technol* 43(11), 4200-4206.

<sup>10</sup> de Boer J, Ballesteros-Gómez A et al. (2016) Flame retardants: Dust - And not food - Might be the risk. *Chemosphere.* 150, 461-464.

<sup>11</sup> Imm P, Knobeloch L, Buelow C, Anderson HA (2009) Household exposures to polybrominated diphenyl ethers (PBDEs) in a Wisconsin Cohort. *Environ Health Perspect* 117, 1890-1895.

<sup>12</sup> Carignan CC, Heiger-Bernays W, et al. (2013) Flame Retardant Exposure among Collegiate U.S. Gymnasts. *Environ. Sci. Technol.*, 47 (23), 13848-13856.

<sup>13</sup> Stapleton HM, Klosterhaus S, et al. (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products *Environ Sci Technol.* 45(12), 5323-5331

<sup>14</sup> Stapleton HM, Sjödin A, et al. (2008) Serum levels of polybrominated diphenyl ethers (PBDEs) in foam recyclers and carpet installers working in the United States. *Environ Sci Technol.* 42(9), 3453-3458.

<sup>15</sup> Bellanger M, Demeneix B, et al. (2015) Neurobehavioral deficits, diseases, and associated costs of exposure to endocrine-disrupting chemicals in the European Union. *Clin Endocrinol Metab.* 100(4), 1256-1266.

<sup>16</sup> Attina TM, Hauser R, et al. (2016) Exposure to endocrine-disrupting chemicals in the USA: a population-based disease burden and cost analysis. *Lancet Diabetes Endocrinol.* 4(12), 996-1003.

<sup>17</sup> Breivik K, Gioia R, et al. (2011) Are reductions in industrial organic contaminants emissions in rich countries achieved partly by export of toxic wastes? *Environ Sci Technol.* 45(21), 9154-9160..

inventory component including screening and instrumental analysis might be useful or might be needed.

Guidance is provided:

- On articles and products possibly containing newly listed POPs present in articles and products (e.g. for POPs listed between 2009 to 2015) (see Annex 1);
- For developing strategies for monitoring of POPs in articles/products and in recycling;
- On inventory development support (Tier III) for the screening of POPs in articles and products and possibly for determining impact factors of recycled materials;
- For import control and possible monitoring at customs or at consumer protection level;
- For the assessment and reduction of human exposure through products and articles in use and through recycled materials.

This document complements the guidance on global monitoring plan, which focuses on the matrices for effectiveness evaluation (air, human milk/blood, and water). Currently the Global Monitoring Plan on POPs does not address POPs in articles<sup>18</sup> and in the Second global monitoring report of POPs<sup>19</sup>, POPs in articles and products were not included.

This guidance can also provide support for addressing SAICM Emerging Policy Issues and Other Issues of Concern. For example all per-/poly fluorinated alkylated substances (PFAS) are considered an emerging issue, which is also reflected in the concern of the research community and the Madrid Statement on the control of PFAS. Furthermore UNEP activities on chemicals in products might also need to a certain extent the screening and analysis of POPs and other chemicals in products where this guidance might provide useful support.

**Note: This guidance does not aim to develop analytical standard procedures similar to e.g. ISO or CEN standards. This document rather gives support and advice for monitoring some POPs listed between 2009 and 2015 with practical information and case studies on sampling, screening, and basic information on extraction and analysis of samples. To the extent possible, the guidance refers to international standards developed for analysis for these chemicals.** However, for a range of POPs in articles and products, no international standard for sampling or for analysis has been developed. The current document aims to fill some of these gaps.

### 1.3 Reference to other guidance under the Basel and Stockholm Conventions

This guidance is part of a larger set of guidance developed to assist parties in developing, updating, and reviewing their national implementation plans. Where appropriate, reference to these guidance documents is provided for further reading. Since support for the inventory of POPs is a major aim, this document is closely linked to inventory guidance development for the respective POPs.

The monitoring of articles and products also links closely to the monitoring of POPs wastes. In the frame of the Basel Convention a set of Technical Guidelines on the environmentally sound management of waste consisting of, containing or contaminated with persistent organic pollutants have been developed. These guidelines can also provide valuable information on the sampling, analytical and monitoring aspects of POPs in wastes and environmentally sound disposal methods.

<sup>18</sup> UNEP (2015) Guidance on the global monitoring plan for persistent organic pollutants. UNEP/POPS/COP.7/INF/39

<sup>19</sup> UNEP (2017) Second global monitoring report. UNEP/POPS/COP.8/INF/38

Useful information on analytical aspects of POPs can be found in the Guidance on the Global Monitoring plan for Persistent Organic Pollutants. Since that guidance focus on effectiveness parameters like air, water and human milk/blood, these guidance documents complement each other.

#### 1.4 Substances considered and related articles and products

As mentioned above, this guidance focusses on industrial and unintentional POPs with the main topic of screening and monitoring of industrial and unintentional POPs in articles and products. Industrial POPs considered are:

- Listed polybrominated diphenyl ethers (POP-PBDEs),
- Hexabrominated biphenyls (HBB),
- Hexabromocyclododecane (HBCD),
- Perfluorooctane sulfonate (PFOS) and related chemicals,
- Polychlorinated naphthalenes (PCNs),
- Pentachlorophenol (PCP), its salts and esters,
- Hexachlorobutadiene (HCBD).

Furthermore all unintentional POPs in products and articles with an emphasis on the recently listed POPs in Annex C (PeCB, PCNs). Since unintentional POPs are often formed in the same processes, other unintentionally produced POPs are also mentioned in this document, as appropriate.

Guidance is not required for the 12 original POPs, other than DDT, HCB, PCDDs, PCDFs and PCBs, because there were no longer any Parties registered for specific exemptions (pursuant to paragraph 9, Article 4), and import/export of these POPs is only allowed for environmentally sound disposal. All unintentional POPs are considered to some extent in chapter 8.

Major articles, products and other material, which may contain industrial POPs and unintentional POPs in articles and products including or possibly including are described in Annex 1.

Where available, case studies on screening and monitoring on new POPs in articles and products are referenced and/or provided in Annex 3.

#### 1.5 Approach to combine screening with confirmation analysis

The guidance gives an introduction to screening approaches. This includes screening technologies for bromine or fluorine as an indication of potential presence of brominated and fluorinated POPs. Such screening enables relatively cheap and simple pre-selection in suspected article groups with regards to their possible POPs content (e.g. polystyrene foam and polyurethane (PUR) foams for bromine as indication of HBCD and POP-PBDEs content respectively, or carpets for fluorine as indication for PFOS and related chemicals). A pre-screening of samples helps to minimise the time and expenses for confirmation analysis, which requires extraction and appropriate clean-up steps and often sophisticated and costly instrumental analysis, which is often not or to a limited extent available in developing countries.

For final confirmation or quantification by instrumental analysis, basic information is provided, including examples of instrumental setting (Annex 2). Where available, the guidance links to case studies (Annex 3) where often sampling and analytical procedures are described.

#### 1.6 National, regional and global coordination of monitoring of POPs for minimizing resources and efforts

Studies on POPs in articles and products can be performed on local, national, or regional (or even global) levels. Considering that resources are often limited and that countries in a region often have similar or the same articles and products that are possibly impacted by POPs, it can be appropriate to aim for a regional concept for monitoring of POPs in products or articles and



avoid repetition in different countries with associated waste of resources. Such regional studies might be coordinated by a Stockholm/Basel Convention Regional Centre or other institutions working at regional or global level. Since most developing countries do not have established analytical capacity for industrial or unintentional POPs, regional approaches have the advantage that an appropriate laboratory might be found and that regional studies can address the relevant products of different countries in a harmonized manner.

For larger countries, national studies might seem more appropriate or even selected local studies in a country (e.g. a federal state might have a specific flammability standard and related POP-PBDEs impacted articles or a region has a PFOS production facility with impact on food from this region).

### 1.7 Approach for presenting case studies

Where available, best practice case studies for key articles/products possibly containing the individual POPs are referenced in the respective chapters and described in **Annex 3**. Where possible, case studies or publications were selected with reports available in the public domain and the information where to access the report or publication is provided.

With the inclusion and link to a range of case studies on monitoring of POPs in articles and products in different countries/regions, the guidance endeavours to provide information on already performed studies, and the approaches used and to give an overview on what has already been done. These case studies can be assessed with e.g. the view of selecting appropriate approaches and methodologies (selection of samples, screening approaches and analysis). The information in the studies might give an idea on what studies and information on POPs in articles, products and materials in recycling are already available and what information is missing. With this kind information already available, countries can avoid duplication of studies and the unnecessary use of resources and time. Since research is developing quickly in this area, Parties and institutions which are planning to monitor POPs and other hazardous chemicals in products, are encouraged to undertake an additional and detailed literature study, since this guidance provides a limited selection of available studies. Only after a thorough assessment of available knowledge, a decision may be made on whether an additional study on selected POPs in articles is needed, as well as the and possibility of any additional chemicals to include in such a study, e.g. SAICM emerging policy issues like PFAS or endocrine disrupting chemicals (EDCs)<sup>20</sup>.

Some of the case studies reveal that former applications of PFOS do not seem to be relevant anymore e.g. in recent surveys PFOS and related chemicals were no longer detected in coated paper (see Annex 3-A).

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<sup>20</sup> UNEP (2017) Endocrine disrupting chemical – An emerging policy issue  
<http://drustage.unep.org/chemicalsandwaste/what-we-do/science-and-risk/endocrine-disrupting-chemicals-edcs>

## 2 General considerations and cross-cutting issues

### 2.1 Capacity building and accreditation

Laboratory personnel needs to be trained on the different analytical procedures and methodologies for POPs monitoring and also on quality assurance and quality control (QA/QC). UNEP has within its activities related to the Global Monitoring plan for Persistent Organic Pollutants (GMP) a program on capacity building for POPs analysis (mainly for governmental laboratories), which could be considered. The programme is implemented in cooperation with the University Amsterdam/The Netherlands and the University Oerebro/Sweden. Furthermore capacity building on POPs analysis is offered by Japan International Cooperation Agency (JICA) or in summer schools (e.g. by RECETOX, Stockholm Convention Regional Centre Brno, Czech Republic).

For continuous education of laboratory personnel on general laboratory QA/QC, information resources such as dedicated publications with training materials on QA/QC could be used.<sup>21</sup> Furthermore, learning options available through the Internet (E-learning or Webinars) could be explored and assessed.

To develop own analytical methodologies, laboratories might consider accreditation schemes such as ISO 17025.

### 2.2 General quality assurance and quality control (QA/QC) considerations

International and national standard procedures for the analysis of chemicals contain dedicated sections on QA/QC. Other measurement protocols often do not contain dedicated sections on QA/QC and, therefore, if no specific international or national standard procedures are available or used by a laboratory, at least the following common procedures for the quality assurance of quantitative analysis of POPs listed in 2009 and 2011 should be considered:

- cleaned laboratory equipment, material, and chemicals to be used to avoid contamination from background;
- system ensuring that effectiveness of the measurements and procedures is continuously supervised through the analysis of procedural blank samples;
- regular injection of solvent blanks and standard solutions;
- tests to be carried out to evaluate the accuracy of the method, e.g. efficiency of the extraction methods, the recovery of the analytes, stability and loss of analytes in solution during storage, calibration using matrix matched standards or standard addition, and use of proper internal standards;
- tests to be carried out to evaluate the precision (repeatability and reproducibility), the limits of detection (LODs) and quantification (LOQs), the robustness and the specificity of the whole method, from sampling to detection;
- clearly defined criteria for identification and quantification need to be applied, and calibration curves to be used;
- storage of analysed samples and data (including instrumental raw data) for a defined time.

### 2.3 International standards for analysis of POPs

Where possible, links are made to existing international standards for analysis of the respective POPs. However, for a number of article matrices, no international standards are available for sampling, extraction and clean-up. A standard for measuring PBDEs in EEE (International Standard IEC 62321) in respect to RoHS compliance has been development and was published

<sup>21</sup> E.g. Wencławiak, B.W., Koch, M., und Hadjicostas, E. (eds.): Quality Assurance in Analytical Chemistry - Training and Teaching. 2nd Edition, p. 247- 272, Springer-Verlag, Berlin Heidelberg 2010.

in 2015<sup>22</sup>. An international standard for extractable PFOS in articles and its analysis has been developed in 2010 (NPR-CEN/TS 15968) but has not been validated yet. Furthermore, no (standard) analytical procedure is available for most of the 160 listed PFOS related chemicals including some non-extractable PFOS precursors.

Also, for PeCB or HCB, the extraction from products like pigments cannot be performed appropriately with available CEN, ISO or EPA standards. Here standard extraction procedures of matrices with e.g. toluene (which is sufficient for most environmental matrices or for sampling adsorbents like PUF filters or XAD resins) do not necessarily lead to satisfying extraction efficiency or reproducibility for products and articles. The analysis of pigments for PeCB/HCB and other unintentional POPs, therefore, needs specific extraction procedures, which are not described (yet) in international standards (see below).

The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of respective articles and mention their limitations for articles/products;
- Describe some standard methodologies used by laboratories experienced in the analysis of POPs contained in certain articles and products;
- Describe case studies with links to reports where monitoring or analytical procedures for a certain matrix are described.

For specific matrices, procedures and standards will further be developed. They would be considered during the updating of this guidance.

## 2.4 Step by step approach

To determine the occurrence and quantities of POPs in different articles, including consumer products, representative samples can be purchased from retail outlets and analysed.

A similar strategy can be used to determine the occurrence and quantities of PFOS and related chemicals in other materials, such as the industrial materials used downstream in a product chain, consumer products, chemical formulas and industrial blends arriving at the borders and possibly identified by the customs or other relevant authorities.

### 2.4.1 Step 1: Survey of products and articles containing respective POPs

Before collecting samples, a survey can be conducted to determine the availability of articles that possibly contain or have been contaminated with POPs chemicals. Sample candidates can be identified from the list provided in Annex 1 for the respective listed POP. If access is easy then the team conducting the study might take samples. Relevant stakeholders might be contacted for support and input and for samples.

### 2.4.2 Step 2: Sample collection

Standard sampling procedures should be established and agreed upon before the start of the sampling campaign. Sampling should comply with specific national legislation, where it exists, or with international regulations and standards. Where no standard procedure exists, the sampling procedure should be documented including the documentation of the storage and shipment until reaching a laboratory accredited for the respective POPs or otherwise accredited for performing an adequate analysis of the respective sample and selected POPs.

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<sup>22</sup> International Electrotechnical Commission (2015) IEC 62321-6:2015 Determination of certain substances in electrotechnical products - Part 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography-mass spectrometry (GC-MS)



A sampling protocol is to be used and should contain the following information:

- Type of sample;
- Location of sampling;
- Any relevant information on the sample.

The sample should be wrapped in aluminium foil and transferred into a vessel or container (e.g. glass or another inert material) with a cap or screw top. The vessel should be labelled (readable, persistent against solvents and water, with unique information e.g. code related to sampling protocol, if the sample represent any hazard this should be noted and the sample labelled respectively). The collected samples should be stored adequately (e.g. appropriate temperature; possibly exclusion of light).

Specific care should be given to cross contamination of and in the laboratory, in particular if the laboratory also analyses other respective POPs in trace quantities (e.g. air samples). Procedural blanks, which are blanks that are treated exactly like the samples, provide good indication if there are background or crossover contamination.

For PFOS and related chemicals listed in the Convention and other PFCs/PFAS (not listed in the Convention but as emerging issue under SAICM)<sup>23</sup> special attention should be paid on contamination in solvents, in the elastomers in the HPLC instruments and in coated septa and filters. Furthermore long chain PFCs can adsorb fast and strongly to glass.

The pre-screening of samples can include specific approaches:

- a) Considerations on the different use areas (see Annex 1-A).
- b) CAS numbers, chemical names or product names (see Annexes in Custom Control Guidance<sup>16</sup>).
- c) Certain risk criteria (e.g. importing company, receiving company or use for a specific purpose) or certain chemical properties or performance properties (e.g. stain repellent).
- d) If applicable, mobile screening methods can be used during the field sampling. Non-destructive methods can even be used for selections of samples in stores and shops. The sensitivity of the screening methodology should cover the regulatory limit for a respective POP for a certain sample category. E.g. mobile screening techniques for fluorine can detect fluorine concentration of approximately 0.1% (e.g. Sliding spark spectroscopy or certain XRF). If legislation requires that PFOS is detected below such a level (see e.g. the European legislation for carpets and textiles with a limit value of 1 µg PFOS/m<sup>2</sup>) then these screening methods cannot be used for pre-selection of samples for assessment of compliance with the limit value.

#### 2.4.3 Step 3: Optional (further) screening in the laboratory

The sampled articles can be screened for the presence of e.g. fluorine or bromine in the laboratory, usually being more sensitive, compared to the mobile equipment used in the field. Screening methods have been developed, which allow determination of presence of the chemical in the sample (see e.g. the DART method described for PFOS and other PFCs or the pyrolysis GC/MS method for POP-PBDEs and other BFRs) (see chapter 3 and chapter 4).

When screening methods are applied, it needs to be ensured that the detection limit of the screening method is more sensitive than the legislation limit required for the content of the chemical.

#### 2.4.4 Step 4: Quantification

Usually quantification requires that the chemical is extracted from the sample and the extract subjected to a clean-up procedure. Extraction methods and the clean-up procedures should be

<sup>23</sup> In the Stockholm Convention only PFOS and related ca. 160 precursor chemicals are considered while all PFAS/PFCs are addressed under the Strategic Approach for International Chemical Management (SAICM) as an emerging policy issue.

validated and where available taken from standard norms. If own procedures are used, they should have proven to lead to correct results and being robust against modifications in the sample matrix.

Finally, instrumental analysis with appropriate sensitivity to achieve the required detection limits needs to be used for the data acquisition and quantification. Quantification is either done with internal standards (e.g. isotope labelled standards, such as carbon  $^{13}\text{C}$ -labelled chemicals for mass spectrometric detection) or other appropriate analytical standards, or by external calibration.

Different analytical methods are described or referenced in the respective sections. For most POPs, an example of instrumental settings is described in Annex 2 in combination with a chromatogram.

#### 2.4.5 Step 5: Documentation and reporting

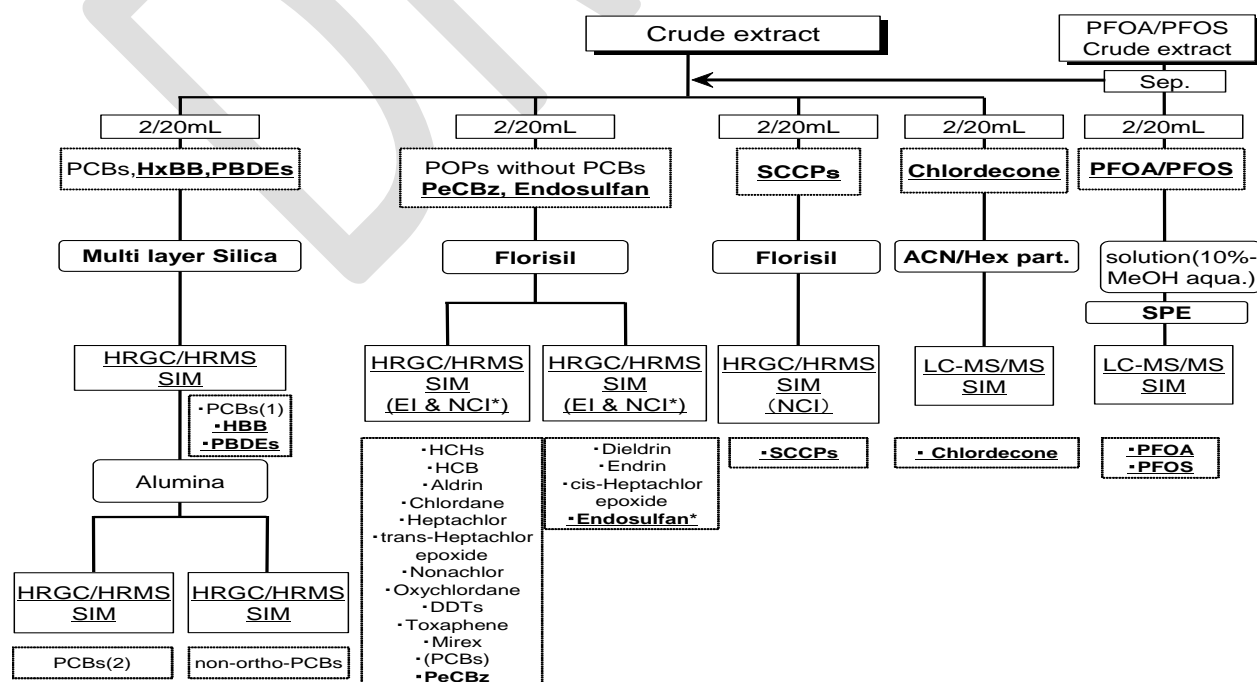
The result of the screening would be documented in an appropriate form. The reporting might include the compilation of a report on the monitoring study including scope, samples, procedures, and results. The documentation could also include the publication in peer reviewed journals, which at the same time would be a further validation of the methodology used and the results. The results would be communicated to the stakeholders concerned or interested.

### 2.5 Overview on instrumentation

Figure 2-1 gives an overview on the clean-up and analytical instruments used for an air sample by a commercial laboratory capable to analyse all listed POPs. For the initial listed 12 POPs all compounds can be measured with gas chromatography (GC) coupled to mass spectrometry (MS) and for basic pesticides or PCBs by GC- Electron Capture Detector (ECD).

For two of the POPs listed in 2009 and 2011 (PFOS and Chlordecone), the use of liquid chromatography (LC) has advantages and is recommended (see Figure 2-1).

Since the concentrations in products or articles are normally high (sometimes in percent range) compared to environmental samples, high resolution MS (HRMS) is not required for most of the article types to be screened, but low resolution MS (LRMS) or ECD can be used. For some articles with low regulation limits more sensitive methods might be necessary (e.g. for PFOS in carpets or unintentionally POPs in food/feed).



**Figure 2-1:** Clean-up of an air sample and instrumentation for analysis of all listed POPs in air (courtesy Prof. Takumi Takasuga; Shimadzu Techno Research, Japan).

**Please note:** SCCP is recommended for listing in the Stockholm Convention at COP 8<sup>24</sup>. PFOA is not listed in the Stockholm Convention but assessed by the POPRC and found to meet the POPs criteria. For analysis of air with low concentrations of POPs HRMS or sensitive LRMS is used, for analysis of respective POPs in articles low resolution GC or ECD is normally sufficient (see respective sections in this document).

DRAFT

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<sup>24</sup> UNEP (2017) Recommendation by the Persistent Organic Pollutants Review Committee to list short-chain chlorinated paraffins in Annex A to the Convention and draft text of the proposed amendment. UNEP/POPS/COP.8/14.

### 3 Sampling, screening and analysis of PFOS and related chemicals in products and articles

#### 3.1 Products and articles possibly containing PFOS and related chemicals

A list of possible applications of PFOS and those of related chemicals are given in Annex 1-A. The list contains applications in articles, which are included in specific exemptions or acceptable purposes as well as former uses and possibly impacted recycling flows. Other potentially contaminated secondary articles from recycled materials or other contamination are also mentioned. This list can be used when selecting samples for screening.

A range of PFOS and related chemicals applications are within products and articles<sup>25</sup> (e.g. specific firefighting foams, chromium plating mist suppressants, pesticides) or used for coating of articles (e.g. carpets, textiles, furniture, paper). Several of these applications were granted specific exemptions or acceptable purposes and therefore such newly produced articles can still be traded at present. Furthermore a range of articles with long life expectancy and formerly produced containing PFOS or related chemicals, might be still in use (e.g. carpets, textiles, furniture and firefighting foams).

The current use of PFOS and related chemicals in China (the largest producer and user) is estimated to be 100 tonnes, mainly used for plating industry (30 – 40 t/y), specific fire-fighting foams (25 to 35 t/y) and sulfluramid insecticides (4-8 t/y) (Zhang et al. 2012)<sup>26</sup>.

#### 3.2 Step by step approach for PFOS and related chemicals analysis in products and articles

The step by step approach for monitoring of POPs in articles and products is described in Chapter 2.4. To determine the occurrence and quantities of PFOS, PFOSF\* and its related chemicals in different articles including consumer products, representative samples can be purchased from retail outlets and analysed. A similar strategy can be used to determine the occurrence and quantities of PFOS and its related chemicals in other materials and wastes, such as the industrial materials used downstream in a product chain, consumer products and chemical formulas arriving at the borders and identified by the customs.

\*Please note: The analysis of PFOSF listed in the Stockholm Convention is only to a limited extent possible or useful since the compound is not stable in the environment, products and in most solvents (including water) and not used in articles/products. Instead PFOSF is only used as intermediate for the production of PFOS related chemicals. Therefore, no description of analysis for PFOSF is needed in this guidance and it should not be requested in tenders for monitoring of PFOS and related chemicals or be included in request from a commercial laboratory.

#### Step 1: Survey of products and articles possibly containing PFOS and related chemicals

Before collecting samples, a survey can be conducted to determine the availability of consumer products that contain or have been treated with fluorinated chemicals. Sample candidates can be identified from the list compiled in Annex A-1. Some case studies on PFOS and other per- and polyfluorinated chemicals (PFC) monitoring described below developed a survey approach. Relevant stakeholders for the different use groups might be contacted for support and input and

<sup>25</sup> A large part of PFOS containing substances have already been disposed to landfills. It is estimated that 200 to 1700 tonnes of the estimated 96000 tonnes (approximately 1%) have reached the ocean (Paul AG, Jones KC, Sweetman AJ (2010) A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environ. Sci. Technol. 43, 386–392.)

<sup>26</sup> Zhang L, Liua J (2012) The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China. Environmental Pollution 165, 193-198.

for samples. Relevant stakeholders to be contacted for the different use categories are listed in Annex 1-A

### Step 2: Sample collection

Samples can be collected e.g. by the customs at the point of import or by respective authorities like factory control or consumer protection authorities and related institutions; see Custom Control Guidance<sup>27</sup>. Sampling campaigns can also be conducted by research institutions.

The following criteria and information may be used by stakeholders:

- a) The article or product contains PFOS and its related chemicals identifiable by the chemical names, CAS numbers or if their structural formulas contain more than three fluorine atoms; or
- b) The article or product contains fluorinated chemicals identifiable by their trade names; or
- c) Articles or products potentially containing PFOS or related chemicals compiled in Annex 1-A; or
- d) The article was identified as having certain properties that are common for articles treated with PFOS and its related chemicals (e.g., stain resistant, water repellent and anti-grease), as can be identified with e.g. the Droplet test.

### Step 3: Screening for presence of fluorine and of fluorinated organic chemicals

Sampled articles can be screened for the presence of fluorine to exclude those with false claims and those that achieved certain surface properties (e.g., anti-grease) without using fluorinated chemicals. Typically, 0.05 to 0.5% of the PFC by weight<sup>28</sup> of the article is used to ensure durable repellence. Thus, samples containing 0.01% cut-off are included for further analysis, provided an adequate safe margin to ensure that all sample articles treated with fluorinated chemicals are included. Sample articles containing less than 0.01% fluorine by weight can therefore be discarded if no specific legislation requires that PFOS is below such a level (see e.g. the European legislation for carpets and textiles). In this case, screening methods cannot be used for a pre-selection of samples.

The fluorine content can be determined by using wavelength dispersive (WD) X-ray fluorescence (XRF) spectrometry. Instrument and operating parameters for this method are provided in Table 2-1. XRF might also be useful as a screening method for fluorinated substances in waste or products but the known limitations of the method are low sensitivity and lack of structure-specific information. Furthermore more sophisticated screening in laboratory with DART, DESI and <sup>19</sup>F NMR (see below) can be applied.

### Step 4: Quantification

Different analytical methods can be applied as e.g. described in Annex 2-D. Some methods have been described in more detail in national surveys with quantifications of PFOS and other PFCs in consumer products (see e.g. USEPA 2009<sup>29</sup> or SWEREA 2004<sup>30</sup>).

<sup>27</sup> Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft).

<sup>28</sup> For articles made of polytetrafluoroethylene (PTFE), such as thread sealant tape, Teflon tubing and some dental floss, the fluorine content can be greater than 70%.

<sup>29</sup> USEPA 2009. Perfluorocarboxylic acid content in 116 articles of commerce. U.S. Environmental Protection Agency, March 2009.

<sup>30</sup> Swerea 2004. Survey, screening and analyses of PFCs in consumer products. Dorte Herzke, Stefan Posner and Elisabeth Olsson. Swerea IVF project report 09/47. Climate and pollution agency in Norway, TA-2587/2009.

### 3.3 Screening methods for fluorine/organofluorine chemicals

#### 3.3.1 Introduction

For a pre-selection of samples, screening methods for PFOS/PFCs are valuable. Most of such screening methods cannot identify specifically PFOS and related chemicals but need then a confirmation analysis for PFOS and to distinguish from other PFCs by MS methods (see below). Some of the screening methods can (semi-)quantify the organofluorine content. Such a measurement might be valuable in cases where PFOS is partly chemically bound or where a larger part of PFOS is present as PFOS precursor for which no analytical standard method exists.

Most screening tools provide only poor semi-quantitative information. In case of spectroscopic approaches (WDXRF, SSS) only fluorine present at the sample surface is detected and semi-quantified.

In case of GC-EPED (Echelle-Plasma-Emission-Detector) coupled to a headspace or a purge & trap sampler, mostly volatile precursors of PFOS are detected and levels of precursors do not necessarily give robust hints on PFOS levels. Fluorine  $^{19}\text{F}$  NMR is a quite sensitive screening technique (LODs around 300 ng/mL solution), which can distinguish fluorine chains bound to different functional groups, such as sulphates, phosphates, acrylates and ethers (Trier 2011, Ellis 2004). Another option is to make extracts of the sample and screen for PFCs by accurate, high resolution mass spectrometry (LC-HRMS) by searching for a combination of 1) typical negative mass defects, 2) homologue series separated by 50 Da or 100 Da 3) typical perfluorinated ions (for perfluorinated compounds, such as PFOS) and/or 4) specific neutral losses, such as HF (for polyfluorinated PFCs containing hydrogen). This methodology has been used to screen industrial blends and paper extracts with (Trier 2011) typical CnFm fragments (i.e.  $m/z$  119, 131, 169, 195, 231, 331).

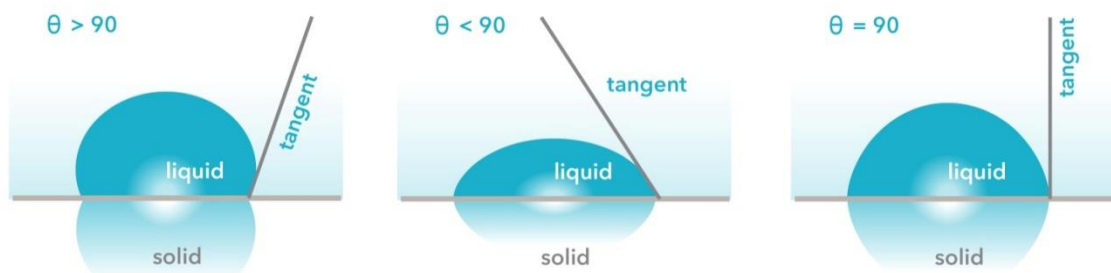
#### 3.3.2 Screening with the “drop test”

When PFOS or other PFCs are coated on a textile substrate and exposed to water (surface tension of 72 mN/m) or oily substances (surface tensions of 20 mN/m and more), they will not spread on the textile surface (Posner 2011). This phenomenon is called “water and oil repellence” and used for water, oil and stain protection of carpets, textiles or leather.

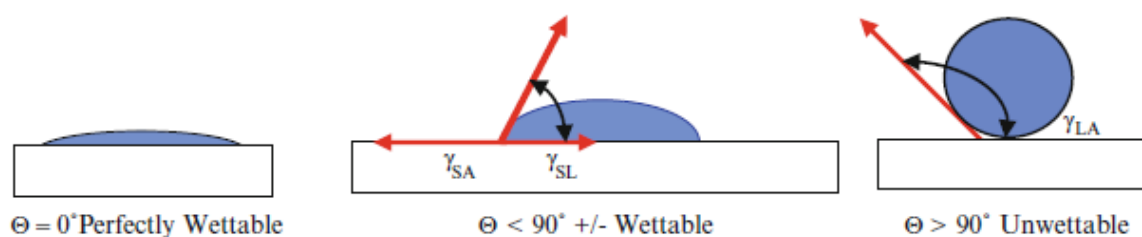
Most alternatives cannot achieve a surface energy lower than 22 mN/m or lower, the surface energy for oil (Posner, 2011). Materials with a high contact angle and low surface energy are therefore likely treated with perfluorinated substances. Highly fluorinated surfaces can be distinguished from non-fluorinated surface treatments, if both a droplet of water and a droplet of oil put on the surface form pellets. If the oil droplet flattens out, the surface is likely treated with a non-fluorinated chemical (hydrocarbon surfactant or a silicone coating). The spreading of a liquid on a surface demonstrates when a fabric is being treated or not by the degree of wetting measured by the contact angle (Figures 3-1 and 3-2). Contact angle,  $\theta$ , is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect as shown in Figure 3-2. It can be seen from this figure that a low values of contact angle ( $\theta$ ) indicates that the liquid spreads, or wets well, while a high contact angle indicates poor wetting. If the angle  $\theta$  is less than 90 degrees the liquid is said to wet the solid. If it is greater than 90 degrees it is said to be non-wetting. A zero contact angle represents complete wetting (Posner 2011, Kissa 2001).

The wetting angle can be used for screening of PFOS (and other PFC) treated materials.





**Figure 3-1:** Contact angle  $\theta$  categories of a droplet on a surface



**Figure 3-2:** Contact angle versus wettability of a substrate surface. When angle  $\Theta$  is  $> 90^\circ$ , liquid will not wet the surface; when angle  $\Theta$  is  $< 90^\circ$ , liquid will wet surface partially; when angle  $\Theta = 0^\circ$ , complete spreading & wetting of the surface by the liquid. Spreading occurs only if  $S > 0$ . Spreading coefficient:  $S = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL})$  (;  $S$  = solid,  $L$  = liquid,  $A$  = air. where  $\gamma_{SA}$  = surface energy of the substrate (e.g., polymer surfaces),  $\gamma_{LA}$  = surface tension of the liquid and  $\gamma_{SL}$  = interfacial tension).

### 3.3.3 Screening of Fluorine with WD-XRF-Analysis

Wavelength dispersive XRF (WD-XRF) systems are able to detect fluorine in vacuum mode. Respective systems (e.g. S8-TIGER; Bruker AXS, Karlsruhe) are used to analyse products and articles on their fluorine content. It is important to understand that for fluorine the depth of signal saturation is limited to the first micrometers, caused by the very low energy of the obtained fluorescence radiation. Applying the WD-XRF of Bruker to the fluorine screening in coated papers an LOD of 0.05% fluorine was elaborated. Taking into account, that per- or polyfluorinated side groups of large coating molecules are expected to form the outer shell of the sample matrix, the LOD of 0.05% is sufficient for perfluorinated structures ( $-C_nF_{2n+1}$ ). If the depth of saturation reaches the non-fluorinated backbone structure of the coating molecules also, the LOD of 0.1% might be too high for very thin coatings or those containing only low levels of fluorine.

**Table 2-1:** WD-XRF method and operating parameters for screen-testing samples for the presence of fluorine (USEPA 2009)

Instrument	Panalytical PW2404 Wavelength Dispersive (WD) X-ray Fluorescence (XRF) Spectrometer equipped with the PW2540 Sample Changer
Software	SuperQ (Panalytical) for instrument control IQ+ (Panalytical) for calibration and quantification
Power of X-ray tube	4000 watts
Measurement atmosphere	Vacuum ( $< 10$ mb) or under helium atmosphere
Scan method	A continuous scan mode followed by fluorine-specific data collection at the peak fluorine wavelength for an additional 10 second measurement.

<sup>a</sup> Liquid samples were tested on filters by wetting a 47-mm paper filter (Whatman) with approximately 0.5 mL sample, and then air drying the filter under an aluminum foil cover.

### 3.3.4 Fluorine screening with $^{19}\text{F}$ NMR spectroscopy

Fluorine has an uneven number of protons, and hence has an unpaired proton with spin  $\frac{1}{2}$ , which couples electromagnetically upon being exposed to a magnetic field. Fluorine is furthermore monoisotopic, and has a high sensitivity (81% compared to Hydrogen). This, together with the high numbers of fluorine present in PFOS and other PFCs, makes  $^{19}\text{F}$  NMR is a sensitive screening technique, capable of screening down to approximately 300 ng/mL (ppb) in samples of e.g. paper and board (Trier 2011)<sup>31</sup>.

Extracts of samples, containing no particulates, are made with organic solvents and evaporated down to approximately 100  $\mu\text{L}$ , and redissolved in deuterated solvent (e.g.  $\text{MeOD}$ ), so that max. 10% of the solvent is hydrogenated (e.g.  $\text{H}_2\text{O}$  or  $\text{MeOH}$ ). The samples are analysed on an NMR instrument (minimum 500 MHz) equipped with a dual H-F probe, and scans up to 24 hours are acquired.  $\text{Cr(III)}$  acetate is added as relaxation agent, and an internal standard with chemical shifts of the PFOS or other PFC analytes is added too (Ellis et al. 2000<sup>32</sup>; Trier 2011<sup>31</sup>). The screening can be made semi-quantitative, and is capable of detection unknown organofluorines. The instrumentation is highly specialised, costly and immobile.

### 3.3.5 Screening of Fluorine: Sliding spark spectroscopy

The basic principle of the method is the thermal vaporization of a small amount of the sample surface using a train of defined high-current sliding sparks (Seidel et al., 1993)<sup>33</sup>. The material components in the spark plasma are vaporized, atomized and activated to emit radiation. Software analysis of the delivered spectra gives information on the content of elementary fluorine on top of the surface. For fluorine a typical double-peak at a wavelength of about 350 nm is obtained. In defining special hardware setup, it is possible to get the absolute intensities of the fluorine emission line. The measurement is repeatedly done at different sites of the sample surface. The system is mobile and can detect organofluorine (such as PFOS) at a concentration of approximately 0.1%.

### 3.3.6 Screening of Fluorine: P&T-GC-EPED

A Plasma Emission Detector with Echelle Spectrometer (EPED, IMT Innovative Messtechnik GmbH) coupled with gas chromatography (AG6890, Agilent) and a purge & trap sampler (PTA3000, IMT, Moosbach) can also be used for screening of volatile organofluorine compounds (Wolz et al. 2011). The EPED detector combines a long term stable pulsing plasma cell with a high resolution Echelle spectrometer. The resulting multi-element gas chromatographic detector shows high sensitivity and selectivity for sulphur and the halogens chlorine, bromine, fluorine and iodine with detection limits for the above elements < 10 pg/s corresponding to approx. 100 pg<sup>34</sup> (peak width of 10 sec) and a linearity about 3-4 orders of magnitude. The equipment is stationary in laboratory and not mobile.

### 3.3.7 Screening of PFOS and related chemicals: HS-GC-EI-MS or HS-GC-CI-MS

A more sophisticated screening tool is a headspace sampler connected to a GC-MS system. About 1 dm<sup>2</sup> of the material is placed into a 10 ml headspace vial. At a temperature of 150°C volatile PFOS precursor compounds are released into the headspace. An aliquot of the headspace volume is transferred onto a GC column and detected by EI-MS after chromatographic separation. Typical CnFm fragments (i.e. m/z 119, 131, 169, 195, 231, 331)

<sup>31</sup> Trier X (2011) Polyfluorinated surfactants in food packaging of paper and board. PhD Danish Technical University, Copenhagen/Denmark.

<sup>32</sup> Ellis DA, Martin JW, Muir DCG, Mabury SA (2000) Development of an  $^{19}\text{F}$  NMR Method for the Analysis of Fluorinated Acids in Environmental Water Samples Anal. Chem. 72, 726-731.

<sup>33</sup> Seidel T, Golloch A, Beerwald H, Böhm G, (1993) Fresenius' Journal of Analytical Chemistry 347, 92-102.

<sup>34</sup> 100 pg may be purged from 10 ml of extract from 0.5 g of coated paper corresponding to 200 pg/g paper.



are then monitored in order to identify the presence of organofluorinated compounds. If run with chemical ionisation even molecular ions can be detected enabling an identification of the detected PFC.

The equipment is stationary in laboratory. It allows a high throughput of samples for screening of volatile PFOS precursors.

### 3.3.8 Screening PFOS and related chemicals in articles with DART-TOF MS

The Direct Analysis in Real Time (DART) - Time of flight (TOF) mass spectrometer (DART-TOF MS) couples the DART ion source with the high-resolution, accurate mass capability of a time-of-flight (TOF) mass spectrometer.

The sample is placed in its native form between the DART ion source and the TOF mass spectrometer inlet. The DART source ionises the sample. Typically no solvents or sample preparation are required. With DART MS chemical composition is determined and high-resolution accurate mass spectra are produced.

While the technology has been applied for screening of PFCs on paper (DiPAPS up to 1500 Dalton) (Ackerman et al. 2009)<sup>35</sup> there is currently no monitoring of PFOS and precursors reported, partly due to the specialised ionisation device/cost of this method.

### 3.3.9 Screening of PFOS and PFCs in articles with accurate mass by HRMS

Filtered extracts can be screened for the presence of organofluorines (soluble in LC eluents) by high-resolution, accurate mass (Quadrupole) Time-of-flight (TOF) mass spectrometry. The search starts with a screening for 1) typical negative mass defects, i.e. the ions have  $m/z$  just below nominal mass, e.g. 412.99 instead of 413.00. The  $m/z$  of the suspect compounds is then used to make EICs (extracted ion chromatograms) to see if they belong to a homologue series separated by 50 Da or 100 Da. The spectra can also be checked for the presence of 3) typical perfluorinated ions (C<sub>n</sub>F<sub>m</sub> fragments (i.e.  $m/z$  119, 169, 219, 269, etc. – these ions are prevalent for perfluorinated compounds, such as PFOS) and/or 4) specific neutral losses, such as HF (loss of  $n$  times HF (20 Da), i.e. look for losses of 20, 40, 60, 80 Da – typical losses for polyfluorinated PFC containing hydrogen).

This methodology has been used to screen industrial blends and paper extracts (Trier 2011). The method is fast, simple and specific, but the instrumentation is costly and not mobile.

## 3.4 Qualitative and quantitative analysis of PFOS and related chemicals

### 3.4.1 Background and general challenges of PFOS/PFC analysis

Analytical standard methods for quantification of PFOS and other PFCs are under development, and some technical standards have been defined (see Table 3-1; and section 3.5.2). Due to their relative low volatility, good solubility in water and lack of chromospheres, the analysis of perfluorinated alkyl substances is a challenging task. The analytical problems associated with the determination of neutral and anionic PFCs are multiple, and include diverse aspects such as unique physico-chemical properties, lack of reliable standards, degradation of standards, impurities, complicated mixtures of isomers and congeners, adhesion of the analytes to the analytical equipment, ion suppression, and contamination during all stages of the analytical procedure, including instrumental sources. When using the different available analytical methods for PFOS and its related chemicals caution should be given to follow the measures needed to assure that they provide reliable results. The challenges associated with

<sup>35</sup> Ackerman LK, Noonan GO, Begley TH (2009) Assessing direct analysis in real-time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 26, 1611-1618.

quantification methods for PFOS and its related chemicals are described in the literature (Martin et al. 2004)<sup>36</sup>.

The analytical detection method of choice for PFOS and most PFCs is currently [LC-MS or LC-MS/MS](#) for the anionic compounds (including PFOS and PFOA), whereas both LC-MS(MS) and GC-MS can be used for the determination of the neutral per- and poly-fluorinated alkylated substances including several precursors of PFOS. Quadrupole tandem mass spectrometry applying negative electrospray ionisation interfaces (HPLC/ESI-MS/MS) seems to be the preferred instrumental method for the determination of ionic PFCs. Recently, atmospheric pressure photo ionisation (APPI)-LC-MS/MS has been reported to give good ionisation of neutral fluorotelomer alcohols (FTOH). In LC-MS of anionic PFCs, usually the dissociated acid (pseudo molecular) ion  $[M-H]^-$  is observed, which can be used for quantitative purposes in LC-single quad MS, or as the precursor ion for multiple ion reaction monitoring in LC-MS/MS. Detection limits of LC-MS(MS) and GC-MS methods are sufficiently low to allow in principle for the determination of environmental levels of PFCs in drinking water and in food samples if a country decides to include them in the monitoring.

Quality assurance measures are required to ensure best possible quality of the data. Liquid samples are diluted and extracted for both volatile and ionic compounds, followed by a cleaning step with activated carbon. Solid samples are homogenized prior to extraction and then treated similar to liquid samples.

Since PFOS and its related chemicals occur in a large range of materials and liquids, it is advisable to use skilled and specialized laboratories where accreditation is one efficient way to verify these skills. A list of laboratories accredited for analysing POPs and using Good Laboratory Practices (GLP) can be found in (<http://www.chem.unep.ch/gmn/gmnlabs/default.htm>).

It has to be underlined, that LC-MS systems have to be especially prepared for PFOS/PFC analysis, due to blank issues related to fluorinated compounds in LC systems (e.g. from teflon parts). In addition, there are further important issues required for a reliable PFC analysis:

- a) use of specific standards for target analytes (not available for most PFOS precursors, mixed chain length PFCs and structural isomers)
- b) use of labelled internal standards (at least for the main target analytes)
- c) purity and stability of the standards. PFOSF, and probably a range of other PFOS precursors including e.g. esters (e.g. polyfluoroalkyl phosphoric acid esters (PAPs)) are prone to degradation (hydrolysis) if stored in alcohols/waters

Both volatile and non-volatile PFOS precursors and other PFCs are analysed using well established analytical methods applying GC/MS and LC/MS techniques. Quality assurance measures are required to ensure best possible quality of the data. Liquid samples are diluted and extracted for both volatile and ionic PFCs, followed by a cleaning step with activated carbon. Solid samples are homogenized prior to extraction and then treated similar to liquid samples. All calculated concentrations are either given in  $[\mu\text{g/L}]$  for liquids,  $[\mu\text{g/kg}]$  for solid materials or in  $[\mu\text{g/m}^2]$  for textiles, paper and leather. Since PFOS/PFCs occur in a large range of materials and liquids, it is advisable to use specialized laboratories where accreditation is one efficient way to verify skills.

<sup>36</sup> Martin JW, Kannan K, Berger U, de Voogt P, Field J, Franklin J, Giesy JP, Harner T, Muir DCG, Scott B, Kaiser M, Järnberg U, Jones KC, Mabury SA, Schroeder H, Simcik M, Sottani C, van Bavel B, Kärrman A, Lindström G, van Leeuwen S. (2004) Analytical challenges hamper perfluoroalkyl research. *Env. Sci. & Tech.* 38, 248A–255A.

### 3.4.2 Specific challenges with analysis of PFOS precursors and bound-PFOS

#### Analysis of PFOS precursors in articles

The OECD compiled a list of 165 PFOS related compounds and chemicals (OECD 2007)<sup>37</sup>. Only for a few of these PFOS related compounds and chemicals a standard analysis is available (Table 3-2). Therefore currently most PFOS related chemicals are not covered by the standard analysis. While for environmental samples this might be of minor relevance due to degradation of these precursors to PFOS (e.g. frequently observed in sewage treatment plants where the PFOS concentrations mass balance of higher PFOS levels in sludge and outflow compared to the inflow)<sup>38</sup>. However, in products and articles PFOS precursors might be used which are not detected then by the routine PFOS analysis or state-of-the-art analysis, including several PFOS precursors (Table 3-2).

#### Analysis of chemically bound PFOS

The current available standard to analyse PFOS in articles focusses on the extractable PFOS (NPR-CEN/TS 15968; see below). In some applications, however, the PFOS related chemicals are chemically bound to the surface. Therefore the analytical standard procedures extract the extractable PFOS and PFOS related chemicals not bound to the surface. The largest part of chemically bound PFOS precursor could remain on/in the article, leading to a considerable underestimation of PFOS related chemicals in these products.

### 3.4.3 Selected international standards for PFOS analysis

Some standards for measuring PFOS in articles have been developed and are shortly introduced. Most standards developed for PFOS relate to water and environmental matrices (Table 3-3).

#### NPR-CEN/TS 15968<sup>39</sup>

The NPR-CEN/TS 15968 standard is currently the only existing international standard for the determination of the extractable content of PFOS in solid items (e.g. textiles, leather, paper) and in chemical products (AFFF, cleaning agents, etc.) within the scope of supporting the EC Regulation 850/2004 on persistent organic pollutants. An international standard has been developed here for "Determination of extractable perfluorooctane sulphonate (PFOS) in coated and impregnated solid articles, liquids and firefighting foams - Method for sampling, extraction and analysis by LCqMS or LC-tandem/MS".

The method is currently a technical specification (TS) meaning it is not fully validated. In order to become a full European standard (EN) some further work needs to be done to ensure accuracy in analytical results with data from proficiency testing.

As stated in the name of the standard, the method only addresses the extractable PFOS and a few PFOS precursors (see Table 3-4 and Table A2-14 in Annex 2). The standard does not address the chemically bound-PFOS related chemicals and also does not describe a holistic analysis of PFOS related chemicals.

It is applicable to concentrations of PFOS in the extract solution in the range from 0.5 to 50 µg/L.

#### ISO Method for water (ISO 25101:2009)

Currently no ISO standard is available to measure PFOS and other PFCs in articles or products. The only ISO standards for PFOS is ISO 25101:2009, which specifies a method for the determination of the linear isomers of PFOS and PFOA in unfiltered samples of drinking water,

<sup>37</sup> OECD (2007) Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals that may degrade to PFCA (as revised in 2007). Organization for Economic Co-operation and Development, 21-Aug-2007 .ENV/JM/MONO 15

<sup>38</sup> Yu J, Hu J, Tanaka S, Fujii S (2009) Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Res. 43:2399-2408.

<sup>39</sup> Preview of NPR-CEN/TS 15968 content: <http://www.evs.ee/preview/cen-ts-15968-2010-en.pdf>

groundwater and surface water (fresh water and sea water) using high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). According to the standard other isomers may be reported separately as non-linear isomers and qualified as such. The method is applicable to a concentration range of 2.0 ng/L to 10000 ng/L for PFOS and 10 ng/L to 10000 ng/L for PFOA. Depending on the matrix, the method may also be applicable to higher concentrations up to 200,000 ng/L after suitable dilution of the sample or reduction in sample size.

#### Validated standards used for compliance measurement of PFOS in articles

National standards for measuring PFOS in articles have been developed in China for specific assessment purposes, e.g. the export into the EU having regulatory limits for PFOS in articles (Table 3-1).

So far, a series of industrial standard testing methods have been issued for the determination of PFOS in main products for import/export. These standards are based on LC-MS/MS.

In addition, China has issued eight industrial standard testing methods of PFOS (Table 3-2).

**Table 3-1:** National standards for testing PFOS in articles in China (all based on HPLC-MS/MS)

No.	Name	Abstract	Date of implementation
GB/T 24169-2009	Determination of PFOS in fluorinated chemical products and consumables	The method specifies the HPLC-MS/MS method for the determination of PFOS in fluorinated chemical products and consumables. The MDL is 0.0002% (calculated in PFOS).	2010-04-01
GB/T 23243-2009	Determination of PFOS in food packaging materials	This method specifies the HPLC-MS/MS method for the determination of PFOS in food packaging materials. The MDL is 0.4 $\mu\text{g}/\text{m}^2$ (calculated in PFOS).	2009-07-01
GB/T 29493.2-2013	Determination of harmful substances in textile dyeing and finishing auxiliaries - Part 2: Dermination of perfluorooctane sulfonates and perfluorooctanoic acid	This method specifies the HPLC-MS/MS method for the determination of PFOS and PFOA in textile dyeing and finishing auxiliaries. The MDL is 10 mg/kg.	2013-09-01

**Table 3-2:** Industrial testing standards for PFOS in articles in China (all based on HPLC-MS/MS)

No.	Name	Date for implementation
SN/T2392-2009	Determination of PFOS in chemical products for import/export: LC-MS/MS method	2010-3-16
SN/T2393-2009	Determination of PFOS in washing products and cosmetics for import/export: LC-MS/MS method	2010-3-16
SN/T2394-2009	Determination of PFOS in extinguisher products for import/export: LC-MS/MS method	2010-3-16
SN/T2395-2009	Determination of PFOS in insecticides for import/export: LC-MS/MS method	2010-3-16
SN/T2396-2009	Determination of PFOS in light industrial products and cosmetics for import/export: LC-MS/MS method	2010-3-16
SN/T2449-2010	Determination of perfluooctane sulfonic acid in leather and leather products: LC-MS/MS	2010-07-16
SN/T2842-2011	Determination of perfluooctane sulfonic acid and perfluorooctanoic acid in textiles: LC-MS/MS method	2011-07-01
SN/T3544-	Determination of perfluorooctanoate (PFOA) and	2013-09-06

No.	Name	Date for implementation
2013	perfluorooctane sulfonate (PFOS) in food for export: LC-MS/MS method	

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**Table 3-3:** Summary of a survey on standardized analytical methods and methods reported in literature to be considered for PFOS analysis in mainly environmental matrices (Please note that the standard for analysis of extractable PFOS in articles NPR-CEN/TS 15968 - have meanwhile been developed and published, see below<sup>40</sup>)

Method	Matrix	Extraction	Clean-up	Detection	Congeners/Standards	Limits of method	Reference
Standard methods for determination of polyfluorinated substances in water							
E DIN 38407-42:2010-05 (D)	Water	SPE	No details available	LC-MS/MS	Polyfluorinated substances	No details available	[DIN 2010]
EPA 537	Drinking water	SPE	-	LC-MS/MS	perfluorinated alkyl acids (incl. PFOS)	1.4 µg/L (DL) 6.5 µg/L (lowest concentration minimum reporting level)	[EPA 2009]
ISO 25101:2009	Water	SPE	-	LC-MS/MS	PFOA and PFOS	2,0 ng/l to 10 000 ng/l	[ISO 25101]
Standard method for determination of PFOS under development							
FprCEN/TS 15968	Coated and impregnated solid articles, liquids, fire fighting foams	Depending from matrix – no details available	Depending from matrix – no details available	LC-MS/MS; LC-MS	PFOS	0,5 ng/ml to 50 ng/ml in extract	[CEN 15968]
Methods for determination of PFOS its salts and PFOA in different matrices reported in scientific literature							
Literature	Water	On-line extraction (turbulent flow chromatography)	-Column wash	LC-APPI/MS	PFOS	18 ng/L (LOQ)	[Takino et al., 2003]
Literature	Waste water STP sludge	Sedimentation, decantation Solvent liquid extraction after drying and grinding (aqueous acetic acid and MeOH)	SPE (OASIS HLB)	LC-APPI/MS	PFOS	2.5 ng/L (LOQ) 10 – 25 ng/g (LOQ)	[Sinclair and Kannan., 2006]
Literature	Water, waste water	Filtration	SPE mixed hemimicelle-based	HPLC-ESI-MS/MS	PFSAs incl. PFOS	0.2 ng/L (LOD)	[Zhao et al., 2007]
Literature	Sediment, sludge	Solvent liquid extraction (aqueous acetic acid and MeOH)	SPE	HPLC-ESI-MS/MS	PFSAs incl. PFOS	0.1 µg/kg (LOD sediment) and 0.9 µg/kg (LOD sludge)	[Higgins et al., 2005]
Literature	Sewage sludge	Freeze drying, Soxhlet extraction, hot vapour extr., PLE	-	HPLC-ESI-MS/MS GC–NCI-MS	PFSAs incl. PFOS	6.000 – 10.000 ng/g (LOD) 10.000 – 20.000 ng/g (LOQ)	[Schröder 2003]
Literature	Dust	Solvent liquid extraction (MeOH) sonication	Centrifugation, filtration	HPLC-ESI-MS/MS	PFSAs incl. PFOS	10 – 50 ng/g (LOQ)	[Moriwaki et al., 2003]
Literature	Dust	Solvent liquid extraction (AcN) sonication	Centrifugation, SPE (C18)	HPLC-ESI-MS/MS	PFSAs incl. PFOS	0.99 – 4.56 ng/g (MDL)	[Kubwabo et al., 2005]

### 3.4.4 Sample pre-treatment

NPR-CEN/TS 15968 proposes grinding of samples to ensure an efficient extraction process without stating particle sizes. As in solid samples PFOS and related chemicals are predominately found on the sample surfaces, a particle size of <1mm may be sufficient. However, for samples, which cannot easily be ground like paper, textiles, or leather, the technical standard recommends cutting leather (and textiles) into pieces of max. 25 mm<sup>2</sup>, whereas for paper a max size of 1 cm<sup>2</sup> is given.

### 3.4.5 Extraction

#### Solid samples

In most cases methanol (MeOH), ethanol or acetonitrile (ACN) as well as mixtures of these solvents with water were chosen as extraction solvents for products. Clean-up is mostly achieved by solid phase extraction (SPE) on reversed phase C18 or WAX columns, which also reduces the presence of ion suppressing inorganic salts/minerals in the extracts.

Extraction techniques reported in these cases include ultrasonic assisted solvent extractions, accelerated solvent extractions (ASE), pressurised liquid extraction (PLE). With these techniques, typically 0.5 to 3 gram of sample matrix is extracted in 2-3 extraction cycles.

Using ASE or PLE Teflon-free tubing and sealing are recommended (special care of the maximal allowed temperatures for the applied sealing materials is necessary). The ground (e.g. by cryohomogenisation, which makes most polymers brittle) or cut samples are mixed with

<sup>40</sup> Determination of extractable perfluorooctanesulphonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LC-qMS or LC-tandem/MS



MeOH pre-washed sea sand or comparable bulk materials and placed into the extraction cartridges. ASE or PLE is then performed at 80-100 °C, for 10-30 minutes per cycle (depending on sample types. The lower the diffusion coefficients of the sample matrix the longer the extraction times).

Ultrasonic extraction is performed with 10-30 ml of extractions solvent (ACN, MeOH) in polypropylene centrifugation tubes. Ultrasonic treatment takes 15-60 minutes (depending on sample type and particle size) and after a centrifugation step the supernatant is removed from the sample. The treatment is repeated once or better twice and the supernatants are combined.

If no clean-up is performed, the final extract is filtered (e.g. syringe filters of cellulose mixed ester (CME)) and reconstituted in MeOH/H<sub>2</sub>O (1/1; vol/vol).

#### **Liquid samples (e.g. AFFF, impregnation sprays)**

Liquid samples are usually diluted with water, a polar organic solvent (MeOH, ACN) or a mixture of both. If LODs greater than 100 µg/L are required, 1:100 (or even higher) dilutions of AFFF can directly be subjected to LC-MS. Lower LODs may be reached by prior clean-up with SPE columns. However, it is highly recommended to produce 1:100, 1:1000 and 1:10000 dilutions, and to start the LC-MS analysis with the highest dilution. This approach enlarges the operating times of the LC-MS system and prevents a PFOS overload.

The diluted sample is filtered (e.g. syringe filters (CME)) and reconstituted in MeOH/H<sub>2</sub>O (1/1; vol/vol).

#### **3.4.6 Clean-up**

Three clean-up procedures can be recommended for PFOS and other perfluorinated carboxylates, phosphates and sulfonate acids. For challenging matrices combinations of these may be applied as well. Descriptions of extractions of neutral PFOS-precursors or volatile PFCs such as FTOHs can be found elsewhere, e.g. Benskin et al. 2012<sup>41</sup>.

A fast and easy clean-up makes use of powders of activated carbon (e.g. Envicarb), which are applied to the sample directly, adsorb interfering matrix components and finally removed from the extracts by filtration (e.g. CME syringe filters) and/or centrifugation. Alternatively, sample extracts are subjected to SPE columns with active carbon. The cleaned extract is then eluted from the column with a suitable solvent (e.g. MeOH, ACN). The approach is applicable to all kinds of extracts (MeOH, ACN, mixtures of both with water, Methyl tert-butyl ether (MTBE)).

Secondly, extracts in MeOH or ACN are diluted with 5-10-fold amounts of HPLC water and subjected to SPE columns containing C<sub>18</sub> or weak anion exchangers. The SPE columns are prepared with 1 SPE volume of methanol and another of water, before the diluted sample is loaded onto the column head. The SPE column is then washed with water (adjusted to pH 4-6), MeOH/water, and/or THF/ACN/MeOH. Finally, PFOS and other perfluorinated carboxylates and sulfonate acids are eluted with 1-2 column volumes of methanol (adjusted to pH 10 with NH<sub>3</sub>).

MTBE extracts from ion-pair extractions can be cleaned with florisil columns (100-1000 mg) prior to solvent change to methanol/water. Florisil columns are pre-washed with MeOH and MTBE before the sample is loaded. After washing with MTBE, target compounds are eluted with 30/70 MeOH/MTBE mixture (vol/vol).

In all cases, the eluents are filtered (e.g. syringe filters (CME)) and dried under nitrogen before reconstitution in MeOH/H<sub>2</sub>O (1/1; vol/vol).

<sup>41</sup> Benskin JP, Ikonomou MG, Gobas FA, Woudneh MB, Cosgrove JR. (2012) Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments. Environ Sci Technol. 46, 6505-6514.

### 3.4.7 Calibration

Calibration standards are normally produced by commercially available mixtures of native and isotope labelled perfluorinated carboxylates and sulphonates and are used for calibration. Isotope labelled analytes are only relevant when mass spectrometry is used for detection. EPA 537 suggests that at least five calibration concentrations are required to prepare the initial calibration curve spanning a 20-fold concentration range and that larger concentration ranges will require more calibration points.

Note, that PFCs are prone to matrix enhancement when analysed by LC-Electrospray ionisation (ESI)-MS, why it is advised that either matrix matched or standard addition calibration curves are used. External calibration curves and precursors for which no native and/or internal standards exist should be used with great care for interpretation.

An example for detailed requirement on calibration is described in the EPA 537 methods. These include e.g. the demonstration and documentation of acceptable initial calibration before any samples are analyzed. After the initial calibration is successful, a continuing calibration check is required at the beginning and end of each period in which analyses are performed.

### 3.4.8 Recovery

According to NPR-CEN/TS 15968 the check of analyte recoveries can be performed by two differently isotope labelled PFOS or PFOA standards. The internal standard applied for quantification is added to the sample at the beginning of the analytical procedure, whereas the other (recovery standard) is added to the final cleaned and volume reduced extract. The alternative way to check recoveries is the fortification of samples with native PFOS.

The EPA Method 537 requires a surrogate recovery in the range of 70-130%, which seems a reasonable approach. If the recovery is out of this range the method also suggests steps to check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance, then to correct the problem and reanalyze the extract.

### 3.4.9 Blank measurements

As a minimum quality assurance, method blank samples are required. The procedural blank shall be at least threefold less than the limit of quantification of the method. Blank samples are treated in the same way as the samples, but do not contain sample matrix. For ultrasonic extracts, the normal volume of extraction solvent (MeOH, ACN) is used, with ASE or PLE cartridges filled with sea sand or a comparable bulk material is used. For ion pair extractions or liquids, HPLC water is used as substitute in method blank samples. Note that ultrasonic extraction risk to decompose labile PFC precursors, e.g. esters.

If PFOS levels in method blank samples increase, it is recommended to compare these with levels in pure solvent blanks, i.e. ACN/water (1/1; vol/vol) or MeOH/water (1/1; vol/vol) or pure HPLC water. This helps to distinguish between solvents or bulk materials as a major source of contamination. Polypropylene tubes and sample containers can be reused, however, are discarded after samples with increased PFOS levels had contact to their surfaces. High concentrated PFOS extracts or solutions can migrate into the plastic walls and cross contaminate low concentrated samples or extracts.

### 3.4.10 PFOS and selected PFOS related chemicals monitored

In Table 3-4 PFOS and related chemicals are included, which can be considered to be part of state-of-the-art analysis of PFCs. However as mentioned above, most of the 165 PFOS related chemicals are not covered by the current used state-of-the-art analysis. In Table A2-14 in the Annex also other PFCs are listed which are covered by state of the art PFC analysis.



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**Table 3-4:** PFOS and related chemicals included in state-of-the-art monitoring. (from approx. 165 PFOS related chemicals; \*Analytes listed in CEN/TS 15968:2010).

Abbreviation	Full name	CAS #	Detection method
<b>Fluorooctane sulfonamides/ sulfonamidoethanols</b>			
<b>PFOSA*</b>	Perfluorooctane sulphonamide	754-91-6	LC-MS
<b>N-Me-FOSA*</b>	N-Methyl-heptadecafluorooctane sulphonamide	31506-32-8	LC-MS
<b>N-Et-FOSA</b>	N-Ethyl-heptadecafluorooctane sulphonamide	4151-50-2	LC-MS
<b>N-Me-FOSE*</b>	N-Methyl-heptadecafluorooctane sulfonamidoethanol	24448-09-7	LC-MS
<b>N-Et-FOSE*</b>	N-Ethyl-heptadecafluorooctane sulfonamidoethanol	1691-99-2	LC-MS
<b>Perfluoro sulfonates</b>			
<b>PFOS*</b>	Perfluorooctane sulfonate	1763-23-1	LC-MS

### 3.5 Example for a LC/MS setting and parameters

#### 3.5.1 LC/MS parameters and mass settings for PFOS

The selected LC/MS conditions differ slightly between laboratories and instruments. In Annex 2-G an example is listed from an accredited commercial laboratory. Mass ions ( $m/z$ ) used for detection are listed in Table 3-2 and for the described method in Annex 2-G.

## 4 Sampling screening and analysis of POP-BFRs in articles, products and recycling streams

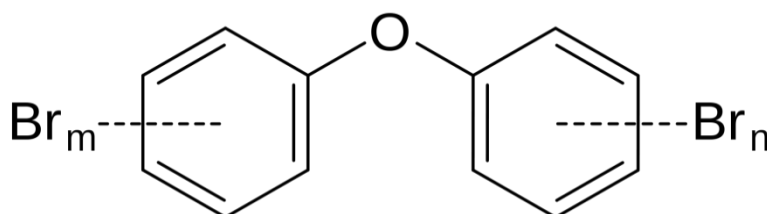
### 4.1 POP-BFRs listed in the Stockholm Convention

#### 4.1.1 POP-PBDEs listed in the Stockholm Convention

Polybrominated diphenyl ethers (PBDEs; Figure 2-1) are a group of industrial aromatic organobromine chemicals that have been used since the 1970s as additive flame retardants in a wide range of - mainly - consumer products. PBDEs were produced with three different degrees of bromination, and marketed as commercial PentaBDE (c-PentaBDE), c-OctaBDE and c-DecaBDE. Typical homologue distributions of c-PentaBDE and c-OctaBDE are shown in Tables 4-1 and 4-2.

Tetrabromodiphenyl ether and pentabromodiphenyl ether<sup>42</sup> from c-PentaBDE as well as hexabromodiphenyl ether and heptabromodiphenyl ether<sup>43</sup> from c-OctaBDE, are listed under the Stockholm Convention. These POPs are listed in Annex A and referred to in this document as POP-PBDEs. Their production and use are to be eliminated by Parties where the amendment has entered into force, subject to the exemptions (recycling) allowed by the Convention after registration.

The octaBDE, nonaBDE, and decaBDE homologues present in the c-OctaBDE mixture are not listed. These highly brominated PBDEs, however, can be degraded to POP-PBDEs by debromination (UNEP 2010<sup>44</sup>). Therefore although c-DecaBDE<sup>45</sup> has not been found to contain POP-PBDEs, it can form POP-PBDEs by debromination during its life cycle, thus, representing an important reservoir of POP-PBDEs (UNEP 2010c). Furthermore DecaBDE has been assessed by the POPs Review Committee and is recommended for listing at COP8 (UNEP 2017<sup>46</sup>).



**Figure 4-1:** Structure of polybrominated diphenyl ethers (PBDEs)

<sup>42</sup> With the main congeners 2,2',4,4'- tetrabromodiphenyl ether (BDE-47 CAS No. 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) and other tetra- and pentaBDEs present in c-PBDE.

<sup>43</sup> With the main congeners 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154), 2,2',3,3',4,5',6-heptabromodiphenyl ether (BDE-175), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183) and other hexa- and heptabromodiphenyl ethers.

<sup>44</sup> UNEP (2010) Debromination of brominated flame retardants. 6th POPs Reviewing Committee meeting Geneva 11-15. October 2010 (UNEP/POPS/POPRC.6/INF/20).

<sup>45</sup> DecaBDE can degrade in thermal processes, environment processes and in biota to lower brominated PBDEs including POP-PBDEs (UNEP, 2010c). Other key degradation products are polybrominated dibenzofurans and, depending on conditions, polybrominated dibenzo-*p*-dioxins.

<sup>46</sup> Recommendation by the Persistent Organic Pollutants Review Committee to list decabromodiphenyl ether (commercial mixture, c-decaBDE) in Annex A to the Convention and draft text of the proposed amendment. UNEP/POPS/COP.8/13

**Table 4-1:** Composition of c-PentaBDE\* (derived from La Guardia et al. 2006; SFT 2009; Schlummer et al. 2011)

Categories of PBDE	Tribromodiphenyl ethers		Tetrabromodiphenyl ethers	Pentabromodiphenyl ethers		Hexabromodiphenyl ethers		Heptabromodiphenyl ethers
Congener	BDE-17	BDE-28	BDE-47	BDE-99	BDE-100/85	BDE-153	BDE-154	BDE-183
Content	Traces	Traces	Major	Major	Minor	Minor	Traces	Traces
Distribution for calculations*	0.5%**		<b>33%***</b>	<b>58%***</b>		<b>8%***</b>		<b>0.5%***</b>

\*The homologue distribution in commercial PBDEs has a variation depending on producer or production lot.

\*\*TriBDEs are not listed as POPs.

\*\*\*The percentage of the PBDE homologues that are POP-PBDEs.

**Table 4-2:** Composition of c-OctaBDE\* (derived from La Guardia, 2006; SFT, 2009; Schlummer 2011)

Categories of PBDE	Hexabromodiphenyl ethers		Heptabromodiphenyl ethers			Octabromodiphenyl ethers			Nonabromodiphenyl ethers		Decabromodiphenyl ethers
Congener	BDE-154	BDE-153	BDE-183	BDE-180	BDE-171	BDE-197	BDE-203	BDE-196	BDE-206	BDE-207	BDE-209
Content	Traces	Minor	Major	Traces	Traces	Major	Minor	Minor	Minor	Minor	Traces
Distribution for calculations*	<b>11%***</b>		<b>43%***</b>			35%**			10% **		1%**

\*The homologue distribution in commercial PBDE has a variation depending on producer or production lot.

\*\*OctaBDE, nonaBDE and decaBDE are not listed as POPs.

\*\*\*The percentage of the PBDE homologues that are POP-PBDEs.

The production of POP-PBDE containing PBDE mixtures - c-PentaBDE and c-OctaBDE) has stopped in 2004<sup>47</sup>. Therefore, the specific issue of POP-PBDEs is their presence in articles in use and second-hand articles. Since POP-PBDEs are also present in certain recycling flows (WEEE plastic and polyurethane foam) products manufactured from these polymers resulting from recycling can become POP-PBDEs contaminated (see Annex 1-B and Annex 3-B).

#### 4.1.2 PBBs listed in the Stockholm Convention

Hexabromobiphenyl (HBB) is listed in Annex A without exemption. The major congeners of commercial HBB (FireMaster FF - 1) were largely 2,2',4,4',5,5'-hexabromobiphenyl (PBB 153), accounting for 50 - 60% of the total mass, followed by 2,2',3,4,4',5,5'-heptabromobiphenyl (PBB 180; 10-15%), and 2,2',3,4,4',5'-hexabromobiphenyl (PBB 138; 5-10%) (Pijnenburg et al.,

<sup>47</sup> With some uncertainty for possible production in China

1995)<sup>48</sup>. Also DecaBB has been produced and used as flame retardant but is not listed in the Stockholm Convention.

#### 4.1.3 HBCD

Hexabromocyclododecane (HBCD) is listed in Annex A with an exemption for production and use in insulation foam (Expanded polystyrene and extruded polystyrene) in buildings. 1,2,5,6,9,10-HBCD has six stereogenic centers and, in theory, 16 stereoisomers could be formed (Heeb et al. 2005)<sup>49</sup>. However, in commercial HBCD only three of the stereoisomers are commonly detected. Depending on the manufacturer and the production method used, technical HBCD consists of 70-95 %  $\gamma$ -HBCD and 3-30 % of  $\alpha$ - and  $\beta$ -HBCD (European Commission 2008)<sup>50</sup>. Two other stereoisomers ( $\delta$ -HBCD and  $\epsilon$ -HBCD) have also been found by Heeb et al. (2005)<sup>49</sup> in commercial HBCD in concentrations of 0.5 % and 0.3 %, respectively.

### 4.2 Products and articles possibly containing POP-PBDEs, PBB and HBCD

A list of potentially POP-PBDE containing articles and materials are listed in Annex 1-B. If a study on the presence of POP-PBDE containing materials is planned, this list can be assessed for possible relevant samples for the country. Case studies on monitoring of POP-PBDEs in articles and products are compiled in Annex 3-B

HBB has been used in the same applications, however, only approx. 5000 tonnes have been produced and used in the 1970s and have to a large extent been landfilled or incinerated. Therefore HBB is not specifically addressed in the sampling, but articles sampled/assessed for POP-PBDEs might be analysed for HBB if required.

A list of potentially HBCD containing articles and materials are listed in Annex 1-C. If a study on the presence of HBCD containing materials is planned, this list can be assessed for sample types. Case studies on monitoring HBCD in articles/products are compiled in Annex 3-C.

### 4.3 Step by step approach for POP-BFRs monitoring in products and articles

To determine the occurrence and quantities of POP-BFRs in different articles, products and materials, representative samples can be purchased from retail outlets, consumer products in use, second hand markets, in end of life phase or from recycling plants (e.g. polymers from WEEE recycling plants) (see Annex 1-B).

#### Step 1: Survey of products and articles possibly containing POP-BFRs

Before collecting samples, a survey would be conducted to preliminarily determine relevant products and articles in use or end of life that might contain POP-BFRs.

A list of major uses and related articles and products containing POP-PBDEs are described in Annex 1-B and include plastic in electronics, polyurethane (PUR) foam products (e.g. furniture, vehicles) and textiles (Annex 1-B).

A list of major uses and related articles and products containing HBCD are described in Annex 1-C and include extruded and expanded polystyrene (XPS/EPS) in buildings and construction, minor use in EPS packaging and in textiles and some other minor uses (Annex 1-C).

<sup>48</sup> Pijnenburg AMC, Everts JW, de Boer J, Boon JP. (1995) Polybrominated biphenyl and diphenylether flame retardants: Analysis, toxicity, and environmental occurrence. *Reviews of Environmental Contamination and Toxicology* 141, 1-26.

<sup>49</sup> Heeb NV, Schweizer WB, Kohler M, Gerecke AC. (2005) Structure elucidation of hexabromocyclododecanes - a class of compounds with a complex stereochemistry. *Chemosphere* 61: 65-73.

<sup>50</sup> European Commission. (2008). Risk Assessment: Hexabromocyclododecane CAS-No.: 25637-99-4 EINECS No.: 247-148-4, Final Report May 2008. Luxembourg

Also some materials known to possibly contain POP-PBDEs or HBCD and further used in recycling (e.g. plastic from WEEE recycling or polyurethane (PUR) or polystyrene foams from different end-of-life products) would be targeted. Stakeholders for the different articles and products would be contacted for support and information input and possibly for providing samples.

### Step 2: Sample collection

Samples can be collected e.g. by the customs at the import or by relevant authorities such as factory control or consumer protection authorities and related institutions. Sampling campaigns might also be conducted by research institutions possibly in collaboration with the ministry or other relevant authorities or directly with the industry or waste management facilities.

Following criteria and information can be used by stakeholders:

- a) The article or product is listed in Annex 1-B (for POP-PBDEs) or Annex 1-C (for HBCD) and contains brominated flame retardants (e.g. the plastic of a computer is labelled as containing brominated flame retardants; the EPS/XPS is marked as containing HBCD).
- b) The article or product is listed in Annex 1-B (for POP-PBDEs) or Annex 1-C (for HBCD) and bromine is being detected by a bromine screening method (see Chapter 4.4.).

Currently there is no standardized method for sampling of HBCD in articles such as foams in buildings or packaging materials, furniture or textiles.

For WEEE a sampling method is described in the Technical Specification TS 50625-3-1: Collection, logistics & treatment requirements for WEEE -- Part 3-1: Specification for depollution – General.

For EEE and WEEE plastic - the major POP-PBDEs contaminated products and material - a detailed sampling methodology and a sampling protocol has been developed and is described in detail in Annexes of [Wäger et al. \(2010\)](#)<sup>51</sup>. This sampling strategy and protocol can be applied (in a modified way) in other countries and regions having shredder plants with related WEEE plastic shredder fractions.

An approach of sampling of single EEE for screening of POP-PBDEs in e.g. Cathode Ray Tube casings of TV and PC is shortly described in Annex 3-B.

### Step 3: Optional (further) screening in the laboratory

Sample articles can be screened for the presence of bromine also in the laboratory where a more sensitive method might be available compared to the mobile equipment used in the field.

Rapid screening methods such as pyrolysis-GC/MS can be used for verifying the presence of POP-BFRs (and other BFRs types). Care has to be taken that by such methods present DecaBDE is not debrominated to lower brominated POP-PBDEs, which would lead to false positive results. Also HBCD is sensitive to degradation and individual methods need to be validated.

Recently a simple wipe test have been developed where respective samples were treated with a pre-cleaned filter paper folded into quarters and wetted with isopropanol and then firmly wiped in concentric circles towards the middle of the area.<sup>52</sup> Rinsing this filter paper resulted in determination of BFRs present even in a semi-quantitative manner<sup>52</sup>.

<sup>51</sup> Wäger P, Schluep M, Müller E. (2010) RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. [Final Report](#) September 17, 2010.

<sup>52</sup> Gallen C, Banks A, Brandsma S, Baduel C, Thai P, Eaglesham G, Heffernan A, Leonards P, Bainton P, Mueller JF.(2014) Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. *Sci Total Environ.* 491-492:255-265.

When screening methods are applied it has to be ensured that the detection limit of the screening method is more sensitive than (below) the limit required for the screening (e.g. required from a certain legislation limit).

#### Step 4: Quantification

Different analytical methods that can be applied for the instrumental quantification of POP-PBDEs and HBCD have been described or reviewed<sup>53,54</sup>. One accredited method used for commercial analysis for PBDEs is described in Annex 2-A and for HBCD in Annex 2-G. Further methods are described in the listed case studies below.

The extraction and clean-up of selected samples are described below.

### 4.4 Screening methods for bromine as indication for POP-BFRs

The screening of bromine can be a simple, rapid and cost-effective method for pre-selection steps of samples to determine which samples to select for the more complex and expensive confirmation analysis of POP-PBDEs, PBB or HBCD (see 4.6).

A range of technologies can be applied for screening bromine in materials like plastics, expanded or extruded polystyrene foams (EPS/XPS), polyurethane foams, textile or rubber. Technologies used include X-ray fluorescence (XRF), Sliding Spark Spectroscopy (Seidel et al. 1993), X-ray transmission (XRT) or Laser-Induced Breakdown Spectrometry (LIBS)<sup>55</sup>. Not every screening method is suitable for each type of material.

Two of these technologies have been approved for BFR screening capability in long term trials for separation of bromine containing polymers (WRAP 2006, Table 4-3)<sup>56</sup> and can be used for the screening of bromine in consumer goods in the field or in recycling plants (see also POP-PBDEs BAT/BEP Guidelines<sup>Error! Bookmark not defined.</sup>).

- X-ray fluorescence (XRF);
- Sliding spark spectroscopy.

Other technologies capable for bromine screening but not practical for a simple screening approach, are for example:

- Neutron activation analysis;
- X-ray transmission (XRT).

The technologies are shortly described below.

#### 4.4.1 X-ray fluorescence (XRF) (Table 4-3)

The X-ray fluorescence (XRF) technology can be used for detection of bromine in polymers and other materials with a detection limit for bromine of 10 to 100 ppm. XRF analysis is limited to the detection of bromine in the material, without any capacity to identify the type of BFR compound.

Using XRF handheld instruments for the analysis of EPS and XPS foams including wastes will take some 10 seconds to gain a quick reading and up to one minute for a standard deviation of less than 10%.

<sup>53</sup> Covaci A, Voorspoels S, Ramos, L, Neels H, Blust R (2007). Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *Journal of Chromatography A* 1153: 145-171

<sup>54</sup> Schlummer M, Brandl F, Mäurer A, van Eldik R. (2005) Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. *J Chromatogr. A*. 1064, 39-51.

<sup>55</sup> Stepputat M, Noll R (2003) On-Line Detection of Heavy Metals and Brominated Flame Retardants in Technical Polymers with Laser-Induced Breakdown Spectrometry," *Appl. Opt.* 42, 6210-6220.

<sup>56</sup> WRAP (2006) Develop a process to separate brominated flame retardants from WEEE plastics Final Report Project code: PLA- 037 November 2006. Banbury, Waste Resources Action Program.



Care has to be taken with the screening methods in case the plastic or other materials are coated. Then the coatings may need to be removed by scratching. In addition, dirt should be removed for an optimized screening. If a sample is heterogeneous (e.g. WEEE with different plastic parts) then the different parts need to be screened.

XRF is a non-destructive method and can, therefore, be used to screen articles in stores or currently in use without damaging them.

The use of XRF instrument requires a specific instruction for the operator of handling such materials according to national guidelines. XRF with different X-ray source are available. Some of the XRF systems use a  $^{63}\text{Ni}$  X-ray source and therefore a radioactive element. These equipment require special waste management at the end of the product's lifetime. Also non-radioactive instruments need careful operation and the personal using the equipment needs to be trained for the specific equipment used. Some of the systems commercially available are :

- [Thermo Scientific Niton;](#)
- [Olympus;](#)
- [Bruker;](#)
- [Analyticon;](#)
- Other providers.

The use area of these XRF instruments is much broader than bromine and chlorine screening. Such instruments can, for example, be used for screening of heavy metals and other elements in consumer goods or contaminated soils. The cost of an instrument is approximately USD 30,000 to USD 50,000.

There are cheaper XRF equipment on the market with reduced functionality for e.g. specifically monitoring of RoHS compliance. These equipment can be used for screening of bromine and might be sufficient for this purpose.

#### 4.4.2 Sliding spark spectroscopy (Table 4-3)<sup>57</sup>

Sliding spark spectroscopy is a surface screening method capable to rapidly detect bromine, chlorine, fluorine and inorganic additives at concentration down to approximately 0.1%. With a comparatively simple system, sliding spark spectroscopy allows direct in-situ analysis of hard, compact non-conductive material without prior sample preparation. Using handheld instruments the time requirement for a measurement lies within seconds.

Care has to be taken with screening methods if the plastic is coated. Then the coatings need to be removed by scratching. Dirt should also be removed for an optimized screening. If a sample is heterogeneous (e.g. WEEE with different plastic parts) then the different parts need to be screened.

Sliding Spark Spectroscopy is a destructive method in a sense that the measurement results in a burn spot from the spark. Therefore the articles to screen must be purchased.

The basic principle of the method is the thermal vaporization, ionization and excitation of a small amount of surface substrate using a train of high-current sliding sparks. The material components in the spark plasma are activated to emit radiation. From the atomic spectrum, information on the composition and the element concentration in the sample can be obtained.

Intense optical emission is observed when positionally stable high-current surface sparks (max. 800 Ampere/pulse) are sliding over compact non-conductive materials such as plastics, glasses, quartz filters or powder pellets. Substrate vaporization, ionization and excitation processes in the surface discharge plasma channel generate emission corresponding to neutral and ionic states. The spectra are essentially composed of lines emitted by the electrode material (e.g. copper and silver), from the substrate under investigation, radiation continuum as well as structured background from the surrounding air. Proper software treatment of the detected

<sup>57</sup> Seidel T, Golloch A, Beerwald H, Böhm G (1993) Sliding spark spectroscopy. *Fresenius' Journal of Analytical Chemistry* 347, 92-102.



spectra allows the rapid multi-element screening of the investigated material. Thus, identification of bromine containing materials and inorganic additives (BFRs, fillers, stabilizers, BFR synergists) or chlorine containing plastics (PVC or chlorinated flame retardants), has been described (Schlummer and Mäurer 2006)<sup>58</sup>. The instrument costs approximately USD 6,000.

#### 4.4.3 Neutron activation analysis

The neutron activation analysis (NAA) is a radiochemical multi-element analysis described as a “*supreme technique*” for elemental analysis. NAA is a sensitive multi-element analytical technique used for qualitative and quantitative analysis of major, minor, trace and rare elements. The method can be applied for the determination of bromine content in plastic; it was used for the Swiss market survey of BFR in products in 2004 and as validation method in the 2009 survey<sup>59</sup>. This technique can only be applied in laboratory. The instruments can be expensive and of limited practicability as nuclear expertise is required.

#### 4.4.4 X-ray transmission technology XRT

The XRT is non-mobile equipment applied in dismantling plants to sort scrap plastic by automatically monitoring the atomic density of materials. Therefore the instrument is not useful for screening for bromine in consumer goods.

**Table 4-3:** Comparison of hand held methods for screening of BFR containing plastic (WRAP 2006 with modifications).

Type:	X-Ray Fluorescence	Sliding Spark spectral analysis
Prime Function	Detect and quantify additives	Detect + quantify bromine and chlorine
Method of operation	Low power X-ray penetrates ~10mm into sample, detector measures distinct energy peaks from fluorescence of a range of elements to give ID and % concentration of additives	High voltage spark on surface creates plasma of vaporised material. Light spectra analysed for know peaks at Br and Cl wavelength to estimate % concentration
Weight approx	1.7 kg	0.75 kg (gun)
Portability	Excellent – battery powered, no cables	Reasonable – light to carry, but needs mains power.
Ruggedness	Excellent – built for on-site use in scrap-yards	Good – but care needed for fibre optic cable
Start-up speed	OK – 2-3 min's	Fast - < 1min
Operator manual	Good	Very good
Ergonomics	Easy – but careful to point away from user	Easy – but low flex cable to gun
Sample presentation & speed	Easy – hold gun on sample for 15 – 30 seconds	Very easy – 1 second to ‘fire’ spark
Read-out	OK – need to interpret ppm numbers on screen	Simple & clear
Adjustment	Not a problem	Easy to adjust base level reading to remove noise. Simple sensor cleaning method
Sample preparation	Thicker samples better (> 5 mm). Will detect surface contamination & coatings. Good for granular plastics	Clean surface required and flat area for good spark contact. Will detect dirt and coatings on surface

<sup>58</sup> Schlummer M, Maurer A (2006) Recycling of styrene polymers from shredded screen housings containing brominated flame retardants. Journal of Applied Polymer Science 102, 1262-1273.

<sup>59</sup> Bantelmann E., Ammann A, Näf U, Tremp J (2010) Brominated flame retardants in products: Results of the Swiss market survey 2008 - pre-publication. Proceedings of the 5th International Symposium on Brominated Flame Retardants. April 7-9 2010, . Kyoto, Japan.

Type:	X-Ray Fluorescence	Sliding Spark spectral analysis
Accuracy	Very good – ppm levels of elements	Sufficient – to nearest 1% on Br/Cl concentration.
Repeatability	Excellent	Good – some noise around 0-1% level
Reliability	Very good	Very good
Speed	5-30 seconds	Fast – 1 second
User confidence	Good on primary elements, lower on chlorine.	High – except < 1% concentration level.
Price	Approx. USD 30000 - 50,000; cheaper if e.g. only RoHS elements are tested	Approx. USD 6,000
Operator skill level required	Technical operator to interpret results	Factory operator with basic training

#### 4.4.5 Screening of Bromine by combustion-ion chromatography

The standard “IEC 62321-3-2 Ed.1 - Determination of certain substances in electrotechnical products” has as Part 3-2 the “Screening of total bromine in electric and electronic products by combustion-ion chromatography (C-IC)”. While this technology is not a mobile screening method it seems a reliable method for the determination of bromine in polymers.

### 4.5 Sample preparation, extraction and clean-up

Key matrices of POP-PBDEs in articles are (see POP-PBDEs BAT/BEP Guidance):

- Flame retarded plastic of electronics (e.g. ABS, HIPS, PP);
- Flexible polyurethane foam (furniture, vehicle seating, mattresses), and rigid polyurethane foam (in construction).

Other materials with less use were textiles, rubber or drilling oils.

#### 4.5.1 Preparation of polymer/plastic samples

The most relevant matrix for monitoring POP-BFRs in articles is plastic/polymer samples. Some BFRs have been specifically used in individual polymers. E.g. 90% of c-OctaBDE has been used in ABS plastic and more than 90% of HBCD has been used in polystyrene (EPS, XPS and HIPS). The largest share of c-PentaBDE has been used in polyurethane.

#### Preparation of samples – international standard

An international standard for sample preparation has been developed and published for electronical and electronic equipment (IEC 62321-2:2013). The standard describes disassembly, disjointment and mechanical sample preparation of EEE/WEEE. The mechanical sample preparation describes the procedures for manual cutting, coarse and fine grinding/milling and homogenizing materials and the related recommended apparatus and equipment.

#### Preparation of single polymer samples

In case of analysis of single polymer item (plastic from a computer, TV set, plastic toy or insulation) no further pre-treatment of the plastic is necessary, if for the extraction the below described dissolution/precipitation approach is chosen.

For other extraction methods single items have to be ground by a suitable mill, preferably using liquid nitrogen. Grinding methods could be evaluated for debromination of PBDE/BFRs and the formation potential of polybrominated dibenzofurans (PBDFs) from PBDEs.

#### Preparation of mixed polymer samples

In case the average POP-BFRs content of mixed WEEE plastic needs to be determined, a careful grinding and homogenisation processes is required to gain a laboratory sample suitable to reflect a bulk sample of several kg to tonnes. This process has to be performed stepwise (50 kg out of a tonne, 1 kg out of 50 kg, 50 g out of 1 kg, 1 g out of 50 g). With decreasing sample size, decreasing particle sizes are recommended, ending up with < 500 µm for the final sample.

Each grinding step should be performed with suitable mills and sieve sizes. The final particle size < 500 µm is recommended for the subsequent solid liquid extraction. The smaller the particle size the more effective is the extraction, especially when polar extraction solvents are chosen, which do not dissolve for example polystyrene based polymers that are frequently a major share in WEEE plastic fractions.

#### 4.5.2 Extraction of POP-BFRs from polymers

A reliable analysis of POP-BFRs in polymers requires an efficient sample extraction process of the additives from the matrix. Extraction is the term given to the process of isolating specific compounds from a bulk matrix. For the determination of additive BFRs in polymeric materials, solvent extraction plays an important role in the overall procedure.

There are two main approaches for extracting POP-BFRs from polymers: A) solid-liquid extraction and B) dissolution/precipitation. The solid-liquid approach extracts PBDE and BFR from ground solid plastics and is applicable, when there is no or only a minor dissolution of solvent and polymer, since partly dissolved polymers contaminate the GC-MS system (if not completely removed in the clean-up).

The dissolution/precipitation approach dissolves both, polymeric matrix and POP-BFRs and the dissolved polymer is removed in a second precipitation step (see below). Dissolution of plastics is described in further detail by Braun (1999).<sup>60</sup>

Since there is no unique solvent to dissolve all polymers in WEEE plastics, the solid-liquid approach is favourable for mixed WEEE plastic fractions, whereas the latter is suitable for polystyrene based WEEE fractions (a major fraction of WEEE plastics) or analysis of single housings of a specific electronic equipment.

##### **Solid-liquid extraction**

Solid liquid extraction is the most commonly used method in trace analysis. The compounds of interest are isolated using a range of procedures, such as vigorous shaking, ultrasonication, Soxhlet extraction and microwave-assisted or pressurized liquid extraction (PLE, e.g. accelerated solvent extraction). Note that light and elevated temperatures created during ultrasonication, microwave-assisted extraction or PLE might cause unintended PBDE or HBCD degradation or isomerisation.

Best recoveries are obtained by Soxhlet extraction applying solvent mixtures like methanol or 1-Propanol with up to 25% of a non-polar solvent like toluene. The extraction time depends on the applied Soxhlet apparatus, but should allow for at least 30 extraction cycles. The Soxhlet extraction is also recommended for other matrices not discussed here (PUR foam, textiles and rubber) with appropriate grinding.

Alternatively PLE with isooctane can be employed in the analysis of PBDE/BFR for WEEE plastic, other plastic items or polyurethane foams. At 100°C three static extraction cycles of 45 minutes each are recommended. However, if there is a considerable amount of polyolefins in the respective WEEE fraction, addition of at least 20% of alcohol (e.g. 1-Propanol) to the extract is required.

##### **Extraction of POP-BFRs by “Dissolution and Precipitation” method**

<sup>60</sup> Dietrich Braun, Simple methods for identification of plastics, 4th ed., 1999, Carl Hanser Verlag, München, Germany.

One effective approach for extraction of POP-BFRs from the polymer is the complete dissolution of the polymer in an appropriate solvent. Selecting a solvent capable of dissolving the polymer at room temperature is most desirable, since elevated temperatures may result in thermal stress that might cause PBDE/BFR degradation. This approach yields good recovery efficiency for the respective BFR. For some polymer types (e.g. polyurethane), however, suitable solvating solvents are not available. Chromatography issues related to system entrapment of the resin and other matrix compounds may also be problematic following a complete polymer dissolution approach. Such entrapment can result in poor chromatographic resolution, hindering the correct detection and identification of compounds and necessitating increased maintenance of the GC–MS system. Adding a second “non-solvent” to the extract to precipitate the interfering components (e.g. resin) can be a useful additional step. Ideally, the polymer and other interfering additives (plasticizers, dye stuffs, etc.) are precipitated and the target analytes remain quantitatively in the extract. This method can, however, also generate analyte losses either via target analyte adsorption in the precipitate, or if the solubility of the target analyte is affected negatively by the non-solvent. Pöhlein and co-workers (2005) also developed two methods to identify and quantify BFRs in styrenic polymers.

The extraction of POP-PBDEs, HBB or HBCD and other brominated flame retardants from the polymers most relevant for POP-BFRs (ABS, PS, ABS/PC blend, PPE/PS blends, PVC,) is performed by dissolution with tetrahydrofuran and precipitation is done with either ethanol (Schlummer et al. 2006)<sup>61</sup>, 1-propanol (Schlummer et al. 2007)<sup>62</sup> or *n*-hexane<sup>63</sup> (Sindikü et al. 2014)<sup>64</sup>. This approach yields high extraction efficiency and short extraction time.

The extraction steps for ABS, PS, PVC, ABS/PC blend, PPE/PS blends are given below:

- 0.5 grams of the plastic samples are weighed into a well-labelled extraction glass vial covered with alumina foil paper. Dark-brown glass vial are recommendable.
- 5 ml of tetrahydrofuran (THF) is added.
- The glass vial is tightly capped and placed on a shaker for two hours.
- After complete dissolution of the polymer sample, 6 – 12 ml of *n*-heptane is added stepwise with rigorous shaking until a good precipitate is formed.
- The glass vial is capped and placed on the shaker for 15 minutes until a clear solution is obtained.
- The glass vial is then allowed to stand for another 15 minutes.
- The extract is then decanted into a well-labelled, pre-weighed collection glass vial covered with alumina foil paper.
- The precipitate is re-dissolved in 5 ml THF and placed on the shaker for 15 minutes.
- Another 6 – 12 ml of *n*-heptane is added stepwise with rigorous shaking and the vial is placed on the shaker for 15 minutes.
- The extract is decanted into the glass vial.
- The entire procedure is repeated thrice.
- The weight of the extract is calculated from the difference between weight of glass vial plus extract and the weight of the bottle.
- The residual polymer is removed from the glass vial and kept in foil paper.

<sup>61</sup> Schlummer M, Mäurer A, Leitner T, Spruzina W (2006) Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE). Waste Management Research 24, 573-583.

<sup>62</sup> Schlummer M, Gruber L, Mäurer A, Wolz G, van Eldik R (2007) Characterisation of polymer fractions from waste electrical and electronic equipment (WEEE) and implications for waste management. Chemosphere 67, 1866–1876.

<sup>63</sup> *n*-hexane can be substituted by the less toxic *n*-heptane

<sup>64</sup> Sindikü O, Babayemi J, Osibanjo O, Schlummer M, Schlupe M, Watson A, Weber R (2014) Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in E-waste polymers in Nigeria. Environ Sci Pollut Res Int. DOI: 10.1007/s11356-014-3266-0

Also the standard analytical procedures with GC-FID developed by PlasticsEurope and Cefic use a dissolution and precipitation method<sup>65</sup>. The polystyrene sample including additives is dissolved in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and then cleaned by precipitation of the polymer through the slow addition of i-propanol (i-PrOH) under stirring. Subsequently an aliquot of the solution is injected and analyzed in the GC-FID system.<sup>65</sup> This dissolution/precipitation step has proven to be reliable by ensuring proper recovery levels of the analyte from the matrix.

***Extraction procedure for polypropylene samples:***

- 0.5 gram of the polymer sample is weighed into a well-labelled extraction glass vial.
- 30 grams of xylene solution is added.
- The glass vial is loosely corked and placed on the heating mantle for 1 hour at a temperature of 105 °C with a magnetic stirrer.
- After complete dissolution of the polymer sample, the glass vial is removed and allowed to cool to room temperature.
- 10 ml of acetone is added step wisely with little shaking until a gel-like precipitate is formed.
- The extract is then filtered using paper filter into a well-labelled, pre-weighed glass vial covered with alumina foil paper.
- The weight of the extract is calculated from the difference between weight of glass vial plus extract and the weight of the bottle.
- The residual polymer is removed from the filter paper and kept in foil paper.

Dissolution of other types of plastics is described in Braun (1999)<sup>66</sup>.

**Clean-up of the polymer/plastic extracts**

The easiest clean-up step consists of a filtration through a 0.45 µm filter disk (PTFE membrane) and the cleaned sample is placed in GC vials prior to chromatographic analysis. However, this approach removes only polymers and oligomers, which may have precipitated upon storage of extracts at lower temperatures.

Considerably better cleaning efficiencies can be reached by column chromatography. For non-polar extracts (isooctane), a Silica SPE column may be used (100-1000 mg) after pre-wash with n-heptane. The sample extracts are loaded on top of the SPE and the collection of target POP-BFRs starts directly with the sample loading. To complete the elution of the analytes another 10 ml n-heptane are added on top and collected after SPE passage.

If the analysis only targets POP-PBDEs, a sulfuric acid treatment is recommended. For this clean-up step a glass column with a diameter of 10 mm is filled with 1 g of neutral silica and 5 to 10 g of H<sub>2</sub>SO<sub>4</sub> impregnated silica (44% by weight). The column is pre-washed with 30 ml of n-heptane, before the sample extract is loaded. The collection of target POP-PBDE fraction starts directly with the sample loading. To complete the elution of the analytes, another 100 ml n-heptane are added on top and collected after passage of the column.

Before GC-MS analysis, the volumes of cleaned extracts are reduced to about 1-100 ml (depending on the expected concentrations in the sample) using a rotary evaporator.

**Gel permeation chromatography for extraction and clean-up**

<sup>65</sup> Cefic PlasticsEurope (2015) Determination of HBCD in Polystyrene Foams with the GC-FID Technique. 25th September 2015.

<http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/AdditionalGuidance/NIPsGuidance/CommentsonDecisionSC710/tabid/5545/ctl/Download/mid/16672/Default.aspx?id=2&ObjID=23306>

<sup>66</sup> Braun D (1999) Simple methods for identification of plastics, 4th ed. 1999, Carl Hanser Verlag, Munich, Germany



Gel permeation chromatography (GPC) provides an alternative separation approach, isolating flame retardants with molecular masses below 1000  $\mu$  from polymers with molecular masses larger than 10,000  $\mu$ <sup>67</sup>. However, this technique is also confined to polymers soluble in organic solvents. Since styrene based polymers cover most of the polymers containing POP-BFRs, GPC can be applied to most of the polymers in question (for the non-soluble PUR foam see below). Since GPC is an LC technique, an online coupling to HPLC systems is possible<sup>67</sup>.

#### 4.5.3 Extraction of POP-PBDEs in flexible and rigid polyurethane foam<sup>68</sup>

For extraction of POP-PBDE from polyurethane, solid-liquid extraction is sufficient to achieve an excellent recovery of POP-PBDEs (Bergmann 2006)<sup>68</sup>. Soxhlet extraction with toluene was found most effective. After 2 hours extraction time, exhaustive extraction is achieved without detection of POP-PBDEs in extracted PUR foam.

#### 4.5.4 Extraction of HBCD from textiles

Kajiwar et al. (2009) compared different extraction methods for HBCD containing textiles: Soxhlet extraction (16 h) with dichloromethane (DCM) and toluene resulted in complete extraction of HBCD. Also ultrasonic extraction (1 h) with DCM resulted in complete extraction. Therefore common extraction methods available in most laboratories result in good extraction yields. However it needs to be highlighted that ultrasonic extraction (1 h) with toluene resulted in low efficiency of less than 5%.

Also Soxhlet extraction using toluene resulted in a slight increase of  $\alpha$ -HBCD and a slight reduction of  $\gamma$ -HBCD. Therefore it seems that  $\gamma$ -HBCD starts isomerization at the temperature at the boiling point of toluene (110.6°C) to some extent. Therefore care needs to be taken with Soxhlet and elevated temperature when the isomer ratio is targeted for specific interpretations and then other extraction methods/solvents than Soxhlet and toluene would be used.

#### 4.5.5 Specific considerations on quality assurance

Common procedures for the quality assurance of analysis of the respective POP are described in chapter 2 above. Specific measures for POP-BFRs (and other BFRs) include:

- measures to minimise exposure of samples to UV-light to avoid losses through degradation;
- all glass vials either covered with alumina foil paper or use of brown glassware;
- lamps in the laboratory to cover with UV-protective film.

### 4.6 Quantitative (and semi-quantitative) analysis

#### 4.6.1 Measurement standards for POP-PBDEs, other PBDEs and interfering BFRs

A measurement method for POP-PBDEs for Stockholm Convention purposes needs to cover the tetraBDEs, pentaBDEs, hexaBDEs and heptaBDEs (major congeners of commercial mixtures are listed in Annex 2-1). The higher brominated homologues (octaBDE, nonaBDE and decaBDE) are currently not considered POP-PBDEs but might be analysed together with POP-PBDEs, in particular when considering that DecaBDE is recommended for listing as POP at COP8 in 2017.

<sup>67</sup> Schlummer M, Brandl F, Mäurer A, van Eldik R. (2005) Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. J Chromatogr A. 1064, 39-51.

<sup>68</sup> Bergmann M (2006) Bestimmung polybromierter Diphenylether in Kunststoffen und Untersuchungen zum Emissionsverhalten. PhD, Technical University Berlin.



## POP-PBDEs standards and interfering BFRs

For the quantification of POP-PBDEs in articles normally external standardization is used. In the standard approach of Fraunhofer Institute, which has been working on recycling of WEEE polymers since a decade ago (Schlummer et al. 2006)<sup>69</sup>, the following PBDE and BFR standards are used for monitoring of POP-PBDEs and other relevant BFRs<sup>70</sup>: major c-OctaBDE congeners (see Figure 4-1), decaBDE, 3,3',5,5'-tetrabromobisphenol A (TBBPA) and tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPE). These standards are recommended depending on the column used; BFRs can co-elute with POP-PBDEs and therefore need to be considered. These main BFR could also be evaluated (possibly determined) to be able to describe the correct peaks in particular when using ECD detectors used preferably in developing countries. The BFRs standard solution is also used to check the chromatographic separation and that other major BFRs do not co-elute with POP-PBDEs (relevant in particular when using ECD technique). In Figure 4-1 the chromatograms of WEEE plastics are shown containing mixtures of flame retardants including POP-PBDEs. On the column used the TBBPA co-elutes with POP-PBDEs 153. Stock solutions of individual standards are prepared by weighing and dissolving the crystalline solids into THF. The concentration of each BFRs standard is approximately 1000 ppm. Working solutions are prepared directly before use by diluting the standard to 5 concentrations between 1 and 100 ppm. A mixture of BFR standards is dissolved together in appropriate portion of THF and *n*-heptane. For Stockholm Convention purposes another calibration range might have to be used if a different 'low POPs' limit would be established from the 1000 mg/kg limit used for RoHS<sup>71</sup>. Currently the Basel guideline includes 1000 mg/kg and 50 mg/kg as low POPs limit.

Also <sup>13</sup>C-labelled PBDE standards are available for quantification by isotope dilution method by different standard suppliers (e.g. Cambridge Isotope Laboratories or Wellington Laboratories).

Also mono- and difluorinated PBDEs are available as analytical standards (F-PBDE®) from Chiron AS. Like C<sup>13</sup>-PBDEs they are closely similar to the parent PBDEs in terms of physico-chemical properties, and are good internal or surrogate standards for GC-MS, GC-ECD, GC-FID and two dimensional GC. Fluorinated PBDE standards are cheaper than the <sup>13</sup>C isotopes. They can be used with GC-ECD detection while <sup>13</sup>C-labelled standards cannot since they coelute with the native standard.

The standards need to be stored under exclusion of lights to prevent photolytic transformation.

### 4.6.2 Instrumental analysis of POP-PBDEs and HBB

#### Separation techniques

The state-of-the-art analytical technique for analysis of POP-PBDEs listed in the Stockholm Convention (tetraBDE to heptaBDE) and for HBB are chromatographic techniques.<sup>72</sup>

As chromatographic technique gas chromatography (GC) is normally used for POP-PBDEs and HBB (see e.g. IEC 62321-6)<sup>73</sup>. Liquid chromatography (LC, HPLC) has rarely been applied, particularly because of the lower separation efficiency. The international standard IEC 62321 describes in addition to GC/MS also a High Performance Liquid Chromatography method

<sup>69</sup> Schlummer M, Maurer A, Leitner T, Spruzina W (2006) Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE). Waste Management Research 24, 573-583.

<sup>70</sup> Major flame retardants should be included in the standard to ensure that BFRs are separated from POP-PBDEs especially when ECD detector is used. Also for the recycling of polymers it is important to know what BFR restricted by RoHS regulation are present. Therefore major BFRs used in EEE polymers are included.

<sup>71</sup> The 0.1% RoHS limit is not based on risk considerations and is 20 times higher than the current provisional 'low POPs' limit for POP pesticides and PCBs.

<sup>72</sup> Covaci A, Voorspoels S, de Boer J (2003) Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers in environmental and human samples - a review. Environ Int 29, 735-756.

<sup>73</sup> International Electrotechnical Commission (2015) IEC 62321-6:2015 Determination of certain substances in electrotechnical products - Part 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography -mass spectrometry (GC-MS)

coupled to Ultra Violet detection (HPLC/UV). GC separation is normally performed on a non-polar 10-30 meter GC column<sup>74</sup>. Injection temperature should be below 260°C or cold on-column injection should be applied, since higher temperature might lead to a degradation of DecaBDE and possibly lead to lower brominated PBDE artefacts. A validated method is described in Annex 2-A for POP-PBDEs and in Annex 2-B for HBB.

### **Detectors: Mass spectrometer, Electron Capture Detector**

Different detection technologies can be used for PBDEs/BFRs analysis. State of the art detection is mass spectrometry. Electron Capture Detector (ECD) is also suitable for analysing POP-PBDEs and has for the monitoring of POP-PBDE in articles and products the advantage of a higher robustness and simpler cleaning of the detector (Table 4-2). The advantages and drawbacks of the main utilized detection techniques are described in the Table 4-2.

As mentioned for the separation unit, it is also important that the detector temperatures are not too low (<300°C) in order to avoid sinks for DecaBDE but also not too high (>340°C) in order to avoid degradation. In conclusion, 330-340°C is recommended for ECD detector temperatures, and 320-330 for the detector side of the column. MS ion source temperatures however, are usually set below 280°C in order to increase the life time of the filaments.

### **PBDE detection with mass spectrometry**

Sensitive EI-MS analysis is performed in single ion reaction mode (e.g. single ion monitoring SIM mode), monitoring the 2 to 3 most abundant isotope clusters of the precursor (molecular) ions (for triBDE to pentaBDE isomers) and the 2 to 3 most abundant M-2 Br isotope clusters for (HexaBDE to DecaBDE). Normally at least 2-3 SIM windows are defined, sometimes SIM windows for each kind of homologues are built-up (see Annex 2-1).

For analysis of PBDE/BFR polymers low resolution mass spectrometry (LRMS)<sup>75</sup> is sensitive enough. Modern GC-EI-LRMS instruments are sensitive enough in the scan mode and can be run with a scan from 400-1000 m/z.

Electron capture negative ionisation (ECNI) coupled to LRMS has been reported to provide better sensitivities for higher brominated PBDE ECNI produces mainly  $m/z=79/81$  (bromine isotopes), which is monitored in one window. The disadvantage of this technique is that the compounds peaks do no longer provide mass spectral information and peaks are allocated by retention times only (as for ECD). The second disadvantage is that <sup>13</sup>C-labelled internal standards cannot be applied due to the same retention time and masses used. ECNI has also the disadvantage that the ionization is highly dependent on the bromine substitution pattern, making quantification inaccurate when <sup>13</sup>C-labelled internal standards cannot be used for each individual analyte.

**Table 4-2:** Advantages and drawbacks of different detection techniques for PBDE/BFRs are highlighted in the table (Covaci et al., 2003 and 2007)<sup>76</sup>

Detection	Advantages	Drawbacks
ECD	purchase cost maintenance cost ease of use	fair sensitivity for BFRs instability of linear range very low selectivity
EI-LRMS	facilitates the use of labelled standards good selectivity	low sensitivity

<sup>74</sup> If also DecaBDE is to be monitored, shorter columns (preferably 15 meter) are normally used.

<sup>75</sup> The more sensitive and expensive HRMS requires highly trained and experienced lab personnel and is not necessary for this matrix.

<sup>76</sup> Covaci A, Voorspoels S, Ramos L, Neels H, Blust R (2007) Recent developments in the analysis of brominated flame retardants and brominated natural compounds. Journal of Chromatography A 1153, 145-171.

ECNI-LRMS	good sensitivity good selectivity for brominated compounds	frequent source maintenance required
EI-HRMS	good sensitivity very good selectivity	purchase cost maintenance cost difficult to use higher "down-time"

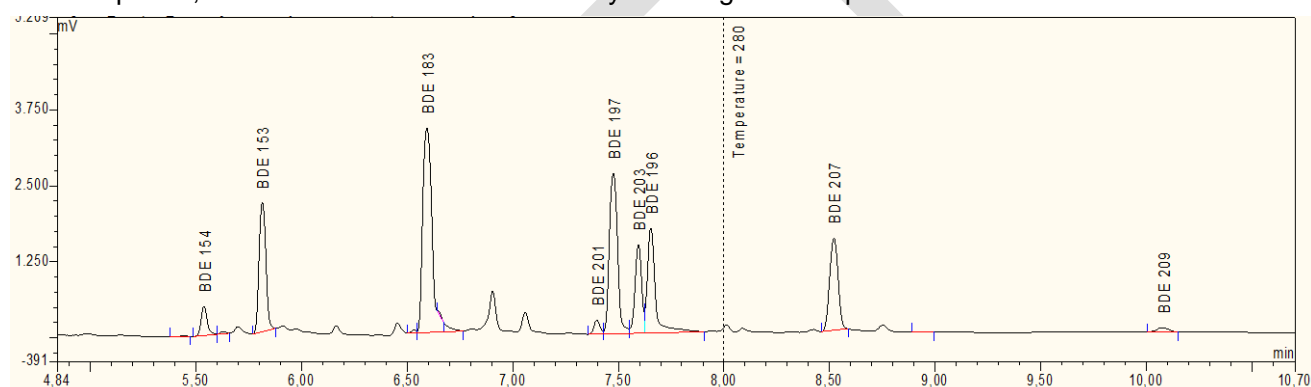
DRAFT

### PBDE analysis with Electron Capture Detector (ECD)

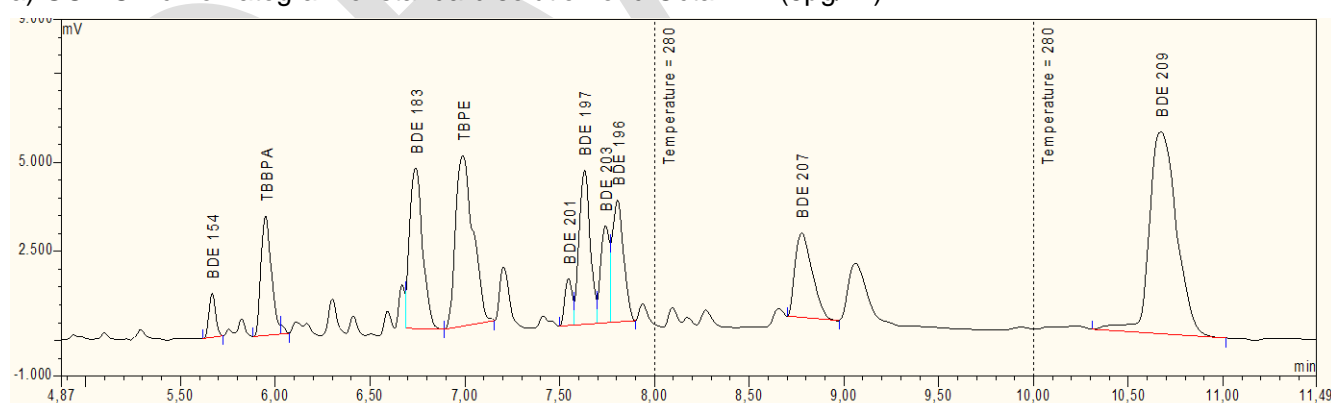
Electron Capture Detector (ECD) is an appropriate detector for brominated aromatic compounds. The advantage of the detector is the robustness, the relative low costs and the ease of use (see Table 4-2). The robustness of the detector and the slightly higher operation temperature is a particular advantage of the ECD detector when analysing “dirty” samples like polymers having often oligomers in the extracts.

However, since the peak in the ECD does not include structural information, only the retention time is used to determine the respective compound. Since PBDEs are present as mixtures in the polymers they have a specific fingerprint which can be used for confirmation. An interlaboratory comparison study revealed a good agreement of GC-ECD and various GC-MS techniques.<sup>77</sup>

The recognition and interpretation of chromatograms from ECD detector need some experience to determine POP-PBDEs in particular if BFR mixtures are present in recycled plastics (see examples in Figure 4-1 below). This might be more critical in future since the number of brominated flame retardants are increasing (according to the bromine industry there are approximately 75 BFRs on the market). In addition other heteroatoms with good electron capturing abilities, such as the chlorinated and fluorinated organic compounds can give high ECD response, which can interfere with the analysis and give false positives.

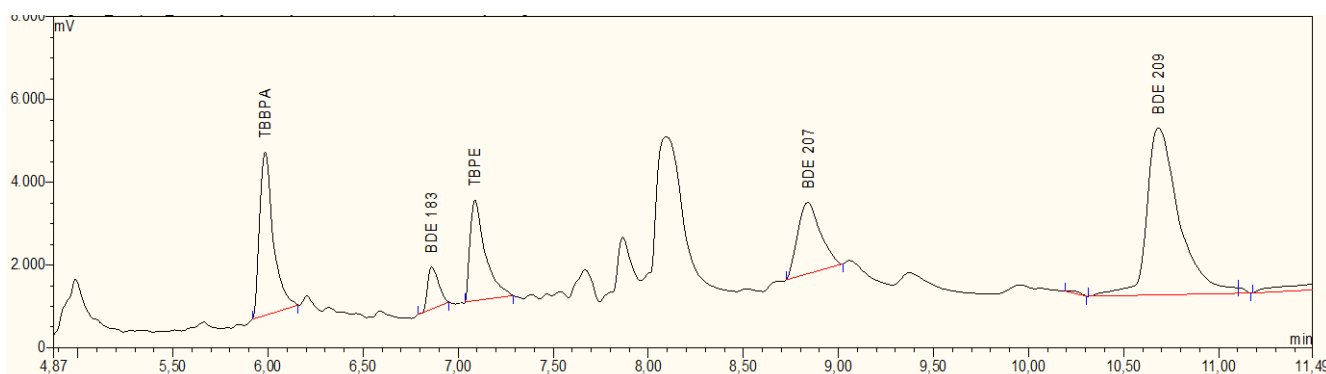


a) GC ECD chromatogram of standard solution of c-OctaBDE (5µg/ml)



b) GC-ECD chromatogram of a sample containing different BFRs including c-OctaBDE as a major BFR (Please note: TBPA co-elutes on this column with BDE 153)

<sup>77</sup> Zeleny R, Voorspoels S et al. (2010) Evaluation of the state-of-the-art measurement capabilities for selected PBDE and decaBB in plastic by the international intercomparison CCQM-P114. Analytical and Bioanalytical Chemistry 396, 1501-1511.



c) Sample containing different technical BFR including traces of c-OctaBDE

**Figure 4-1:** GC/ECD chromatograms of a) c-OctaBDE standard compared to two extracts from WEEE plastic (b) and c) with BFR mixtures including c-OctaBDE and other BFRs (GC separation was obtained with a Phenomenex Zebron™ ZB-5HT Inferno™ (15 m x 0.25 mm x 0.1 µm), temp. program: 140°C (1 min), 20 °C/min (280°C), 4 °C/min (300°C), 20 °C/min (320°C, 5 min)

#### 4.6.3 Example of a GC/MS setting for POP-PBDEs and HBB

The selected GC/MS conditions differ slightly between laboratories. Also different GC columns can be used. In Annex 2-A an example of GC/MS condition for the analysis of POP-PBDEs and in Annex 2-B for HBB are given along with the respective chromatograms. Also the exact masses for the MS settings are listed.

#### 4.6.4 International and national standards for PBDE analysis

##### International Standard for determination of regulated substances in electronics

An International Standard IEC 62321 ed.1<sup>78</sup> has been developed for “*Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)*”.

For the analysis of PBDE (monoBDE to decaBDE) and PBB (monoBB to decaBB) in plastics used for electrical products, standard IEC 62321-6 “*Determination of certain substances in electrotechnical products - Part 6: Determination of polybrominated biphenyls and polybrominated diphenyl ethers in polymers and electronics by GC-MS, IAMS and HPLC-UV*” has been developed. It includes three instrumental standard methodologies:

- Determination of PBB and PBDE in polymers by gas chromatography mass spectrometry (GC-MS);
- Determination of PBB and PBDE in polymers by ion attachment mass spectrometry (IAMS);
- Determination of PBB and PBDE in polymers by high-pressure liquid chromatography – Ultra violet detection (HPLC-UV);

The method has especially been optimized for the concentration range of 100 mg/kg and 1000 mg/kg due to the requirements of EU RoHS Directive compliance. The published IEC 62321-6 standard is only commercially available.

##### German national standard for determination of c-PentaBDE and c-OctaBDE in plastic materials in respect to the RoHS directive<sup>79</sup>

<sup>78</sup> International Electrotechnical Commission (2008). International Standard IEC 62321 Electrotechnical products -Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers). Edition 1.0 2008-12 (also adopted as EN 62321:2009), IEC Technical committee TC 111.

A standard method for determination of c-PentaBDE and c-OctaBDE in plastic materials in respect to the RoHS directive (Directive 2003/11/EC, Directive 76/769/EEC) has been developed on behalf of the German Environmental Agency (Kemmlein et al. 2005)<sup>79</sup>. The method includes extraction, clean-up and measurement procedures. The study has also validated the method for different polymers and assessed for reproducibility and repeatability. The compounds analysed in this method are however limited to certain PentaBDE (BDE85 (2,2',3,4,4'-pentaBDE), BDE99 (2,2',4,4',5-pentaBDE), BDE100 (2,2',4,4',6-pentaBDE)) and OctaBDE (BDE203 (2,2',3,4,4',5,5',6-octaBDE), BDE196 (2,2',3,3',4,4',5,6'-octaBDE), BDE197 (2,2',3,3',4,4',6,6'-OctaBDE)) since the current RoHS limit is defined for  $\Sigma$ PentaBDE and  $\Sigma$ OctaBDE with a limit of 0.1% each.

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<sup>79</sup> Kemmlein S, Bergmann M, Jann O (2005) Standard measurement method for the determination of polybrominated flame retardants (pentabromo diphenylether, octabromo diphenylether) in products Nr. 31/2005 UBAFBNr 000839/e.Förderkennzeichen 202 67 300, Umweltbundesamt.



### US EPA method 1614<sup>80</sup> for PBDE in water, soil, sediments and tissue

The US Environmental Protection Agency (USEPA) has developed a standard for the analysis of polybrominated diphenyl ethers in water soil, sediment and tissue by HRGC/HRMS ([US EPA method 1614](#))<sup>80</sup>.

The GC/MS analysis described in this standard available on the internet can also be used for the analysis of POP-PBDEs from articles and products after appropriate clean-up. One important consideration is the concentration range defined in the method. This range needs possibly to be adjusted by dilution of the sample.

#### 4.6.5 Interlaboratory comparison test for PBDE analysis in plastic

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC) of the European Commission operates the International Measurement Evaluation Programme® (IMEP). Within their interlaboratory comparisons (ILC's) they performed a proficiency test on PBDE analysis using PET spiked with PBDE and PBB<sup>81</sup>. The Interlaboratory comparison included the determination of total bromine, the total sum of polybrominated biphenyls (PBB), total sum of polybrominated diphenylethers (PBDEs) and several individual brominated diphenylethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209) in plastic. The study is available in the internet.<sup>81</sup>

#### 4.6.6 Instrumental analysis for HBCD

##### Separation techniques for HBCD

Both gas chromatography (GC) and liquid chromatography (LC) methods are used for the instrumental quantification of HBCD. However, the separation of the isomers is only possible with LC methods<sup>82</sup>.

##### Gas chromatography

Determination of individual HBCD diastereoisomers by GC is not feasible due to the thermal inter-conversion of HBCD isomers at 160°C. Total HBCD (i.e., the sum of all HBCD diastereoisomers) can be approx. determined with gas chromatography mass spectrometers (GC-MS). Since the three diastereoisomers have different response factors, the concentration of HBCD cannot be determined accurately by GC-MS<sup>83</sup>.

HBCD degrades at 240 °C, therefore there may be significant losses of HBCD during GC analysis. Any GC method needs to consider degradation in injection and on the column. Therefore the injection temperature and temperature program need to be carefully selected. Cold on-column injection, short GC columns, and thin, stationary films can minimize the degradation of HBCD<sup>84</sup>. When analysing for HBCD by GC-MS, the liner should be changed after each batch of samples to keep it as clean as possible. Co-elution of HBCD with certain PBDEs can also be a problem.<sup>84</sup>

<sup>80</sup> US EPA method 1614

[http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007\\_09\\_11\\_methods\\_method\\_1614.pdf](http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_09_11_methods_method_1614.pdf)

<sup>81</sup> Cordeiro F, Verbist I, Robouch P, Linsinger T, de la Calle B (2011) IMEP-26: Determination of Brominated Flame Retardants in Plastic. Interlaboratory Comparison Report. European Commission Joint Research Centre Institute for Reference Materials and Measurements. June 2011

<sup>82</sup> Frederiksen M., Vorkamp K., Bossi R., Svensmark B., Analysis of HBCD and TBBPA by GC-MS versus LC-MS-MS – indications of systematic differences in obtained results, 4th International Symposium On Flame Retardants BRF2007, Amsterdam, Netherlands 2007.

<sup>83</sup> de Boer J, Wells DE (2006) Pitfalls in the analysis of brominated flame retardants in environmental, human and food samples – including results of three international interlaboratory studies

<sup>84</sup> Webster L, Bersuder P, Tronczynski J, Vorkamp K, Lepom P (2009) Determination of hexabromocyclododecane (HBCD) in sediment and biota. ICES Tech. Mar. Environ. Sci. 44 (i), 1–14. [http://www.ices.dk/sites/pub/Publication%20Reports/Techniques%20in%20Marine%20Environmental%20Sciences%20\(TIMES\)/times44/091207-TIMES%2044%20FINAL3.pdf](http://www.ices.dk/sites/pub/Publication%20Reports/Techniques%20in%20Marine%20Environmental%20Sciences%20(TIMES)/times44/091207-TIMES%2044%20FINAL3.pdf)

Mainly non-polar columns are used, for example, HT-8, DB-5, and STX-500. Splitless, pulsed-splitless, programmed temperature vaporizer (PTV), and on-column injectors have been used for the determination of HBCD<sup>84</sup>. Automatic sample injection should be used if possible, to improve the reproducibility of injection and the precision of the overall method<sup>84</sup>.

### **Liquid chromatography**

A liquid chromatography (LC) method using a chiral HPLC column is required to separate the three diastereoisomers, with separation of enantiomers being possible. Liquid chromatography-mass spectrometers (LC-MS) and high performance liquid chromatography-mass spectrometers (HPLC-MS or HPLC-MS/MS).

It is recommended to use a reverse-phase column for analysis of HBCD by LC-MS.<sup>84</sup> The three diastereoisomers found in the technical mixture should separate easily using a column, such as a C18 and either methanol/water or acetonitrile/water, usually with ammonium acetate (10 mM) as the mobile phase and a gradient programme will be required.<sup>84</sup> HPLC with chiral columns, such as permethylated  $\beta$ -cyclodextrin columns, can also be used to separate the enantiomers of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD diastereoisomers.<sup>84</sup>

A validated/accredited method for analysis of HBCD with HPLC-MS is described in Annex 2-H.

### **HBCD detection**

For the analysis of HBCD in materials such as PS foams and textiles different analytical approaches with different detectors can be applied and have been documented. In general these approaches target the pure identification of HBCD and/or the quantification of HBCD in the different matrices. Regarding quantification the determining parameter for the selection of the analytical approach will depend on the expected quantities since the detection limits of the methods need to be taken into account. Basically all detectors described for PBDEs such as MS, EDC, (Table 4-2) can be used for HBCD. In addition also FID and NMR has been used to detect HBCD for specific

#### **HBCD detection with mass spectrometry**

The LC, HPLC or GC can all be coupled to mass spectroscopy. Both high- and low resolution GC-MS can be used in conjunction with either electron ionization (EI) or ECNI. ECNI provides more sensitivity than EI or positive-impact chemical ionization (PCI). Either ammonia or methane may be used as the reagent gas when using chemical ionization<sup>84</sup>. When GC-ECNI-MS is used, the bromine ion only is monitored; therefore, isotopically labelled standards (<sup>13</sup>C) cannot be used as internal standards for quantification purposes. Larger fragment ions, required for structural confirmation, are not formed in ECNI mode<sup>84</sup>.

Either electrospray or atmospheric-pressure chemical-ionization (APCI) can be used. However, electrospray is more sensitive and is therefore recommended for samples with low concentration (e.g. biota, food). The deprotonated molecular ion ( $m/z = 640.7$ ) should be the major ion, fragment ions may also be identified to be used as qualifier ions. LC-MS has poorer detection limits than GCI-MS, with the sensitivity being approximately ten times less than that of the GC-NCIMS method. LC-MS-MS can usually overcome the problem of higher detection limits<sup>84</sup>.

#### **HBCD detection with Flame Ionization Detector (FID)**

A standard method for determination of HBCD in polystyrene foams with the GC-FID Technique has been developed by the HBCD Industry Group.<sup>85</sup> If the total amount of HBCD needs to be determined, gas chromatography coupled with a Flame Ionization Detector (FID) represents a sensitive, reliable and less cost intensive solution. The FID can reach detection limits of low ppm for the developed standard for HBCD in EPS/XPS. While the developed standard state to

<sup>85</sup> Cefic PlasticsEurope (2015) Determination of HBCD in Polystyrene Foams with the GC-FID Technique. 25th September 2015.  
<http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/AdditionalGuidance/NIPsGuidance/CommentsonDecisionSC710/tabid/5545/ctl/Download/mid/16672/Default.aspx?id=2&ObjID=23306>

aim for a reliable detection of 1000 mg/kg<sup>85</sup>, it needs to be assured that also 100 mg/kg are robustly detected since the Basel Convention low POPs limit list 1000 mg/kg or 100 mg/kg<sup>86</sup> in the technical guideline.

Low injector temperature (split or splitless Injector) and an appropriate oven program used in the method have shown that they do not lead to significant HBCD degradation during injection and/or elution. The quantification of HBCD in a given sample is performed by using the Internal Standard (ISTD) technique<sup>85</sup>.

#### **HBCD monitoring/detection in articles and products with NMR spectroscopy**

For the pure identification of HBCD in XPS/EPS treated with HBCD or brominated polymer, spectroscopic methods can be applied such as NMR spectroscopy which does not require any complex sample preparation<sup>87</sup>. However, HBCD concentration needs to be in the range of >2000 mg/kg for obtaining an appropriate signal intensity. Since the levels in HBCD treated articles are normally above 5000 mg/kg, NMR can be used for the detection of such originally HBCD treated articles and products. However NMR cannot be used for the assessment of low POPs limits defined by the Basel Convention at 100 mg/kg or 1000 mg/kg in e.g. polystyrene for/from recycling.

Please note: The interpretation of the NMR signals requires expertise and is more applicable in the academic fields.

#### **4.6.7 Example of a LC/MS setting for HBCD**

The selected LC/MS conditions differ slightly between laboratories. Also different GC columns can be used.

In Annex 2-H an example of LC/MS condition for the analysis of HBCD are given along with the respective chromatogram. Also the exact masses for the MS settings are listed.

#### **4.6.8 International standards for HBCD analysis**

For the analysis of HBCD in plastics used for electrical products, standard IEC 62321-6 '*Determination of certain substances in electrotechnical products - Part 6: Determination of polybrominated biphenyls and polybrominated diphenyl ethers in polymers and electronics by GC-MS, IAMS and HPLC-UV*' can be applied. However this needs a validation of this standard for HBCD.

There are currently no other international standards for the analysis of HBCD in articles and products. Analytical standard procedures have been developed for environmental matrices like biota and sediments<sup>88</sup>.

#### **4.6.9 Rapid determination techniques for HBCD, POP-PBDEs and PBB**

For more rapid analysis (compared to the standard GC methods with clean-up) some techniques have been developed. Fast analytical techniques might be important for high throughput of samples and for a quick monitoring (e.g. for waste management/recycling decisions). In most cases this is achieved by faster (but less effective) extraction techniques and to omit the clean-up steps.

<sup>86</sup> It is noted that further work to agree on one value will be undertaken according to decision BC-12/3

<sup>87</sup> Jeanerat D, Pupier M, Schweizer S, Mitrev YN, Favreau N, Kohler M (2016) Discrimination of hexabromocyclododecane from new polymeric brominated flame retardant in polystyrene foam by nuclear magnetic resonance, *Chemosphere* 144, 1391-1397.

<sup>88</sup> Webster L, Bersuder P, Tronczynski J, Vorkamp K, Lepom P (2009) Determination of hexabromocyclododecane (HBCD) in sediment and biota. *ICES Tech. Mar. Environ. Sci.* 44 (i), 1–14. [http://www.ices.dk/sites/pub/Publication%20Reports/Techniques%20in%20Marine%20Environmental%20Sciences%20\(TIMES\)/times44/091207-TIMES%2044%20FINAL3.pdf](http://www.ices.dk/sites/pub/Publication%20Reports/Techniques%20in%20Marine%20Environmental%20Sciences%20(TIMES)/times44/091207-TIMES%2044%20FINAL3.pdf)

### **Rapid onsite distinction between EPS/XPS containing HBCD and brominated polymeric alternatives**

For future management of HBCD containing EPS and XPS an appropriate and rapid field method is required to distinguish between foams containing HBCD and foams free from HBCD including the brominated polymeric systems when e.g. buildings with EPS/XPS are demolished or insulation is replaced. Schlummer et al. (2014)<sup>89</sup> developed a screening method for identifying HBCD containing expanded and extruded polystyrene foams and to distinguish from brominated polymeric systems. The test principle is based on the fact that PolyFR (a brominated polymeric macromolecule) is not extractable whereas HBCD (a low molecular weight substance) is extractable<sup>89</sup>. Following rapid extraction of HBCD with acetone the brominated flame retardant is identified and quantified by bromine screening using a handheld XRF instrument. A robustness test revealed a high degree of correctness and a high repeatability for the test system<sup>89</sup>.

### **Combination of XRF screening and wipe testing and analysis**

Gallen et al. (2014)<sup>90</sup> developed a simple non-destructive wipe test where samples are treated with a pre-cleaned filter paper wetted with isopropanol and then firmly wiped. Simple extraction of the filter paper with a direct analysis without clean-up resulted in determination of BFRs even in a semi-quantitative manner.

### **Rapid extraction and analysis**

Pöhlein et al. (2008)<sup>91</sup> developed a rapid screening method for BFR including PBB and PBDEs in polymer samples using ultra sonic extraction and GC-MS analysis.

### **Direct injection without extraction**

An alternative method to screen brominated flame retardants including PBDE in a selective mode without extraction and clean-up has been established. Danzer et al. (1997)<sup>92</sup> used online pyrolysis of pulverised plastic and analysed samples with gas chromatography coupled to mass spectroscopic detection (py-GC/MS).

A thermo-desorption method for polymers was developed for rapid screening of polymers of 100 TV sets and 80 computers (Riess et al. 2000)<sup>93</sup>. The pyrolysis GC/MS method has since been developed to a commercially available application by Shimadzu with a 48 sample auto-sampler (Shimadzu 2010)<sup>94</sup>.

### **Further considerations regarding the rapid screenings**

An independent evaluation of the quality of results of such rapid screenings has not been performed yet. The pyrolysis of matrices might lead to some degradation of PBDE including debromination reactions which have been reported for GC/MS analysis.

<sup>89</sup>Schlummer M, Vogelsang J, Fiedler D, Gruber L, Wolz G (2015) Rapid identification of polystyrene foam wastes containing hexabromocyclododecane or its alternative polymeric brominated flame retardant by X-ray fluorescence spectroscopy. *Waste Management & Research*, 33(7), 662-670.

<sup>90</sup>Gallen C, Banks A, Brandsma S, Baduel C, Thai P, Eaglesham G, Heffernan A, Leonards P, Bainton P, Mueller JF. (2014) Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. *Sci Total Environ.* 491-492:255-265.

<sup>91</sup>Pöhlein M, Bertran RU, Wolf M, van Eldik R (2008) Versatile and fast gas chromatographic determination of frequently used brominated flame retardants in styrenic polymers. *J. of Chromatography A* 1203, 217-228.

<sup>92</sup>Danzer B, Riess M, Thoma H, Vierle O, van Eldik R (1997) Pyrolysis of Plastics Containing Brominated Flame Retardants. *Organohalogen Compounds* 31, 108-113

<sup>93</sup>Riess M, Ernst T, Popp R, Müller B, Thoma H, Vierle O, Wolf M, van Eldik R (2000) Analysis of flame retarded polymers and recycling materials. *Chemosphere* 40, 937-941.

<sup>94</sup>Shimadzu (2010). Pyrolysis GC/MS of Brominated Flame retardants  
[http://www2.shimadzu.com/applications/gcms/Applications/GCMS\\_PBDE\\_07C\\_070\\_en.pdf](http://www2.shimadzu.com/applications/gcms/Applications/GCMS_PBDE_07C_070_en.pdf)

Furthermore such rapid analytical techniques with reduced (or no) clean-up steps reduces the number of injections between GC/MS (or other instrument) maintenance and shortens the lifetime of the GC columns (even if pre-columns are used). Both possible drawbacks need to be assessed if such rapid analysis might be used as options for POP-BFRs screenings. This is in particular relevant for developing countries where maintenance/repair of instruments is often a challenge and costly.

#### 4.6.10 Commercial availability of PBDEs and HBCD analysis

Standard commercial GC/MS analysis of PBDEs or LC/MS analysis of HBCD in plastic and other materials is widely available in industrial countries. For PBDEs this is largely because of the requirement of RoHS compliance. The Commercial GC/MS analysis of brominated flame retardants are, however, still relatively expensive. The price in Europe for PBDEs analysis starts from approximately 100 EURO per sample<sup>95</sup>.

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<sup>95</sup> This can be compared to PCBs analysis in transformer oil, which is currently available with GC/MS for approx. EURO 50 per sample. Much of this cost difference can be explained by the more complex and time consuming extraction and clean-up of the polymer matrix required for PBDE analysis compared to a PCB oil.



## 5 Sampling, screening and analysis of PCP and its salts and esters in articles, products and recycling

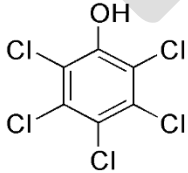
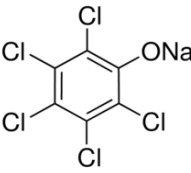
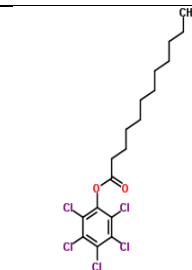
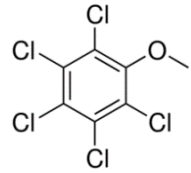
A “Draft guidance on preparing inventories of pentachlorophenol and its salts and esters and on identifying alternatives for the phase-out of those chemicals”<sup>96</sup> has been developed, which for specific Tier III inventory tasks suggests screening and analysis of PCP for selected articles and products in use and stock. For the sampling and monitoring of PCP related wastes, the Basel Convention “Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with pentachlorophenol and its salts and esters” can be consulted.<sup>97</sup>

### 5.1 PCP listed in the Stockholm Convention

PCP is a chlorinated aromatic hydrocarbon of the chlorophenol family, consisting of a chlorinated benzene ring and hydroxyl group. Taking note of the POPRC recommendation, the Conference of the Parties decided to amend Part I of Annex A to the Convention to list pentachlorophenol and its salts and esters with specific exemptions for the production and use of pentachlorophenol for utility poles and cross-arms and to insert note (vi) to reflect that pentachlorophenol (CAS No: 87-86-5), sodium pentachlorophenate (CAS No: 131-52-2 and 27735-64-4 (as monohydrate)), pentachlorophenyl laurate (CAS No: 3772-94-9) and pentachloroanisole (CAS No: 1825-21-4) are identified as persistent organic pollutants (decision SC-7/13).

Parties to the Stockholm Convention must prohibit and/or eliminate the production of PCP and its salts and esters, unless they have notified the Secretariat of their intention to produce it for use in utility poles and cross-arms with the time-limited specific exemption listed in Annex A.

**Table 5-1:** Structural formulas of PCP, its salt Na-PCP, ester PCP-L, and metabolite PCA

	Pentachloro-phenol	Sodium penta-chlorophenate	Pentachlorophenyl laurate	Pentachloroanisole
Chemical name and abbreviation	2,3,4,5,6-pentachlorophenol (PCP)	Na-PCP	PCP-L	PCA
CAS number	87-86-5	131-52-2 and 27735-64-4 (as monohydrate)	3772-94-9	1825-21-4
Molecular formula	C <sub>6</sub> HCl <sub>5</sub> O	C <sub>6</sub> Cl <sub>5</sub> ONa	C <sub>18</sub> H <sub>23</sub> Cl <sub>5</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>3</sub> Cl <sub>5</sub> O
Molecular Mass	266.34 g/mol	288.32 g/mol	448.64 g/mol	280.362 g/mol
Structural formulas of PCP, its salt and ester, as well as the main transformation product				

<sup>96</sup> Secretariat of the Stockholm Convention (2017) Draft guidance on preparing inventories of pentachlorophenol and its salts and esters and on identifying alternatives for the phase-out of those chemicals. UNEP/POPS/COP.8/INF/20.

<sup>97</sup> UNEP (2016) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with pentachlorophenol and its salts and esters. UNEP/CHW.13/6/Add.3.



## 5.2 Products and articles possibly containing PCP

PCP has been produced commercially since the 1930s.<sup>96</sup> At the height of its production, global output of PCP was around 90,000 tonnes per year (IEP, 2008). Total historic production is likely in the million tonne scale. However, by the 1990s, widespread use of PCP was discontinued in most countries (UNEP, 2013d). PCP and its salt and esters are currently produced in Mexico and in India, with formulation taking place in the US. (UNEP, 2014c).

PCP is a general biocide and has been used extensively as a fungicide, bactericide, herbicide, molluscicide, algacide, insecticide, disinfectant, defoliant, anti-sap stain agent and anti-microbial agent in various industries including agriculture, wood treatment, textiles, paints, oil drilling and forestry (UNEP, 2013d).

A list of potentially PCP containing articles and materials are listed in Annex 1-D. If a study on the presence of PCP containing materials is planned this list can be assessed for possible relevant samples for a Tier III monitoring (see Annex 1-D and the SC inventory guidance for PCP<sup>114</sup>).

## 5.3 Step by step approach for PCP monitoring in products and articles

To determine the occurrence and quantities of PCP, NaPCP and PCP-L in different articles, products and materials, the former use of PCP in the country would be assessed (see PCP inventory guidance<sup>96</sup>).

Depending on the matrices screened, other POPs can be integrated in the monitoring of PCP. Since PCP is always contaminated to a different degree with PCDD/PCDF, these unintentional POPs can be integrated in a monitoring for selected samples. For wood treatment also PCNs, lindane, DDT and endosulfan has been used in some countries/regions and could be integrated in such screening.

### Step 1: Survey of products and articles possibly containing PCP

Before collecting samples, a survey would be conducted to preliminarily determine relevant products and articles in current use or end of life that might contain PCP.

A list of major uses and related articles and products and wastes containing PCP are described in Annex 1-D and include treated wood, leather, textiles and pesticides (see also Annex 1-E).

PCP is also formed unintentionally in some processes in organochlorine production and in thermal processes but has not been listed in Annex C.

The screening of PCP in the end of life can be combined with Basel Convention activities (Synergy) and the Basel Convention *“Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with pentachlorophenol and its salts and esters”*<sup>97</sup> would be consulted.

### Step 2: Sample collection

Samples can be collected, for example, by customs at the import point of entry or by relevant authorities such as factory control or consumer protection authorities and related institutions.

Sampling campaigns might also be conducted by research institutions in collaboration with the relevant authorities or directly with the industry or waste management facilities.

Since treated wood is a major sample matrix related stakeholders would be included in the sample collection including importers of wood treatment, importers of treated wood, stakeholders for recycling of wood and operators of biomass boilers.

Following criteria and information can be used by stakeholders:

- a) The article or product is listed in Annex 1-D and has been produced or applied during the time when PCP has been produced and used.
- b) Certain risk criteria (e.g. treated wood (utility poles; railway sleepers, window frames, wood in roof structure); treated leather; wooden or textile art work in museum)

c) For chemicals; CAS numbers, chemical names or product names.

For treated wood and other articles it is important to clarify if and when PCP has been banned or restricted from use in the country/region or if the use is still allowed. This would influence the sampling strategy. Articles and products categories compiled in Annex 1-D can be used as a starting point for monitoring.

### Step 3: Screening of products in the field and in the laboratory

Sample articles can be screened for the presence of chlorine in the field or in the laboratory.

PCP in articles and products has been screened with XRF in wood and in textiles.

In some cases also visual inspection of potentially treated wood for white surface of crystals ("blooming" of organochlorine) can indicate the treatment with pesticides.

When screening methods are applied it has to be ensured that the detection limit of the screening method is below the limit required for the screening e.g. required from a certain legislation limit or below the Basel Convention low POP content is [1-100] or [1000] mg/kg<sup>97</sup>.

### Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of PCP and have been described<sup>98,99</sup>. One accredited method used for commercial analysis is described for PCP in Annex 2-C. Further methods are described in the listed case studies in Annex 3-D.

The extraction, clean-up of selected samples are described below.

## 5.4 Screening methods as indication for PCP

### 5.4.1 XRF screening of treated wood

XRF screening of chlorine can be used for a pre-screening of samples for further analysis. XRF and  $\mu$ -XRF is used for screening of PCP and other POPs pesticides in wood in particular for wooden art objects. In some countries the screening of chlorine in wood with XRF is relative specific for POPs pesticides (DDT or PCP) when mainly these pesticides have been applied for wood applications.<sup>100</sup> Also if it is known that only PCP or only POPs pesticides have been used for wood treatment in a certain applications (e.g. electricity poles or railway sleepers) countries only might just screen for chlorine to identify or to separate in recycling<sup>101</sup>.

A method for XRF screening of waste wood in a wood recycling plant for PCP has been patented indicating the relevance for such screening and separation approach.<sup>102</sup>

### 5.4.2 Screening of treated textiles

XRF spectroscopy has also been used for screening of POPs in textiles in a museum.<sup>103</sup>

<sup>98</sup> Covaci A, Voorspoels S, Ramos, L, Neels H, Blust R (2007). Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *Journal of Chromatography A* 1153: 145-171

<sup>99</sup> Schlummer M, Brandl F, Mäurer A, van Eldik R. (2005) Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. *J Chromatogr. A*. 1064, 39-51.

<sup>100</sup> Bartoll J, Unger A, Püschner K, Stege H (2003) Micro-XRF investigations of chlorine containing wood preservatives in art objects, *Studies in Conservation* 48, 195–202.

<sup>101</sup> Due to the use of heavy metals in wood treatment such as chromium copper arsenate (CCA) also these pollutants can be screened out by XRF.

<sup>102</sup> Bensch H, Engelhardt J, Katzung W, Jürgen Prof. Leonhardt Method and device for patterning of waste wood translated from German. Patent DE 19941124 B4.

<sup>103</sup> Krug S, Hahn O (2014) Portable X-ray fluorescence analysis of pesticides in the textile collection at the German Historical Museum, Berlin. *Studies in Conservation* 59, 355-366.

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## 5.5 Sample preparation, extraction and clean-up

### Extraction and clean-up

For the development of the German standard method for analysis of PCP in wood two extraction methods were compared in an inter-calibration test.<sup>104</sup> Method 2 is a more complex procedure in that sonication and shaking in relatively nonpolar toluene are applied without temperature control and the polar analyte needs to be extracted from the wood matrix treated with polar acid by the relatively nonpolar toluene. It is assumed that this produces greater variability between different laboratories compared to the more straightforward sonication in methanol at elevated and controlled temperature. Results indicated that method 2 tends to yield lower recoveries in less experienced laboratories due to incomplete collection of PCP. It should also be noted that the extraction step is carried out twice in case of method 1. Based on a reproducibility expected from practical experience and being regarded as more robust when applied without prior training, the methanol method has been annexed to the German waste wood regulation as a reference method for the determination of PCP.

Also accelerated solvent extraction (ASE) with cyclohexane and in situ acetylation. This method has been shown to be equivalent to the methanol extraction.<sup>105</sup>

After extraction of PCP from the matrices, PCP is normally not subjected to a column clean up but is separated by derivatization and extraction procedure by liquid-liquid extraction (see Figure 5-1). Also other derivatization with methyl or ethyl ether or acetic anhydride has been described.<sup>106</sup>

These methods can also be applied for textiles or leather.

Furthermore a standardized method for determining the content of PCP, its salts and esters in leather has been developed by DIN/ISO (DIN EN ISO 17070:2015-05).<sup>107</sup> As extraction procedure the method use a steam distillation.<sup>107</sup> The German reference method for determining PCP in leather and textiles considers these extraction methods. In a laboratory proficiency test for PCP in leather all listed four extraction methods (Ultrasonic; ASE; KOH, steam distillation) achieved good extraction efficiency.<sup>108</sup> The proficiency test with more than 60 laboratories showed also a high variability even when using the standard tests. The highest differences were observed with in-house methods.

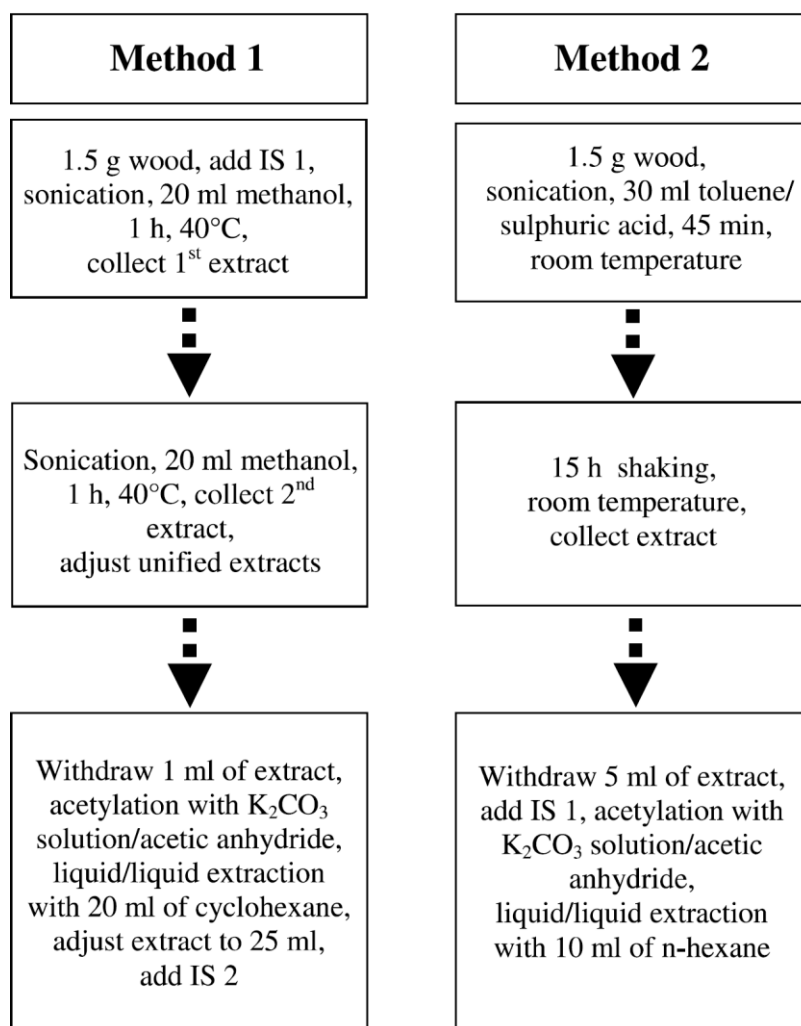
<sup>104</sup> Becker R, Buge HG, Win T (2002) Determination of pentachlorophenol (PCP) in waste wood--method comparison by a collaborative trial. *Chemosphere*. 47(9), 1001-1006.

<sup>105</sup> Win T (2001) Determination of pentachlorophenol (PCP) in wood. In: *Catalogue of Reference Methods Provided by BAM*. Federal Institute for Materials Research and Testing (BAM), Berlin, Germany, pp. 46–47 (ISSN 1617- 6634).

<sup>106</sup> Buhr, A., Genning, C., Salthammer, T (2000) Trace analysis of pentachlorophenol (PCP) in wood and wood-based products—comparison of sample preparation procedures. *Fresenius J. Anal. Chem.* 367, 73–78.

<sup>107</sup> DIN EN ISO 17070:2015-05 (E) (2015) Leather - Chemical tests - Determination of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers and pentachlorophenol content (ISO17070:2015). <https://www.iso.org/obp/ui/#iso:std:iso:17070:ed-2:v1:en>

<sup>108</sup> Noordman-de Neef AS (2016) Results of proficiency test PCP in leather. Report for Institute for Interlaboratory Studies Spijkenisse, The Netherlands. [www.iisnl.com/pdf/iis16A06.pdf](http://www.iisnl.com/pdf/iis16A06.pdf)



**Figure 5-1:** Extraction procedure of PCP and PCPNa from wood<sup>104</sup> (IS: Internal Standard)

## 5.6 Quantitative (and semi-quantitative) analysis

Analytical detection of PCP, its salts or esters is typically performed by capillary gas chromatography.<sup>104,107,109</sup>

One study compared GC with micellar electrokinetic capillary chromatography (MEKC) methodology and found comparable results.<sup>110</sup>

As detectors standard methods use normally either GC-ECD<sup>104,107</sup> or GC/MS.<sup>107,109</sup>

PCP can also be detected by UV spectroscopy or thin layer chromatography.

A quantitative methods for measuring PCP concentrations in textile samples by isotope dilution liquid chromatography-mass spectrometry were calibration range of 1 to 50 ng/g<sup>111</sup> not validated for PCP levels above Basel Convention low POP content.

DIN EN ISO 17070:2015-05<sup>107</sup> specifies a method for determining the content of PCP, its salts and esters in leather.

An accredited standard GC/MS analysis for PCP is described in Annex 2-C.

<sup>109</sup> USEPA METHOD 8270. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). <https://www.epa.gov/sites/production/files/2015-07/documents/epa-8270d.pdf>.

<sup>110</sup> Mardones C, von Baer D, Hidalgo A, Contreras A, Sepúlveda C.(2008) Determination of pentachlorophenol and tribromophenol in sawdust by ultrasound-assisted extraction and MEKC. J Sep Sci. 31(6-7):1124-1129.

<sup>111</sup> Su F, Zhang P (2011) Accurate analysis of trace pentachlorophenol in textiles by isotope dilution liquid chromatography-mass spectrometry. J Sep Sci. 34(5), 495-499.

## 5.7 International standards for PCP in articles and products

### 5.7.1 ISO standard for the determination of PCP in leather

An ISO standard (DIN EN ISO 17070:2015-05)<sup>107</sup> has been developed for the determination of PCP (and other chlorophenols) in leather articles. The standard includes extraction and clean-up procedure and instrumental analysis with GC-ECD.<sup>107</sup>

### 5.7.2 German Reference method for determination of PCP in leather and textile

A reference method (LFGB B 82.02-8 2001-06)<sup>112</sup> has been developed for determination of PCP content leather and textile for the (reference method);

### 5.7.3 German Reference method for the determination of PCP in wood

A standard procedure for the determination of PCP in wood has been developed for the German waste wood ordinance<sup>113</sup>. The Waste Wood Ordinance sets out concrete requirements governing the recycling, energy recovery and disposal of waste wood and ensures that pollutants are not recycled or do not accumulate during recovery. The standard includes extraction and clean-up procedure and instrumental analysis with GC-ECD.<sup>113</sup>

### 5.7.4 USEPA Method 8270<sup>109</sup> for determination of semi-volatile organic compounds by GC/MS

USEPA Method 8270<sup>109</sup> is used to determine the concentration of semi-volatile organic compounds by GC/MS in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method.<sup>109</sup>

<sup>112</sup> LFGB B 82.02-8 2001-06 Nachweis und Bestimmung von Pentachlorphenol in Bedarfsgegenständen, insbesondere aus Leder und Textilien.

<sup>113</sup> Verordnung über Anforderungen an die Verwertung und Beseitigung von Altholz (Altholzverordnung - AltholzV). Altholzverordnung vom 15. August 2002 (BGBl. I S. 3302), die durch Artikel 6 der Verordnung vom 2. Dezember 2016 (BGBl. I S. 2770) geändert worden ist



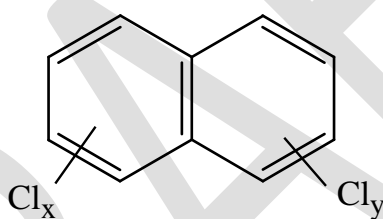
## 6 Sampling, screening and analysis of PCNs in articles and products

A “Draft guidance on preparing inventories of polychlorinated naphthalenes (PCNs)”<sup>114</sup> has been developed, which for specific Tier III inventory tasks suggests screening and analysis of PCNs for selected articles and products in use and stock. For the sampling and monitoring of PCNs in wastes, the Basel Convention technical guidelines considering PCNs<sup>115</sup> can be consulted.

### 6.1 PCNs listed in the Stockholm Convention

Polychlorinated naphthalenes (PCNs) comprise of 75 possible congeners in eight homologue groups, as listed in Table 2-1, with one to eight chlorine atoms substituted around the planar aromatic naphthalene molecule. The basic structure of the PCNs is shown in Figure 5-1 and has the molecular formula  $C_{10}H_{8-n}Cl_n$ , where  $n=2-8$ .

The homologue groups listed in the Stockholm Convention by decision SC-7/14 and considered in this inventory are dichlorinated naphthalenes (di-CNs), trichlorinated naphthalenes (tri-CNs), tetrachlorinated naphthalenes (tetra-CNs), pentachlorinated naphthalenes (penta-CNs), hexachlorinated naphthalenes (hexa-CNs), heptachlorinated naphthalenes (hepta-CNs), and octachlorinated naphthalene (octa-CN), hereinafter collectively referred to as PCNs. Mono-CNs are not listed in the Stockholm Convention.



**Figure 5-1:** General structure of polychlorinated naphthalenes (PCNs)

### 6.2 Products and articles possibly containing PCNs

PCNs as commercial mixtures were mainly produced and used between 1920 and 1970<sup>114</sup>. Some companies have used PCNs in products until around 2000.<sup>116,117</sup> The total production volume of commercial PCNs is estimated to 150,000 t.<sup>114</sup>

Similarly to PCBs, PCNs have been used in closed applications (e.g. capacitors and transformers) and in a wide range of open applications including cable insulation, wood preservation, as additive in paints and dye carriers, feedstock for dye, and in engine oils.<sup>114</sup>

A list of potentially PCN containing articles and materials are listed in Annex 1-E. If a study on the presence of PCN containing materials is planned this list can be assessed for possible relevant samples for the country. Since the production of PCNs has largely been phased out in the 1980s and 1990s, most articles and products containing PCNs have reached end of life or

<sup>114</sup> Secretariat of the Stockholm Convention (2017) Draft guidance on preparing inventories of polychlorinated naphthalenes. UNEP/POPS/COP.8/INF/19

<sup>115</sup> UNEP (2017) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls, polychlorinated terphenyls, polychlorinated naphthalenes or polybrominated biphenyls including hexabromobiphenyl. UNEP/CHW.13/6/Add.4.

<sup>116</sup> Yamashita N, Kannan K, Imagawa T, Miyazaki A, Giesy J P (2000) Concentrations and Profiles of Polychlorinated Naphthalene Congeners in Eighteen Technical Polychlorinated Biphenyl Preparations. Environ. Sci. Technol. 34, 4236-4241.

<sup>117</sup> Yamamoto T, Noma Y, Sakai S (2016) Thermal destruction of wastes containing polychlorinated naphthalenes in an industrial waste incinerator. Environ Sci Pollut Res DOI 10.1007/s11356-016-7100-8.

have already been disposed. Some PCNs are unintentionally formed in the production of organochlorine chemicals and in thermal processes (see Annex 1-E).<sup>114</sup>

Since PCBs and SCCP (recommended for listing at COP 8 in 2017<sup>118</sup>) have been used in many of these applications, the screening and analysis of the selected samples for PCNs can be combined with the screening of PCBs and, if listed, for SCCPs, where appropriate.

### 6.3 Step by step approach for PCN monitoring in products and articles

To determine the occurrence and quantities of PCNs in different articles, products and materials, the former use of PCNs in the country would be assessed (see draft PCN inventory guidance<sup>114</sup>). Since PCBs were also used in the same open and closed applications<sup>114</sup>, such a monitoring could be combined with the screening of PCBs in these applications. Since PCNs and PCBs have been phased out in the 1980s until 2000 and have partly been substituted by short chain chlorinated paraffins (SCCPs), which are recommended for listing in the Stockholm Convention at COP8 in 2017, SCCPs could be included in such a monitoring plan if eventually listed in the Convention.

#### Step 1: Survey of products and articles possibly containing PCNs (and PCBs)

Before collecting samples, a survey would be conducted to preliminarily determine relevant products and articles in current use or end of life that might contain PCNs.

A list of major uses and related articles and products and wastes containing PCNs are described in Annex 1-E and include capacitors, transformers, certain paints and coatings, cables, Neoprene rubber and textiles (see Annex 1-E).

Furthermore, PCNs are formed unintentionally in certain organochlorine production and in thermal processes. Therefore, these products, articles and wastes can also be considered and assessed (see Annex 1-E and Stockholm Convention PCN draft inventory guidance<sup>114</sup>).

The screening of PCNs in the end of life can be combined with Basel Convention activities (Synergy) and also the related Basel Convention technical guideline<sup>115</sup> should be consulted.

#### Step 2: Sample collection

Samples can be collected e.g. by the customs at the import or by relevant authorities such as factory control or consumer protection authorities and related institutions. Since PCNs (like PCBs) have been used in open applications like paints and sealants in construction, this sector is also relevant for assessment and collection.

Sampling campaigns might also be conducted by research institutions possibly in collaboration with the ministry or other relevant authorities or directly with the industry or waste management facilities.

Following criteria and information can be used by the stakeholders:

- a) The article or product is listed in Annex 1-E and has been produced or applied during the time where PCNs have been produced and used.
- b) CAS numbers, chemical names or product names.
- c) Certain risk criteria (e.g. age of condenser, same product contained PCNs like Neoprene FB).

The procedures developed to sample PCBs oils in transformers and condensers can be applied in the same manner for PCNs in these applications (see below). The difference is the final instrumental analysis which can be combined with analysis of PCBs in these samples.

<sup>118</sup> UNEP (2017) Recommendation by the POPs Review Committee to list short-chain chlorinated paraffins in Annex A to the Convention and draft text of the proposed amendment. UNEP/POPS/COP.8/14

For PCNs in open application there is currently no standardized method such as sampling of PCNs in paints and coatings in construction or ships or PCNs in products like cables or rubber. The different articles and product categories are described in Annex 3-E. If monitoring of PCNs in some of these product categories would be considered relevant, samples would be collected considering the time when PCNs have been used in these applications (see Annex 3-E and Stockholm Convention draft PCN inventory guidance<sup>114</sup>). For the sampling of unintentional PCNs organochlorine see Annex 1-E.

### Step 3: Screening of products in the field and in the laboratory

Sample articles can be screened for the presence of chlorine in the field or in the laboratory. Transformer and transformer oils can be screened with test kits for chlorine such as Clor-N-Oil or Dexsil test. Within those assessments, PCNs are also tested positive through the same mechanism as PCBs. However, this screening for chlorine in capacitor or transformer oil is not specific for PCNs for all the types of samples since PCBs have been used in larger quantities in these applications. Since PCBs need to be assessed in such screenings the test for chlorine has to be applied in any case.

The “density test” for oils can be used for a pre-screening to detect pure PCN or PCB oil containing transformers or capacitors. PCB transformers, pure PCN-containing transformers would also be tested positive since the density of PCNs is similar to that of PCBs (1.2 to 1.5).

Paints, coatings, sealants or rubber can also be screened with XRF for chlorine. In this case a chlorine positive sample is not specific for PCNs. However it indicates that the material might contain PCNs or PCBs or SCCPs (recommended for listing at COP8), with other chlorine containing materials like chloroprene rubber or PVC giving a positive signal.

Rapid screening methods such as pyrolysis-GC/MS might be used for quick verification of the presence of PCNs.

Recently a simple wipe test has been developed for POP-BFRs where respective samples were treated with a pre-cleaned filter paper folded into quarters and wetted with isopropanol and then firmly wiped in concentric circles towards the middle of the area.<sup>119</sup> Rinsing this filter paper resulted in determination of BFRs present even in a semi-quantitative manner<sup>52</sup>. Such a simple screening might also be possible for PCNs (and PCBs) in open applications like paints, coatings, sealants or rubber but need to be evaluated.

When screening methods are applied it has to be ensured that the detection limit of the screening method is below the limit required for the screening e.g. required from a certain legislation limit or below the Basel Convention low POP content of 50 mg/kg or 10 mg/kg<sup>120</sup>.

### Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of PCNs and have been described<sup>121,122</sup>. One accredited method used for commercial analysis is described for PCNs in Annex 2-D. Further methods are described in the listed case studies in Annex 3-E.

<sup>119</sup> Gallen C, Banks A, et al (2014) Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. *Sci Total Environ.* 491-492:255-265.

<sup>120</sup> UNEP (2016) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls, polychlorinated terphenyls, polychlorinated naphthalenes or polybrominated biphenyls including hexabromobiphenyl. UNEP/CHW.13/6/Add.4

<sup>121</sup> Covaci A, Voorspoels S, Ramos, L, Neels H, Blust R (2007). Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *Journal of Chromatography A* 1153: 145-171

<sup>122</sup> Schlummer M, Brandl F, Mäurer A, van Eldik R. (2005) Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. *J Chromatogr. A.* 1064, 39-51.

The extraction, clean-up of selected samples are described below.

## 6.4 Screening methods for chlorine as indication for PCN

### 6.4.1 Screening for oils in capacitors and transformers

A major former use of PCNs was in capacitors from 1930 to 1980s. Since capacitors are closed applications only those capacitors would be screened for PCNs and PCBs.

The screening steps for categorising capacitors are the following:

1. Check year of manufacture: If manufactured in or after 1990 → “PCN/PCB free”
2. Check nameplate: If there is an indication about presence/absence of PCN/PCB → categorise accordingly.
3. If unclear then either drill, sample and analyse capacitor - or categorise as PCB/PCN containing.

For screening the oils of capacitors or transformers for PCNs (or other chlorinated POPs used in transformers or capacitors like PCBs or HCBd), screening test kits for oil such as Clor-N-Oil or Dexsil test or the L2000 PCB/Chloride Analyzer can be used.<sup>123</sup> Samples tested positive for chlorine can be further analysed in laboratory for POPs content (PCN, PCB or HCBd).

The density test with water can be used for pre-screening. This test compares the density of the transformer/capacitor oil to water to determine the presence of PCBs or another organochlorine oil by observing if the oil sample floats. However when using the density test only pure or highly PCN (or PCBs) contaminated transformers and capacitors would be tested positive since the density of PCNs is similar to that of PCBs (1.2 to 1.5) while the density of low contaminated oil with PCNs or PCBs is below 1.

XRF can also be used for screening of organochlorine in oils. However the detection limit of some XRF equipment might not reach a detection limit of 50 ppm chlorine for oil.

### 6.4.2 Screening of coatings, paints, rubber and cables

XRF and sliding spark spectroscopy can detect chlorine. The detection limit depends on the instrument. For XRF the detection limits of chlorine is higher compared to bromine. Hand held XRF have detection limits for chlorine around 100 mg/kg. Laboratory XRF equipment can reach detection limits of 10 ppm.

For sealants and chinks screening with XRF can detect PCN and PCB containing sealants. Additive levels in sealants are normally between 5 and 25%<sup>124</sup>. Since chlorinated paraffins have also been used in sealants, the detection of chlorine needs a further confirmation analysis for the determination of the additive.

In anticorrosion coatings PCBs and PCNs additives were mainly used in chloroprene paints and chloroprene lacquers as well as in PVC copolymers at 5 to 35% after drying (BUWAL 2000). Also all PVC and chloroprene coatings give a chlorine positive signal with XRF or other screening technologies not specific for PCNs or PCBs. Also for chloroprene rubber (e.g. Neoprene FP) or PVC cables chlorine screening is positive and does not inform on the additive used. For these samples only an instrumental analysis can reveal the related additive.

<sup>123</sup> UNEP (1999) Guidelines for the Identification of PCBs and Materials Containing PCBs.

<sup>124</sup> PCBs have been detected in sealants in lower concentration. Levels below 0.5% stem probably from secondary contamination from concrete when sealants have been removed and were replaced by a new sealant.

## 6.5 Sample preparation, extraction and clean-up

### Extraction

Samples are normally extracted with standard method like Soxhlet extraction. Soxhlet extract with toluene was used by Yamamoto et al.<sup>125</sup> for a wide range of sample matrices including rubber, printer belts, car shredder residues, refused derived fuel and fly ashes.

Details on extraction approaches used can be found in the references of the case studies compiled in Annex 3-E.

### Clean-up

Depending on the matrix, different clean-up methods need to be applied possibly with multi-layer columns or a sequence of clean-up columns.

PCNs can finally be cleaned on an activated carbon cartridge column (e.g. Carboxen, Supelco). The cartridge column is washed with solvents (e.g. 25% dichloromethane/hexane; volume depending on column size) and the PCNs recovered by reverse flush with hot toluene (with appropriate volume depending on the column size).

Clean-up methods have been developed for the separation of PCNs from PCBs due to possible interference in the analysis.<sup>126</sup> Here e.g. silica gel-impregnated activated carbon columns can be applied.

Details on some clean-up procedures used can be found in the references of the case studies compiled in Annex 3-E.

## 6.6 Quantitative analysis of PCNs

PCNs are normally analysed by GC-LRMS or GC-HRMS or other GC-MS systems.

PCNs can also be detected with EDC detector.

GC-ECD can be applied for PCN samples if PCNs are major contaminants in a sample with low levels of PCBs. If however PCBs are present in higher concentrations compared to PCNs (e.g. PCB oils then PCN) then the co-eluting PCBs interfere with the quantification of PCNs. For such samples GC/MS would need to be used for quantification of PCNs.

As GC-columns the isomer specific separation of PCNs has been described for e.g. Ultra 2 column (5% Phenyl)-methylpolysiloxane) by Falandys et al.<sup>127</sup> and for a DB 1701 column (low/mid-polarity, bonded, cross-linked and solvent-rinsable) by Yamashita et al.<sup>128</sup>

One accredited method used for commercial analysis is described for PCNs in Annex 2-D. Further methods are described in the listed case studies in Annex 3-E.

## 6.7 International standards for analysis of PCNs

Currently no international standard is available for the analysis of PCNs in products.

The only international validated international standard methods of analysing PCNs has been developed for water by the International Organization for Standardization (ISO): ISO/TS 16780<sup>129</sup>

<sup>125</sup> Yamamoto T, Noma Y, et al. (2005) Congener-specific analysis of Polychlorinated Naphthalenes in the waste samples. *Organohalogen Compounds* 67, 708-711. <http://www.dioxin20xx.org/pdfs/2005/05-453.pdf>

<sup>126</sup> Yamashita N, Kannan K, et al. (2000) Concentrations and Profiles of Polychlorinated Naphthalene Congeners in Eighteen Technical Polychlorinated Biphenyl Preparations. *Environ. Sci. Technol.* 34, 4236-4241.

<sup>127</sup> Falandysz J; Nose K; et al. (2006) HRGC/HRMS analysis of chloronaphthalenes in several batches of Halowax 1000, 1001, 1013, 1014 and 1099. *J. Environ. Sci. Health Part. A* 2006, 41(10), 2237–2255.

<sup>128</sup> Yamashita N, Taniyasu S, et al. (2003) Polychlorinated naphthalene contamination of some recently manufactured industrial products and commercial goods in Japan. *J Environ Sci Health A* 38:1745–1759.

<sup>129</sup> ISO (2015) ISO/TS 16780 Water quality– Determination of polychlorinated naphthalenes (PCN)—Method using gas chromatography (GC) and mass spectrometry (MS). <https://www.iso.org/standard/68420.html>



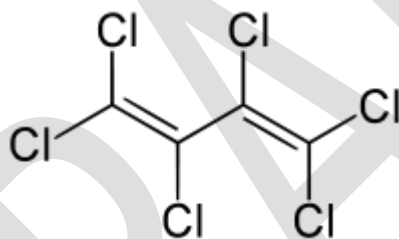
## 7 Sampling, screening and analysis of HCBd in articles and products

A “Draft guidance on preparing inventories of hexachlorobutadiene”<sup>130</sup> has been developed, which suggests, for specific Tier III inventory tasks, the screening and analysis of HCBd for selected articles and products. For the sampling and monitoring of HCBd in wastes the Basel Convention “Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene”<sup>131</sup> can be consulted.

### 7.1 HCBd in the Stockholm Convention

HCBd (CAS number 87-68-3) is a halogenated aliphatic substance, mainly generated as a by-product in the manufacture of chlorinated solvents (tri- and tetrachloroethylene<sup>6</sup> and tetrachloromethane<sup>7</sup>) or hexachlorocyclopentadiene (intermediate of cyclodiene pesticide). Anthropogenic emission sources of HCBd are intentional production (see chapter 2.2), unintentional production (see chapter 2.3) and waste from historical application (see chapter 2.5) and related potentially contaminated sites (see chapter 2.6) (UNEP 2012). HCBd was used in a range of applications (see chapter 2.4). HCBd has an ozone depleting potential (ODP) higher than some ozone damaging substances which are banned under the Montreal Protocol (UNEP 2001). There are no known natural sources of HCBd (BUA 1991).

Basic information on HCBd including its chemical structure is compiled in Table 2-1. Information about chemical and physical properties of HCBd is listed in Table 2-2.



**Figure 7-1:** Structure of hexachlorobutadiene (HCBd)

### 7.2 Products and articles possibly containing HCBd

The primary source of HCBd production/formation was and likely still is during the manufacturing of chlorinated solvents such as tetrachloroethylene/perchloroethylene, trichloroethylene and tetrachloromethane/carbon tetrachloride.<sup>132, 133, 130</sup> For intentional production, HCBd is separated from the heavy fraction of the production of these solvents and is possibly marketed for various uses. Former uses of HCBd are listed in the HCBd in Chapter 2 of the inventory.

HCBd was produced in high volumes between 1970 and 1980. Worldwide production of HCBd was estimated to be about 10,000 tonnes in 1982. Monitoring data from East Asia suggest that

<sup>130</sup> Secretariat of the Stockholm Convention (2017) Draft guidance on preparing inventories of hexachlorobutadiene (HCBd). UNEP/POPS/COP.8/INF/18

<sup>131</sup> UNEP (2017) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene. UNEP/CHW.13/6/Add.2.

<sup>132</sup> BUA (1991) Hexachlorobutadiene. BUA Report 62. German Chemical Society, S. Hirzel Wissenschaftliche Verlagsgesellschaft Stuttgart.

<sup>133</sup> Lecloux A (2004) Hexachlorobutadiene – Sources, environmental fate and risk characterisation Science Dossier for Euro Chlor. October 2004.



intentional production and/or unintentional generation and release have continued at least until recently.<sup>134</sup>

HCBD is also generated in the production of other organochlorine chemicals such as hexachlorocyclopentadiene.

The major use areas were in purification of gas streams in industry (lubricants; rubber production), in industrial manufacture (lubricants; solvents rubber/polymer production); Electrical and other technical equipment (transformer; heat-transfer liquid; hydraulic fluid) and in agriculture as pesticide and biocide. More details are compiled in the HCBD inventory guidance in Chapter 2. The major current use areas remaining are considered transformers and heat exchange/hydraulic equipment and obsolete HCBD insecticide stockpiles and fungicide waste.<sup>131,130</sup> In countries where HCBD is still produced and marketed, other uses might still be present.

### 7.3 Step by step approach for HCBD monitoring in products and articles

To determine the occurrence and quantities of HCBD in different products, processes and materials, the generation and current and former use of HCBD in the country would be assessed (see HCBD inventory guidance<sup>96</sup>).

Depending on the matrices screened, other POPs can be integrated in the monitoring of HCBD. In transformers, the monitoring can be combined with PCBs and PCNs inventory; in hydraulic oils and heat transfer oils the monitoring can be combined with PCBs, PCNs and short chain chlorinated paraffins (recommended to be listed as POPs at COP8 in 2017<sup>135</sup>). In some production/products where HCBD might be formed unintentionally, the monitoring can be combined with the monitoring of other unintentionally POPs.

#### Step 1: Survey of products and articles possibly containing HCBD

Before collecting samples, a survey should be conducted to preliminarily determine relevant products and articles in current use or end of life that might contain HCBD. A list of major uses and related articles and products and wastes containing HCBD are described in Annex 1-F.

The screening of HCBD in waste and end of life can be combined with Basel Convention activities (Synergy) and the Basel Convention *“Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with pentachlorophenol and its salts and esters”*<sup>97</sup> would also be consulted.

#### Step 2: Sample collection

Samples can be collected by responsible authorities such as factory control at production sites or consumer protection authorities or customs. Sampling campaigns might also be conducted by research institutions possibly in collaboration with the ministry or other relevant authorities or directly with the industry or waste management facilities.

Since production of organochlorine solvents where HCBD could be separated for commercial use are major stakeholders would be included.

Following criteria and information can be used by the stakeholders:

- a) CAS number of HCBD as chemical (87-68-3), chemical names (HCBD; perchloro-1, 3-butadiene; perchlorobutadiene; 1,3-hexachlorobutadiene; 1,3-butadiene, 1,1,2,3,4,4-hexachloro-; 1,3-butadiene, hexachloro-; hexachlorobuta-1,3-diene). CAS numbers of

<sup>134</sup> Risk management evaluation on hexachlorobutadiene. Addendum Report of the Persistent Organic Pollutants Review Committee on the work of its ninth meeting. UNEP/POPS/POPRC.9/13/Add.2

<sup>135</sup> UNEP (2017) Recommendation by the POPs Review Committee to list short-chain chlorinated paraffins in Annex A to the Convention and draft text of the proposed amendment UNEP/POPS/COP.8/14

- organochlorine solvents possibly containing HCBd (Carbon tetrachloride CAS # 56-23-5; tetrachloroethylene 127-18-4; trichloroethylene 79-01-6; hexachlorocyclopentadiene 77-47-4)
- b) The products, materials and samples listed in Annex 1-F.
  - c) Wastes listed in the Basel Convention guidelines<sup>131</sup> as potentially HCBd containing or contaminated (see also Table A1-3 in Annex 1-F).

Articles and products categories compiled in Annex 1-F can be used as a starting point for monitoring.

### Step 3: Screening of products in the field and in the laboratory

Samples listed in Annex 1-F or other selected can be screened for the presence of chlorine in the field or in the laboratory (Clor-N-Oil or Dexsil test or the L2000 PCB/Chloride Analyzer). Since most products potentially containing HCBd are organochlorine chemicals these screenings are not specific for HCBd. However these tests can be used for pre-screening of transformer oils or oils in hydraulic equipment or heat exchanger for the presence of HCBd and other POPs containing oil.

When screening methods are applied it has to be ensured that the detection limit of the screening method is below the limit required for the screening e.g. required from a certain legislation limit or below the Basel Convention low POP content which is [1][100] mg/kg.<sup>131</sup>

### Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of HCBd mostly using GC/MS or GC-ECD and have been described e.g. for water<sup>136</sup>, soil<sup>137</sup> and might be applied with an appropriate extraction method also for products, materials and wastes but considering the possible different concentration levels possibly present in the products and materials. One accredited method used for commercial analysis is described for HCBd in Annex 2-E. Further methods are described in Chapter 5.6 and in the listed case studies in Annex 3-F.

Information on extraction, clean-up of selected samples are described below.

## 7.4 Screening methods as indication for HCBd

### 7.4.1 Screening of oils in transformers, capacitors and hydraulic equipment

A major former use of HCBd was in transformers and heat exchangers and hydraulic equipment.

For screening the oils of transformers, heat exchangers and hydraulic equipment for HCBd (or other chlorinated POPs partly used in these applications like PCBs or PCNs), screening test kits for oil such as Clor-N-Oil or Dexsil test or the L2000 PCB/Chloride Analyzer can be used.<sup>138</sup> Samples tested positive for chlorine can be further analysed in laboratory for POPs content (PCNs, PCBs, and after listing also for SCCP suggested for listing at COP8 in 04/2017<sup>135</sup>).

Also the density test with water can be used for pre-screening. This test compares the density of the transformer/capacitor oil to water to determine the presence of PCBs or another organochlorine oil. By observing if the oil sample float or sinks, one can determine if an organochlorine compound is present in high concentration.<sup>138</sup> However when using the density

<sup>136</sup> Covaci A, Voorspoels S, Ramos, L, Neels H, Blust R (2007). Recent developments in the analysis of brominated flame retardants and brominated natural compounds. *Journal of Chromatography A* 1153: 145-171

<sup>137</sup> Schlummer M, Brandl F, Mäurer A, van Eldik R. (2005) Analysis of flame retardant additives in polymer fractions of waste of electric and electronic equipment (WEEE) by means of HPLC-UV/MS and GPC-HPLC-UV. *J Chromatogr. A*. 1064, 39-51.

<sup>138</sup> UNEP (1999) Guidelines for the Identification of PCBs and Materials Containing PCBs.

test only pure or highly HCBd (or PCNs, or PCBs) contaminated transformers or other oil would be tested positive since the density of HCBd is similar to that of PCBs ( $1.66 \text{ g/cm}^3$  at  $25^\circ\text{C}$ ) while the density of low contaminated oil with HCBd, PCBs or PCNs is below 1.

#### 7.4.2 XRF screening samples

XRF screening of chlorine can be used for a pre-screening of samples for further analysis. Also XRF can be used for screening of organochlorine in oils. However the detection limit of some XRF equipment might not reach a detection limit of 50 ppm chlorine for oil.

### 7.5 Sample preparation, extraction and clean-up

Standard procedures for water, fish or soil has been developed. Standard methods for clean-up of HCBd in products, materials and wastes have not been published.

Depending on the sample matrix a clean-up might be required.

#### Chemicals or organochlorine waste

For the analysis of HCBd in raw products of the organochlorine industry or products such as solvents, samples might be directly injected without clean-up. This approach was used by Zheng et al.<sup>139</sup> in the assessment of the heavy fraction from chloromethanes production<sup>139</sup>.

For samples with low levels of HCBd an enrichment step of HCBd might be needed as described below for water and air.

#### Extraction and clean-up of water

HCBd is normally extracted from unfiltered water with hexane, pentane or cyclohexane.<sup>140</sup>

When a water sample (100 ml) is extracted with 1 ml pentene then a detection limit of 1 ng/l or lower can be reached.<sup>140</sup> When using a volume of approx. 10 litre and hexane, a detection limit of 0.01 ng/l was reached.<sup>140</sup>

When clean-up is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate clean-up procedures.

#### For air

HCBd is sampled in air on Tenax TA sorbent<sup>141</sup> or an active carbon<sup>140</sup>. For the analysis direct thermal desorption can be used for the Tenax TA sorbent. For other active carbon methods extraction e.g. with p-xylene.<sup>140</sup>

### 7.6 Quantitative (and semi-quantitative) analysis

Analytical detection of HCBd is typically performed by capillary gas chromatography.<sup>142,143</sup>

As detectors, standard methods use normally either GC-ECD<sup>142</sup> or GC/MS.<sup>142,143</sup>

<sup>139</sup> Zhang L, Yang W, Zhang L, Lib X (2015) Highly chlorinated unintentionally produced POPs generated during the methanol-based production of chlorinated methanes: a case study in China. *Chemosphere* 133, 1–5.

<sup>140</sup> BUA (1991) Hexachlorobutadiene. BUA Report 62. GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA).

<sup>141</sup> ISO (2011) Indoor air — Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID. ISO 16000-6:2011(en). <https://www.iso.org/obp/ui/#iso:std:iso:16000:-6:ed-2:v1:en>

<sup>142</sup> USEPA (1984) Method 612: Chlorinated Hydrocarbons  
[https://www.epa.gov/sites/production/files/2015-10/documents/method\\_612\\_1984.pdf](https://www.epa.gov/sites/production/files/2015-10/documents/method_612_1984.pdf)

<sup>143</sup> ISO (1997) Water quality - Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods (ISO 10301:1997). <https://www.iso.org/standard/18345.html>

A standard analysis HCBD with gas chromatography with electron-capture (GC-ECD) as well as gas chromatography with/mass spectrometer (GC-MS) have been developed for at least fish, vegetable, eggs, milk extracts, wastewater and soils.<sup>131</sup>

Also GC-FID analysis is used in standard analysis for HCBD in air.<sup>141</sup>

### Analysis of HCBD in water.

The analysis of HCBD in water is relevant for drinking water and ground water around production sites. According to EPA method 612 and ISO 10301 the GC-ECD is used for analysis.<sup>142,143</sup> Also headspace GC/MS can be used.<sup>143</sup>

The methods used should be able and be calibrated to detect HCBD well below regulatory and health guiding values. WHO has establishing a limit for HCBD of 0.6 µg/litre considering current TDI.<sup>144</sup> Due to the genotoxic potential of HCBD<sup>145</sup>, Switzerland set a drinking water limit of 0.075 µg/l.<sup>146</sup> These limit values could be used for considering a groundwater contaminated in particular if the water is used as drinking water.

### Chemicals or organochlorine waste

For the analysis of HCBD in raw products of the organochlorine industry or products such as solvents, samples might be directly injected to GC-MS without clean-up. This approach was used by Zheng et al.<sup>147</sup> in the assessment of the heavy fraction from chloromethanes production<sup>139</sup>.

Also suspected organochlorine solvent (e.g. perchloroethylene, trichloroethylene or tetrachloromethane) can be directly analysed with GC-ECD or GC-MS.

A validated and accredited method for analysing HCBD by GC/MS is described in Annex 3-F.

## 7.7 International standards for HCBD in articles and products

Currently no international standard is available for the analysis of HCBD in products or wastes.

### 7.7.1 HCBD in water (ISO 10301:1997)<sup>143</sup>

An ISO method has been established to detect HCBD in water.<sup>143</sup>

### 7.7.2 HCBD in water (USEPA 612 and 625)

EPA Methods 612 and 625 can be used for analysis of HCBD in industrial and municipal wastewater.

### 7.7.3 HCBD in air (ISO 16000-6:2011)<sup>141</sup>

An ISO method has been established to detect HCBD in indoor air. Air is sampled on a Tenax TA sorbent and then analysed by thermal desorption by either gas chromatography using MS or MS-FID.<sup>141</sup>

<sup>144</sup> Hexachlorobutadiene in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.

<sup>145</sup> Brüscheiler BJ, Märki W, Wülser R (2010) In vitro genotoxicity of polychlorinated butadienes (Cl4-Cl6). Mutation Research - Genetic Toxicology and Environmental Mutagenesis 699, 47-54.

<sup>146</sup> Swiss Federal Office of Public Health (2010) Toxikologische Beurteilung von polychlorierten Butadienen im Trinkwasser. Faktenblatt, Bern, 27.4.2010.

<sup>147</sup> Zhang L, Yang W, Zhang L, Lib X (2015) Highly chlorinated unintentionally produced POPs generated during the methanol-based production of chlorinated methanes: a case study in China. Chemosphere 133, 1–5.

## 8 Sampling and analysis of PeCB/HCB and other unintentionally produced POPs in products and articles

Unintentional PeCB and HCB are formed and released in parallel to PCDD/PCDF and therefore are present in the same processes and products as PCDD/PCDF (see [UNEP Toolkit](#); Weber et al. 2008, [Takasuga et al. 2009](#)<sup>148</sup>). HCB and PeCB are formed in some chemical productions in particular high concentrations including certain pigments ([Government of Japan 2006](#)<sup>149</sup> and [2007](#)<sup>150</sup>) or production of major organochlorine solvents (Jacoff et al. 1986<sup>151</sup>; [Weber et al. 2011](#)<sup>152</sup>). The ratio of PeCB to HCB depends on the level of chlorination. In productions of perchlorinated compounds (e.g. tetrachloroethene), HCB might be present in considerable higher concentration compared to PeCB. In other processes of only partly chlorinated organic compounds (trichloroethene, dichloroethane) the PeCB might be present in concentration comparable or possibly even higher compared to HCB. Systematic studies on such basic relationships of HCB, PeCB and other unintentionally POPs are missing up to now. Depending on the purification process of these chemicals, PeCB and HCB (and other unintentionally POPs) remain as production residues (e.g. heavy distillates) or are transferred into the product.

### 8.1 Products and articles possibly containing PeCB/HCB

Articles and products possibly containing PeCB, HCB or other unintentionally produced POPs are listed in Annex 1-3. Furthermore all organochlorine chemicals might be suspected to contain unintentionally produced POPs at some level.

### 8.2 Extraction of articles/products possibly containing PeCB and clean-up

For the range of chemicals and some articles and products that dissolve in solvents, specific extraction procedures are not required. For those chemicals and articles which do not dissolve readily in solvents, the chosen extraction process needs to have proven high or exhaustive extraction of the unintentionally POPs from the articles and products.

#### 8.2.1 Analysis of solvents

The solvent is directly spiked (with <sup>13</sup>C<sub>6</sub>-HCB and <sup>13</sup>C<sub>6</sub>-PeCB), the volume is reduced by rotary evaporator and injected without clean-up. For solvents with larger impurities a clean-up with alumina column might be performed.

<sup>148</sup> Takasuga T, Takemori H, Yamamoto T, Higashino K, Sasaki Y, Weber R. (2009) The fingerprint of chlorinated aromatic compounds in contaminated sites from chloralkali process and a historic chlorine production using GC-HR-TOF-MS screening. [Organohalogen Compounds 71, 2239-2244](#).

<sup>149</sup> Government of Japan (2006) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in TCPA and Solvent Red 135. November 2006.

<sup>150</sup> Government of Japan (2007) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in Other Pigments Derived from TCPA and Phthalocyanine

<sup>151</sup> Jacoff F, Scarberry R, Rosa D (1986) Source assessment of hexachlorobenzene from the organic chemical manufacturing industry, in Morris, C.R.; Cabral, J.R.P. Hexachlorobenzene: Proceedings of an International Symposium; pp. 31-37.

<sup>152</sup> Weber R, Watson A, Malkov M, Costner P, Vijgen J (2011) Unintentionally produced hexachlorobenzene and pentachlorobenzene POPs waste from solvent production – the need to establish emission factors and inventories. [Organohalogen Compounds 73, 2205-2208](#).

### 8.2.2 Extraction and analysis of chemicals dissolving in solvent

Most organochlorine chemicals will dissolve in solvents such as dichloromethane, toluene or n-heptane<sup>153</sup>. A test of dissolution of a few milligrams in a few ml solvent can be done (e.g. in a 5 ml sample vial) possibly assisted by ultrasonic treatment.

Some pesticides might contain inorganic materials in the formulation, which will not dissolve. However the organic fraction is normally dissolved in particular when the inorganic matrix is just an additive in the pesticide formulation. However in some cases the organic trace contaminants are partly incorporated in the inorganic matrix as in the case of pigments or certain ashes. In these cases the inorganic matrix has to be broken up by appropriate pre-treatment (see below).

### 8.2.3 Extraction of pigments and other samples where matrix need to be broken up

The structure of pigments needs to be dissolved, so that unintentional POPs possibly included in the pigment layers can be sufficiently extracted. For this first step pigments are treated with sulphuric acid. 0.01 g of a pigment sample is spiked (with <sup>13</sup>C<sub>6</sub>-HCB and <sup>13</sup>C<sub>6</sub>-PeCB or other unintentional POPs standards) and dissolved in sulphuric acid for a constant volume of 50 ml and a clean-up spike added.

The dissolved pigment solution is extracted three times with n-heptane. The n-heptane is concentrated to approx. 1 ml for the clean-up.

### 8.2.4 Clean-up

Different clean-up procedures are used depending on the levels, which needed to be detected for the different unintentional POPs (e.g. for HCB/PeCB detection in the high ppb range might be sufficient while for PCDD/PCDF ppt level (ng/g and lower) needs to be detected). Extraction and clean-up procedures are described e.g. in respective publications/report that have analysed unintentionally POPs in pigments or pesticides (see references for case studies below such as Holt et al. 2010; [Government of Japan 2006](#) and [2007](#); Liu et al. 2012).

## 8.3 Quantitative instrumental analysis

For PeCB and HCB the measurement can be performed with low resolution MS or ECD. Conditions for GC/MS are described in Annex 2-F.

For the PCDD/PCDF analysis different international standards have been developed (e.g. EN 1948-3; [USEPA Method 8290A](#)<sup>154</sup>).

<sup>153</sup> The use of heptane is preferred compared to hexane (neurotoxic; should be substituted were feasible).

<sup>154</sup> [US EPA method 8290A](#)



## ANNEX 1 Selected articles and products which might contain industrial or unintentional POPs

### Annex 1-A PFOS and related chemicals in articles and products

#### PFOS and related chemicals in production and as products

PFOS and related chemicals are currently produced in at least three countries (China, Germany, and Italy). Some trade names and product names are available and have been listed in an Annex of the "POPs Customs Control Guidance"<sup>155</sup>.

#### PFOS in fire-fighting foams

Specific fire-fighting foams (aqueous film forming foams (AFFF)) with PFOS or other PFCs are used for extinguishing liquid fuel fires. They are especially used at installations and plants where large quantities of flammable liquids are stored. PFOS containing fire-fighting foams are still on the market.

Firefighting foam is listed as an acceptable purpose. Therefore, countries can register for this use, which has to be considered then for monitoring.<sup>156</sup> Firefighting foams can be sampled at import from customs. Additionally stocks on the fire-fighting services level would be sampled and analysed. Box A-1 list firefighting services and locations with a high probability of AFFF use which could be inspected and where samples could be taken. However, firefighting services from the city/region also might have AFFF for specific uses and these would be assessed.

#### Box A-1: Fire-fighting services and locations where AFFF foams are mainly used

- fire-fighting training sites
- airports
- oil refineries
- military areas
- offshore installations, mobile rigs
- onshore gas terminals, onshore installations for gas and oil extraction
- storage facilities at industrial sites
- tank farms
- waste management installations
- hospitals
- car parks
- ships and ferries

#### Metal plating industries

<sup>155</sup> Stockholm Convention (2017) Guidance for the control of the import and export of POPs (Draft).

<sup>156</sup> As stated in Part III of Annex B (paras 3 and 4), the goal is to reduce and ultimately eliminate the product and use of these chemicals, and that countries must report on the progress made to eliminate PFOS its salts and PFOSF under Article 15.

PFOS and related chemicals are mainly used as surfactant/wetting agent/mist suppressants in hard and decorative chrome plating, which can reduce the emission of chromium and improve the working environment in this sector. PFOS containing performance chemicals are also possibly used in copper plating, nickel plating, tin plating, plating plastic, and plating with precious metals.

PFOS use in metal plating in closed loop systems is listed as an acceptable purpose, and use in hard metal plating and decorative metal plating as a specific exemption. Therefore, countries can register for this use and several countries have already registered. This use has to be considered then for monitoring.

The main stakeholders to monitor the import and presence of PFOS in PFOS containing performance chemicals are customs and in particular the relevant authority, which controls the plating industries. The association of metal/plastic plating industry and individual metal and plastic plating industries would be informed and encouraged to participate in a survey of the presence of PFOS and related chemicals in mist suppressant. Samples can be taken at the respective industries.

### **Oil industry**

PFOS and related chemicals may be used as surfactants in the oil and gas industries to enhance oil or gas recovery in wells, as evaporation inhibitors for gasoline, as jet fuel, and hydrocarbon solvents. These uses are listed as specific exemptions and countries can register.

The main stakeholders to monitor the import and presence of PFOS in PFOS containing performance chemicals for these uses are customs officers, in particular the relevant authority controlling these industries. From the industrial side, the relevant association and individual facilities should be informed and asked for information. Samples might be provided directly by the industrial associations or individual companies.

### **Other relevant industrial uses of PFOS having exemptions**

PFOS and related chemicals used in photo imaging, photo resist and anti-reflective coatings for semi-conductors, and as etching agent for compound semi-conductors and ceramic filters have already been registered for as exemptions by several countries.

The main stakeholders to monitor the import and presence of PFOS in PFOS containing performance chemicals for these uses are customs officers, in particular the relevant authority controlling these industries. From the industrial side, the relevant association and individual facilities would be informed and asked for information. Samples might be provided directly by the industrial associations or individual companies.

### **Aviation hydraulic fluids**

Hydraulic oils containing PFOS have been used as an anti-erosion additive in civil and military airplanes since the 1970s to prevent evaporation, fires, and corrosion. This use of PFOS is listed as an acceptable purpose and if registered, it should be monitored and controlled.

The main stakeholders to monitor the import and presence of PFOS in aviation hydraulic fluids are customs, and in particular the competent authorities responsible for repair shops at airports and military air bases. Industrial stakeholders are airlines and workshops at airports using hydraulic oils for airplanes. Other stakeholders may include the military air force of the country and possibly other air forces stationed in the country. Samples might be received from the mentioned stakeholders.

### **Insect baits and insecticides**

A PFOS related substance (sulfluramid/Mirex-S<sup>157</sup>) is used as insecticide against ants,

<sup>157</sup> CAS: 4151-50-2; N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonamide

cockroaches, termites, etc. The use for control of leaf-cutting ants is listed as an acceptable purpose and the use to control red fire ants and termites is listed as a specific exemption.

The main stakeholders to monitor the import and presence of PFOS and related chemicals in insecticides are customs and the Ministry of Agriculture. Relevant authorities could check for the presence of sulfluramid containing insecticides at pesticide producers, formulators, and in stores selling pesticides. Samples might be obtained from these stakeholders or purchased on the market.

### **Industries where specific exemptions has been stopped in 2015 (surface treatment of carpet, leather, paper, textile)**

The specific exemption for surface treatment of carpets, leather, paper and textiles expired in 2015 and countries cannot register for this exemption. For these uses often alternative PFAS are used, although these are considered an emerging issue under SAICM. Therefore these chemicals may also be assessed and best alternatives could be selected including non-fluorinated alternatives.

The related industries include carpet industries, paper industry, textile industry, and leather industry. The main stakeholders to monitor the import and presence of PFOS and related chemicals in these industries are the relevant authorities responsible for supervision of these industries (enforcement), the customs and related industry (compliance). Additionally, the industrial stakeholders would be included in the monitoring. Samples might be received from the mentioned stakeholders.

### **Articles treated with PFOS and related chemicals**

A part of PFOS and related chemicals and other PFCs might enter a country by impregnated products (see *PFOS and related chemicals Inventory Guidance*<sup>2</sup> Chapter 2.4 and 5). This includes articles currently produced and articles in use (see section below).

Currently these articles are not labelled to indicate that they contain PFOS or other PFCs (for details on labelling approach see “POPs labelling Guidance” (Stockholm Convention 2017<sup>158</sup>)). Therefore, it is currently not possible to identify such articles by labels.

While the impregnated articles listed above are currently not labelled to contain PFOS or other PFCs, an indication for furniture, carpets, textile, leather, stone or other fabrics that possibly contain PFOS or other PFCs is a “stain resistant” label or advertisement for this property. For paper and paperboards, an indication for possible use of PFOS and other PFCs containing coatings are properties of water, oil, and grease resistance.

The main stakeholders to monitor the import and presence of articles impregnated with PFOS and related chemicals are customs and market surveillance authorities. The industrial stakeholders are companies producing, importing/exporting, or marketing these articles and products. Samples might be received from these stakeholders or purchased on the market.

These articles might include:

#### ***Synthetic carpets***

A large share of synthetic carpets has been treated with PFOS and related chemicals and other PFCs for stain resistance. For details see Section 2.1.3 of “Guidance on BAT and BEP for the use of PFOS and related chemicals”

#### ***Textiles and leather***

PFOS and other fluorinated surfactants and polymers have been used to treat textiles and leather to provide oil and water repellency and soil and stain release properties. For details see

<sup>158</sup> Guidance on labelling of products or articles that contain new POPs or use new POPs during manufacture – initial considerations.

## Section 2.1.2 of “Guidance on BAT and BEP for the and use of PFOS and related chemicals”

### ***Furniture***

PFOS and related chemicals have been used in particular in couches, chairs and other furniture with potentially stain resistant surfaces. For details see Chapter 2 of “Guidance on BAT and BEP for the use of PFOS and related chemicals”<sup>5</sup>

### ***Impregnated paper/food contact paper***

PFOS and other PFCs containing chemicals have been used in food contact paper to provide oil, grease and water repellence (see Box A-2, below). PFOS derivatives, such as N-Me-FOSE and

N-Et-FOSE was previously marketed under the tradename Scotchban (by 3M) and used to impregnate paper for e.g. margarine. While these applications seems to have been phased out in European countries, these and other PFOS based chemicals (e.g. SN-diPAPs also called SamPAPs, Trier 2011a and Benskin 2012)<sup>159</sup> were until recently sold in China, as industrial blends for paper coating purposes (Trier 2011). The industrial blends contained considerable amounts of PFOS impurities.

#### **Box A-2: Some categories of food contact paper/packaging possibly using PFOS or other PFCs for oil, grease, or water repellency**

- Wrapping paper used for fast food
- Burger boxes, pizza boxes
- Popcorn bags
- Muffin paper cups
- Baking paper, microwave paper
- Paper coffee cups
- Disposable crockery
- Cake and biscuit boxes (long-time storage of fatty foods)
- Sandwich wrapping paper (to wrap lunch boxes)
- Chewing gum cardboard boxes
- Other food packaging

### **Further uses of PFOS and related chemicals in products and articles considered less relevant**

Some other former PFOS uses that are not considered to be of priority today include:

- Industrial and household surfactants;
- Paint and varnishes;
- Toner and printing ink;
- Sealants and adhesive products.

The use of PFOS and related chemicals in these applications is not exempted and is therefore prohibited by the Convention. However, a country might decide to assess the current status of the presence of PFOS in these applications and to ensure that PFOS is not used and

<sup>159</sup> Trier X, Granby K, Christensen JH (2011a) Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging, Environ. Sci. Pollut. Res. 18, 1108-1120.

additionally to evaluate what alternative chemicals are currently used including their environmental/health performance. For a more detailed description of these (former) PFOS applications, see “PFOS inventory guidance”<sup>2</sup>. Samples might be received from stakeholders or purchased on the market.

### **Monitoring of PFOS and related chemicals in articles in use (stocks)**

The historic production of PFOSF from 1970 to 2002<sup>160</sup> is estimated to be approximately 96,000 tonnes and 26,500 tonnes of related production wastes<sup>161</sup>. A large share of the produced PFOS and related chemicals was applied for surface treatment of carpets, textiles, paper, leather, and furniture. Therefore, the stock of PFOS and related chemicals in use and in particular deposited in landfills might have major relevance (in particular when considering the minor use volume today). Therefore, monitoring efforts need also to consider the stocks of articles currently in use. The same articles mentioned in above section “PFOS and related chemicals in production and as products” might be considered for the assessment of stocks. An overview on sectors might have been gained in the development of the PFOS inventory.

Samples might be taken from private households and businesses (e.g. carpets from hotels). Also samples might be purchased on the second-hand market.

### **Monitoring of PFOS and related chemicals in reuse and recycling**

The “PFOS Inventory Guidance” considers carpet recycling as one inventory activity. Other articles potentially in recycling or reuse (possibly) treated with PFOS and related chemicals are textiles, paper, leather, and (textiles/leather on) furniture. Of these former relevant PFOS uses, the recycling of furniture and leather seems to be of minor relevance. Paper is recycled to a high degree in some countries, but due to the rather short use phase the paper formerly impregnated largely before 2002 (when 3M stopped such PFOS use) has entered the recycling chain some years ago.

The main stakeholders to monitor the recycling of PFOS containing carpets (and possibly other materials) are the relevant authorities in the waste management sectors and factory inspection. Industrial stakeholders are the carpet (recycling) industry. Stakeholders for the monitoring of reuse of furniture impregnated with PFOS and related chemicals are market surveillance authorities in cooperation with second-hand furniture retailers. Samples might be taken from recycling facilities (e.g. for carpets or paper) and might be purchased on the second-hand market.

### **PFOS and related chemicals in biosolids and sludge**

Sewage sludge and related “biosolids” are a sink for a range of POPs released from consumer goods (e.g. POP-BFRs, PFOS) or industrial processes. In some countries, regulation limits exist for POPs in sewage sludge and/or biosolids (e.g. PCBs, PCDD/PCDF or PFOS). The application of PFOS contaminated biosolids (originating from wastewater treatment plants related to PFOS/PFC productions and industrial use)<sup>162, 163, 164</sup> on agricultural areas have

<sup>160</sup> In 2002, 3M ended PFOS production.

<sup>161</sup> Paul AG, Jones KC, Sweetman AJ (2009) A First Global Production, Emission, And Environmental Inventory for Perfluorooctane Sulfonate. *Environ Sci Technol.* 43, 386-392.

<sup>162</sup> Oliaei F, Kriens D, Weber R, Watson A (2012) Assessment of PFOS and PFC pollution from a PFC production plant in Minnesota (USA). *Environ Sci Pollut Res Int.* DOI 10.1007/s11356-012-1275-4.

Oliaei F, Kriens D, Weber R. (2010) Discovery and investigation of PFOS/PFCs contamination from a PFC manufacturing facility in Minnesota – environmental releases and exposure risks. *Organohalogen Compounds* 72, 1338-1341. <http://www.dioxin20xx.org/pdfs/2010/10-1507.pdf>.

<sup>163</sup> USEPA (2011) Q&A's - Perfluorochemical (PFC) Contamination of Biosolids near Decatur, AL Prepared by U.S. Environmental Protection Agency.

<sup>164</sup> Kröfges P, Skutlarek D, Färber H, Baitinger C, Gödeke I, Weber R (2007) PFOS/PFOA Contaminated Megacities in Germany Polluting the Drinking water Supply of Millions of People. *Organohalogen Compounds* 69, 877-880.

resulted in large scale contaminated sites, e.g. in Germany<sup>164</sup> and the USA (Decatur Alabama)<sup>163</sup> including groundwater and drinking water contamination. In the German case, PFOS/PFOA containing sludge has been imported into the country (Germany) and by further application as biosolid has resulted in large contaminated sites and the contamination of drinking water for approximately 5 million inhabitants<sup>164</sup>.

Therefore, the use and import of biosolids can be a relevant source of PFOS/PFCs. Limit values of 100 µg PFOS+PFOA/kg (0.1 ppm) have been set e.g. in Germany by the fertilizer ordinance<sup>165</sup>.

The customs would monitor the import of biosolids/organic fertilizers in cooperation with the agricultural ministry, which controls and monitors the overall use of sewage sludge and other biosolids in the country. Companies exporting or importing biosolids/organic fertilizer need to guarantee certain pollutant levels including POPs and heavy metals. Samples might be received from mentioned stakeholders and might be sampled directly from sewage treatment plants. PFOS/PFC levels in sewage sludge can reveal and direct to point sources.

### **PFOS and related chemicals in feed, food and drinking water**

The monitoring of feed, food and drinking water goes above the scope of this guidance and matrices are not covered by described methodologies. Due to the relevance for human exposure these articles are shortly mentioned here.

Food, feed and drinking water can in particular be contaminated with PFOS and related chemicals in connection with contaminated sites of former PFOS production, use and disposal. This includes e.g. lakes and rivers with elevated PFOS levels, fruits and vegetables from areas with soil and ground water is contaminated. Also drinking water can be contaminated with PFOS in areas with polluted ground water or surface water. If a country decides to include feed, food or drinking water into the monitoring of PFOS containing articles and products then the development of the monitoring concept should be linked with the development of the inventory of PFOS contaminated sites (developed during the NIP update). A first priority selection of samples can be done based on the findings of the PFOS contaminated site inventory. Samples might be received from stakeholders, purchased on the market or taken from households.

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<sup>165</sup> Düngemittelverordnung (BGBl. I S. 2482), Verordnung über das Inverkehrbringen von Düngemitteln, Bodenhilfsstoffen, Kultursubstraten und Pflanzenhilfsmitteln (Düngemittelverordnung - DüMV). last modified 23. April 2015 (BGBl. I S. 886).



## Annex 1-B: POP-PBDEs and HBB in articles and products

Since production of c-PentaBDE (consisting of POP-PBDEs listed in Annex A) and c-OctaBDE (containing hexaBDE and heptaBDE listed in Annex A) is considered to have stopped in 2004, the monitoring can largely concentrate on articles and products in use, recycling, and end-of-life. Since production of HBB stopped in 1970s it is not considered for monitoring of articles.

For c-OctaBDE, the material flow with the largest amount of c-OctaBDE are certain polymers used in Electrical and Electronic Equipment (EEE) and related Wastes (WEEE).<sup>166</sup> Large amounts of EEE and WEEE have been exported from industrial countries with former major use of c-OctaBDE (e.g. USA and Europe) to developing countries. Furthermore, polymers from recycling of WEEE are partly sent for recycling to developing/transition countries (e.g. China or India). Recent studies have shown that recycled polymers containing PBDE have been used to produce articles for which no flame retardancy is required including, for example, children's toys, household goods, and video tapes.<sup>167</sup> This shows that the flows of polymers containing PBDEs for recycling are not well controlled and need to be monitored and better managed.

For c-PentaBDE, the main use was PUR foam in transport (cars, buses, trains, etc.) and furniture and for some regions possibly insulation in construction.

Therefore, the reuse and recycling of these two major material flows need to be monitored. Details on the POP-PBDEs material flows are given in the "POP-PBDEs inventory Guidance"<sup>Error! Bookmark not defined.</sup> and "POP-PBDEs BAT/BEP Guidelines"<sup>Error! Bookmark not defined.</sup>. Considering these major uses of c-PentaBDE and c-OctaBDE, the following reuse of articles and goods and recycling would be assessed (in country and in imports):

### POP-PBDEs as chemical and in chemical products

Although production has officially stopped, some companies still offer c-PentaBDE (CAS 32534-81-9) and c-OctaBDE (32536-52-0) for sale in the public domain although production and marketing is banned under the Convention. Therefore, illegal trade of these chemicals might still take place. Companies offering POPs are listed in the „POPs Customs Control Guidance“<sup>168</sup>.

C-DecaBDE is still produced as flame retardant. The production of c-DecaBDE by bromination of diphenylether has POP-PBDEs as intermediates. Therefore c-DecaBDE could possibly contain POP-PBDE as contaminant and could be monitored. C-DecaBDE debrominates under various conditions (UNEP 2010)<sup>169</sup>. Therefore articles containing c-DecaBDE and articles recycled from c-DecaBDE containing materials would be monitored for POP-PBDE.

### Second hand EEE in import and on the local market

Polymers of used EEE (produced before 2005) can contain POP-PBDEs<sup>170</sup>. The most relevant WEEE fractions are Cathode Ray Tube (CRT) housing from TVs and computers. Imported used EEE is, in many countries, subjected to assessment of their functionality to avoid illegal import of WEEE<sup>171</sup>. Therefore, customs are already monitoring used electronics. Within this monitoring, screening of bromine for indication of POP-PBDEs might be performed. However, since other brominated flame retardants are mainly present in today's used electronics, confirmation analysis would need to be considered. Samples might be received from stakeholders, purchased on the market, from households or end-of-life treatment facilities.

<sup>166</sup> See Chapter 4 of Guidance for the inventory of PBDEs listed under the Stockholm Convention (Draft).

<sup>167</sup> UNEP (2010) Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. ([UNEP/POPS/POPRC.6/2](#))

<sup>168</sup> Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft)

<sup>169</sup> UNEP (2010) Debromination of brominated flame retardants. 6th POP Reviewing Committee meeting Geneva 11-15. October 2010 (UNEP/POPS/POPRC.6/INF/20).

<sup>170</sup> Plastic in electronics produced from 2005 on can contain trace amount of c-OctaBDE from recycling of c-OctaBDE containing polymers.

<sup>171</sup> Basel Convention (2011) Technical guidelines on transboundary movements of e-waste, in particular regarding the distinction between waste and non-waste. 15. July 2011, UNEP/CHW.10/INF/5.

## Import of Waste Electrical and Electronic Equipment (WEEE)

The largest amount of POP-PBDEs of c-OctaBDE is present in WEEE, in particular Cathode Ray Tube (CRT) housing from TVs and computer monitors and office equipment. WEEE subject to a transboundary movement, for example, imported by a country, for the recovery of metals, can be subject to the provisions of the Basel in addition to the specific legislation of a country.

Depending on further treatment of this WEEE and in particular the treatment of the polymer fraction, this POP-PBDE-containing material can cause environmental pollution (e.g. from the practice of open burning) or hazards if recycled into sensitive products (Table A-1). Therefore, relevant authorities and industries treating the WEEE need to assure the appropriate management and treatment of the associated polymer material of such WEEE imports (see Chapter 4 of the “POP-PBDEs BAT/BEP Guidelines”<sup>172</sup>). If the polymer is subjected to further recycling, the relevant authority would monitor or ask the companies for monitoring data and assure pollutants like POP-PBDEs are separated according to the recommendations of the Conference of Parties if no exemption for recycling is granted. If the country has asked for exemption of recycling PBDE containing materials, it should take care that, in particular, such polymers are not recycled into sensitive uses (see also Chapter 4 of POP-PBDEs BAT/BEP Guidelines<sup>172</sup>).

### WEEE plastic for recycling

The polymer fractions from recycling of WEEE are the most relevant recycling material flow possibly containing POP-PBDEs. Mainly ABS plastic but also mixed WEEE plastic fractions might be impacted. Such polymer fractions are partly exported – often from industrial countries to developing countries for material recycling purposes to produce new plastic products. Such polymers might be plastic flakes from WEEE shredders or pelletized plastic. The monitoring for the recycling of this polymer might also include, in addition to POP-PBDEs, other RoHS Directive<sup>173</sup> relevant substances.

**Table A1-1:** Examples of sensitive use areas\* where POP-PBDE-containing recycled plastic should not be used\*\*<sup>172</sup>

#### Some sensitive uses of plastic

- Toys
- Food packaging; food containers
- Kitchen equipment
- Refrigerator interior\*\*\*; freezer interior\*\*\*
- Water tanks (in particular tanks used for drinking water)
- Water pipes (in particular drinking water pipes)
- Silos, storage, and piping for food and animal feed
- Polymer parts with direct contact
- Furniture, handles of tools, doors, etc.

\* In such applications generally recycled polymer fractions containing heavy metals, or critical softeners, brominated flame retardant, phosphor organic flame retardant or other critical chemical should not be used.

\*\* The list provides key examples of sensitive uses and is not considered comprehensive.

\*\*\* The recycling of polymers from WEEE plastics containing no critical chemicals is encouraged following the cradle to cradle principle, e.g. polymers from refrigerators/fridges to refrigerators/fridges.

<sup>172</sup> UN Environment (2017) Guidance on best available techniques and best environmental practices for the recycling and disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants; Updated January 2017.

<sup>173</sup> Directive on the restriction of the use of certain hazardous substances in EEE 2002/95/EC.

### Used cars, buses, and other vehicles (produced before 2005)

C-PentaBDE has been applied in cars, buses, and trucks for treating polyurethane foam in e.g. the upholstery of seats, headrests, or armrests until 2004 in some regions. C-OctaBDE has been used to a minor extent in dashboards and other plastic parts until 2004 in some regions.

Depending on the phase-out of POP-PBDEs in different regions, vehicles produced within a region can be regarded as not or low<sup>174</sup> impacted:

- In Europe: POP-PBDEs have been used until late 1990s;
- In the US: POP-PBDEs have been produced/used until 2004;
- In Japan: POP-PBDEs have been used until late 1990s;
- In China: POP-PBDEs have been produced until approx. 2004.

Vehicles produced until these dates in these countries/regions can contain POP-PBDEs.<sup>175</sup> Therefore, POP-PBDEs are imported to developing countries with second-hand vehicles containing such treated polymers.

Currently there are no data on which producers have used POP-PBDEs in which series. Therefore, currently only screening of the vehicles by non-destructive XRF in current used vehicles (or screening of end-of-life vehicles) could clarify the presence/absence of POP-PBDEs/BFRs in the respective vehicles. A positive detection of bromine in PUR foam (seat, headrest, etc.) in vehicles produced before 2005 is a strong indication of the presence of c-PentaBDE. A confirmation analysis by GC/ECD or GC/MS can then be performed.

### Furniture and mattresses containing PUR-foam (produced before 2005)

The use of c-PentaBDE (and other flame retardants) in furniture depends on the flammability standard of a country (Shaw et al. 2010)<sup>176</sup>. Due to flammability standards for furniture in the US and UK in particular furniture in North America and UK are often flame retarded. Therefore older furniture in these region/countries may contain c-PentaBDE (or other flame retardants).

The extent of furniture exported from North America or UK for re-use to other regions has not been assessed and need to be considered as a possible source for c-PentaBDE input for other countries.

Mattresses have to a minor extent been flame retarded with c-PentaBDE (in particular from institutions like prisons, military, hospitals or hotels) (see POP-PBDEs BAT/BEP Guidelines). Samples can be taken from mattresses which in field screenings were bromine positive.

These applications can be sampled easily in end-of-life phase.

### PUR foam in other applications

Also other PUR-foam applications have partly been treated with c-PentaBDE such as various baby products (Stapleton et al. 2011) pillows or for packaging. PentaBDE was also used in rigid PUR foam in construction. Therefore (formerly used) foams in construction might contain POP-PBDEs.

These applications can be sampled in the end-of-life phase.

<sup>174</sup> Plastic parts from vehicles are partly recycled and could have been used in new vehicles.

<sup>175</sup> Please note that Japanese and European car manufacturers have also produced within the US and therefore these cars produced in the US might contain POP-PBDEs until 2005.

<sup>176</sup> Shaw SD, Blum A, Weber R, Kannan K, Rich D, Lucas D, Koshland CP, Dobraca D, Hanson S, Birnbaum LS. (2010) Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? [Reviews on Environmental Health 25\(4\) 261-305.](#)

### Textiles and rubber

PentaBDE have been used<sup>177</sup> in limited quantities for the treatment of textiles for uses including back-coating, for curtains and for functional textiles (UNEP 2009). Functional textiles might be screened for their bromine content.

PentaBDE has also been used in rubber for e.g. conveyor belts and other minor uses. If a country has larger use of rubber conveyor belts also these could be monitored.

### Articles produced from recycled plastic

Currently no regulation exists on the labelling of articles produced from recycled polymers. Therefore these materials can currently only be monitored by analytical screenings. The main stakeholders to monitor the import and presence of POP-PBDE containing articles made from recycled polymers are customs and authorities for market surveillance. Industries using recycled polymers from WEEE or transport would monitor for POP-PBDEs and report to the environmental ministry or NIP coordinator on levels of POP-PBDEs.

The articles can be assessed in a similar way as the polymers described above. A similar screening approach as for other materials (XRF screening combined with confirmation analysis) might be applied. Sliding spark spectroscopy is not sensitive enough (1000 ppm bromine) for such a screening. Possible articles for a screening are, for example, those listed in the negative list (see Box 3, above).

### PUR foam for recycling

PUR foam from end-of-life products (ELV vehicles, furniture, mattresses) might be gathered for recycling purposes. Such PUR foam for recycling might be used in the country, exported or imported from other countries.

### Articles produced from recycled PUR foam

PUR foams for recycling might be used in different new articles and products.

**Carpet re-bond:** Large scale recycling of PUR foam into carpet padding/re-bond is currently practised in the US and Canada (Luedeka 2011, see Chapter 6 POP-PBDEs BAT/BEP Guidance). Since Penta-PBDE is not intentionally added, the quantity of residual PentaBDE in Canada in re-bond carpet cushion is in decline.<sup>178</sup> The extent of this recycling activity for other regions is unknown but appears to be limited (DiGangi et al. 2011). If carpet rebond is imported from this region, it might contain POP-PBDEs. Relevant exposure of workers in PUR recycling and carpet installers has been demonstrated in a first study from the US (Stapleton et al. 2008) and there are risks of further exposure of consumers.

**Other uses:** While the majority of polyurethane foam scrap is processed into carpet rebond (in the U.S. market), scrap can also be shredded and used as packaging and stuffing for pillows, pet bedding, insulation and stuffed animals for kids. Foam scrap might also be used for some furniture cushioning, sound insulation or gymnastic mats or (school) bus seats (UNEP 2010b, USEPA 1996, Zia et al. 2007).

**Regrinding:** PUR foam is partly grinded to ultrafine powder and added to the virgin material in the manufacture of new foams. If POP-PBDE-containing PUR foam is used then also new PUR foam can become polluted.

### POP-PBDEs in biosolids, sewage sludge and industrial sludges

Sewage sludge and related “biosolids” are a sink for a range of POPs released from consumer goods (e.g. POP-BFRs, PFOS) or industrial processes. In some countries, regulation limits

<sup>177</sup> C-DecaBDE and HBCDD are still used in the impregnation of textiles.

<sup>178</sup> Environment Canada (2016) Socio-Economic Study and Mass Balance Study for Products Containing Polybrominated Diphenyl Ethers (PBDEs) in Canada (2013, confidential). Comment on the guidance.

exist for POPs in sewage sludge and/or biosolids (e.g. PCBs, PCDD/PCDF or PFOS). Also POP-PBDEs are detected in sewage sludge/biosolids. POP-PBDE contaminated biosolids and sewage sludge might originate from wastewater treatment plants related to (former) PBDE production and industrial use. Biosolids/organic fertilizer imports and exports may therefore be added to the list of products to be considered in developing an inventory with related control of companies.

### **PBDEs in feed and food**

The monitoring of feed and food goes above the scope of this guidance and matrices are not covered by described methodologies here. Due to the relevance for human exposure these articles are shortly mentioned here.

Food and feed can in particular be contaminated with POP-PBDEs in connection with contaminated sites of former POP-PBDE production, use and disposal. This includes e.g. fish from lakes and rivers with former PBDE inflow, eggs and milk from areas where formerly PBDE contaminated sludges or bio-solids have been applied or landfill where POP-PBDE containing materials has been disposed. If a country decides to include feed and food into the monitoring of POP-PBDE containing articles and products then the development of the monitoring concept would best be linked to the development of the inventory of POP-PBDE contaminated sites. A first priority selection of samples can be done based on the findings of the POP-PBDEs contaminated site inventory then.



## Annex 1-C: HBCD in articles and products

The major uses of HBCD are described in the HBCD inventory guidance<sup>179</sup>. HBCD is still produced and used in particular in polystyrene in construction. Also the material stock and flow with the largest HBCD volume used is EPS and XPS. A recent study has shown that HBCD is also present to some extent in EPS/XPS packaging including food packaging and in buoy indicating recycling of HBCD containing EPS/XPS. The second largest use was on flame retarded textiles (e.g. in transport or indoor use such as curtains). HBCD has also been used in high impact polystyrene (HIPS) in casings of electronic equipment.

Considering these major uses of HBCD, the following use, reuse of articles, products and material/recycling flows could be assessed in the country or in imports:

### HBCD as chemical and chemical product

HBCD is still produced, traded and used in product (CAS numbers 3194-55-6 (non specific); 25637-99-4 (isomer mixture); 134237-50-6 ( $\alpha$ -HBCD); 134237-51-7 ( $\beta$ -HBCD); 134237-52-8 ( $\gamma$ -HBCD)). Chemicals imported or used for flame retarding materials (in particular polystyrene and textiles) could be monitored for HBCD if the chemical identity is unclear.

### HBCD in polystyrene used in construction (EPS, XPS)

The major use of HBCD has been in EPS and XPS in the construction sector. Insulation foam in buildings is the only use exempted under the Stockholm Convention. There are a large variety of EPS and XPS uses in the construction sector (see HBCD inventory guidance). Depending on the flammability standards in a country and production policy all or only some of these materials might be flame retarded. For countries with flammability standards requirements, for all EPS/XPS applications in construction flame retardants might be needed (e.g. Germany, Netherlands, UK). Other countries might only require for wall and ceiling insulation or might not have standards at all. For an overview of the use and presence of HBCD in construction different EPS and XPS application can be screened in particular if the use of HBCD is unclear in the country.

### HBCD in polystyrene used in EPS and XPS in uses other than construction

While EPS/XPS packaging does normally not need flame retardants, HBCD has been found in some packaging including food packaging (Rani et al. 2013).

HBCD has also been detected in EPS buoy used for fish/muscle farming with associated contamination (Hong et al. 2013)<sup>180</sup>. The total HBCD levels were lower than used for flame retarding and therefore most likely resulted from recycling of EPS.

Therefore EPS and XPS in packaging including food packaging and disposal dishes and drinking cups might be assessed for cross contamination from recycling. Also other uses of EPS/XPS might be screened for (cross) contamination.

### HBCD in textiles

The second most important application of HBCD has been in polymer dispersion on cotton or cotton mixed with synthetic blends and synthetic. Treated textiles are mainly used in upholstery fabrics such as upholstery in residential and commercial furniture and vehicle seating upholstery, draperies and wall coverings, interior textiles (e.g. roller blinds) and automobile interior textiles. Therefore monitoring in textile would address such potentially flame retarded textile applications.

<sup>179</sup> Secretariat of the Stockholm Convention (2015) Guidance for the inventory, identification and substitution of Hexabromocyclododecane (HBCD) (Draft April 2015).

<sup>180</sup> Hong SH, Jang M, Rani M, Han GM, Song YK, Shim WJ. (2013). Expanded polystyrene (EPS) buoy as a possible source of HBCDs in the marine environment. *Organohalogen Compounds* 75, 882-885.



### **HBCD in cars and other vehicles**

HBCD has been applied in vehicles in textiles and other synthetic materials such as carpets and floor mats. An initial screening of car interior have revealed possibly impacted parts and materials (Kajiwara et al. 2014)<sup>181</sup>. Also other vehicles (busses, trains, air planes, ships) can contain HBCD in treated synthetics in different uses.

### **HBCD in minor uses (Latex binders; adhesives and paints)**

A minor use of HBCD was as additive to latex binders, adhesives and paints. Within a screening latex binders and fire resistant paints could be screened.

### **Waste polystyrene (EPS, XPS, HIPS) used for recycling and related products**

Polystyrene can be recycled. However the Convention is restricting the recycling of HBCD containing polystyrene. Therefore some control and monitoring would be done for polystyrene materials (EPS, XPS and HIPS) used for recycling. The materials can be assessed by screening approach (XRF) combined with confirmation analysis. Also products and articles made from recycled EPS/XPS or HIPS. E.g. the assessment of EPS buoy<sup>182</sup> showed that HBCD containing EPS has been partly used. Also in some countries EPS beads are used in potting soil.

HBCD-containing HIPS has been used in electric and electronic appliances, such as in audio visual equipment cabinets, in refrigerator lining as well as in distribution boxes for electrical lines and certain wire and cable applications (UNEP 2010)<sup>183</sup>. Overall EEE polymers are a minor HBCD use and PBDE and other BFR are/have been used in higher volumes. However in particular for HIPS HBCD can be present as flame retardant. Therefore HIPS from WEEE for recycling from import or generated in the country could be monitored for HBCD.

### **HBCD in biosolids, sewage sludge and industrial sludges**

Industrial/sewage sludge and related “biosolids” are a sink for a range of POPs released from consumer goods (e.g. POP-BFRs, PFOS and related chemicals) or industrial processes. In some countries, regulation limits exist for POPs in sewage sludge and/or biosolids (e.g. PCBs, PCDD/PCDF or PFOS and related chemicals). HBCD contaminated sludge and biosolids might originate from wastewater treatment plants related to HBCD production and industrial use. Companies exporting or importing biosolids/organic fertilizer need to assure the origin of the biosolids and guarantee certain pollutant levels including POPs and heavy metals.

<sup>181</sup> Kajiwara N, Takigami H, Kose T, Suzuki G, Sakai S. (2014). Brominated flame retardants and related substances in the interior materials and cabin dusts of end-of-life vehicles collected in Japan. *Organohalogen Compounds* 76, 1022-1025.

<sup>182</sup> Hong SH, Jang M, Rani M, Han GM, Song YK, Shim WJ. (2013). Expanded polystyrene (EPS) buoy as a possible source of hexabromocyclododecanes (HBCDs) in the marine environment. *Organohalogen Compounds* 75, 882-885.

<sup>183</sup> UNEP. (2010). Risk profile on hexabromocyclododecane. UNEP/POPS/POPRC.6/13/Add.2.

## Annex 1-D: PCP and its salts and esters in articles and products

The major uses of PCP and its salts and esters are described in the PCP inventory guidance<sup>184</sup>. PCP has been produced since the 1930s. It is still produced and used in particular as wood preservative for utility poles and cross arms listed as exempted use in the Stockholm Convention.

Due to the contamination of PCP with polychlorinated dibenzo-p-dioxin and dibenzofuran the monitoring for PCP can integrate a monitoring for PCDD/PCDF for selected samples.

### PCP as chemical and in chemical products

PCP is still produced, traded and used in chemical product (Pentachlorophenol (CAS No: 87-86-5), sodium pentachlorophenate (CAS No: 131-52-2 and 27735-64-4 (as monohydrate)), pentachlorophenyl laurate (CAS No: 3772-94-9) and pentachloroanisole (CAS No: 1825-21-4)). Chemicals imported or used for wood treatment or leather treatment could be monitored for PCP if the chemical identity is unclear or suspicious.

Related to the production of PCP are highly PCDD/PCDF contaminated residues.<sup>185</sup> Production residues and landfill leachates where production residues have been disposed can be sampled and analysed for PCP and PCDD/PCDF.

### PCP and Na-PCP in treated wood

The major worldwide use of PCP has been as a heavy-duty wood preservative, used for utility poles and pilings, railway sleepers, laminated beams for bridge construction, sound barriers, fence posts and other outdoor construction materials and as a surface biocide for masonry (UNEP, 2013d). In the USA and Canada PCP is only allowed as a heavy duty wood preservative for industrial use, primarily for the treatment of utility poles and cross-arms, which account for more than 90% of PCP-consumption in those countries with the remainder being wood treated for other uses (and railway sleepers) (UNECE 2010).

Na-PCP is currently used in India, mainly for wood preservation purposes-impregnated wood/particle boards.

### Waste wood used in recycling

Waste wood is recycled in a range of articles. The recycling of PCP treated waste wood into bedding in stables has resulted in PCDD/F and PCP exposure of chicken and resulting PCDD/F contamination in eggs.<sup>186</sup>

### Recovery of PCP treated wood in biomass incineration and related products

The incineration of PCP-treated wood can result in high PCDD/F release and has resulted in contamination of animal feed and animal products.<sup>187, 188</sup> Ashes from incineration of PCP treated wood can contain high levels of

<sup>184</sup> Secretariat of the Stockholm Convention (2017) Guidance on preparing inventories of pentachlorophenol (PCP) and its salts and esters and on identifying safer alternatives for the phasing out of these chemicals (Draft 2017).

<sup>185</sup> UNEP (2013) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on Persistent Organic Pollutants. Source Group II.7 Production and use of chemicals [http://toolkit.pops.int/Publish/Main/II\\_07\\_Chemicals.html](http://toolkit.pops.int/Publish/Main/II_07_Chemicals.html)

<sup>186</sup> Brambilla G, Fochi I, De Filippis SP, Iacovella N, di Domenico A (2009) Pentachlorophenol, polychloro dibenzodioxin and polychloro dibenzofuran in eggs from hens exposed to contaminated wood shavings. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 26, 258-264.

<sup>187</sup> Fiedler H, Hutzinger O, Welsch-Pausch K, Schmiedinger A (2000) Evaluation of the Occurrence of PCDD/F and POPs in Wastes and Their Potential to Enter the Foodchain. Study on behalf of the European Commission, DG Environment, 30. September 2000.

<sup>188</sup> Hoogenboom R, Bovee T, et al. (2004) Short communication The German bakery waste incident; use of a combined approach of screening and confirmation for dioxins in feed and food Talanta 63 1249–1253

### **PCP in leather**

PCP was used as major preserve in leather treatment. In some countries PCP might still be used in leather treatment and the UNEP. Leather products produced from 1950s to 1990s have a higher probability to contain PCP and related PCDD/PCDFs.

### **PCP in textile**

PCP and PCPL was used in the preservation of textiles and fabrics, particularly those used in heavy-duty military applications, which are subject to attack by fungi and bacteria during storage and use. These include wool, cotton, flax and jute fabrics and yarns used in covers, tarpaulins, awnings, tents, webbing, netting, sails and ropes (OSPAR, 2004).

### **PCP in artwork**

PCP and other POPs pesticides has been used to treat art work in museum including wood and textiles from 1950s to 1980s.

### **PCP in biosolids, sewage sludge and industrial sludge**

Sewage sludge and related biosolids are final sinks for a range of POPs (e.g. PCBs, PCDD/PCDFs, HCB). PCP was the main source of PCDD/PCDF in sewage sludge until around 1990s/2000.<sup>189, 190</sup> In recent years the impact of PCP on sewage sludge was minor. Companies exporting or importing biosolids/organic fertilizer need to assure the origin of the biosolids and guarantee certain pollutant levels including POPs and heavy metals. Sludge with impact from wood treatment facilities can still be contaminated.

<sup>189</sup> Zennegg M, Munoz M, Schmid P, Gerecke AC. (2013) Temporal trends of persistent organic pollutants in digested sewage sludge (1993-2012). *Environ Int.* 60, 202-208.

<sup>190</sup> Hagenmaier H, Brunner H, Haag R, Berchtold A (1986) PCDDs and PCDFs in sewage sludge, river and lake sediments from south west Germany. *Chemosphere* 15, 1421-1428.

## Annex 1-E: PCNs in articles and products

The major former uses of PCNs are described in the PCN inventory guidance<sup>191</sup>. PCNs were mainly produced and used from 1930 to 1970s with the stop of production for the use in products and articles around 2000. Furthermore PCNs are unintentionally produced in organochlorine production and in thermal processes.

### PCNs as chemical and intermediate

Parties to the Stockholm Convention shall prohibit and/or eliminate the production of PCNs, except if they have notified the Secretariat of their intention to utilize the time-limited specific exemption for production and use of PCNs as intermediate for the production of polyfluorinated naphthalenes, as provided in Annex A to the Convention. The Party registering the specific exemptions should provide to the Secretariat the information on the production and use of PCNs. PCN and PCN mixtures produced for the production of fluorinated PFNs as well as the PFNs produced from PCNs can be analysed for PCN content and contamination.

Wastes and stocks from PCN production and former PCN productions could be analysed for PCN content and contamination including waste disposed in landfills of such productions.

### PCNs as chemical and in chemical products

The production of PCNs as intermediate for the production of polyfluorinated naphthalenes has a time-limited specific exemption in the convention. The PCN products, the PFNs and wastes from these productions could be analysed for PCN content and compositions.

### PCNs (and PCBs) in transformers and condensers

A major use of PCNs was in capacitors, particularly in the impregnated paper, since the 1930s.<sup>192</sup> PCNs have been used in capacitors from 1930s until 1980s. PCNs have been used for a slightly longer period than PCBs, which were mainly used from 1940s to 1980s. However the product and overall use volume of PCBs were ca. 10 times larger than that of PCNs.<sup>217</sup> Therefore capacitors produced from 1930 and 1980 can be monitored for PCNs together with the monitoring with PCBs.

The amount of PCNs in transformer oils was considerably smaller than PCBs. There has been no report of a transformer containing pure PCNs in the frame of the Stockholm Convention inventory work until now.<sup>217</sup> Therefore the amount of pure PCN transformers can be considered small. However PCNs exist as unintentional contaminants in all PCB transformer oils since commercial PCBs contained traces of PCNs (0.01–0.09% of PCB content).<sup>217</sup>

### PCNs (and PCBs) in hydraulic oils

PCNs - like PCBs - have been used in hydraulic fluids in the mining sector at least until 1989.<sup>193</sup>

### PCNs (and PCBs) in paints and coatings

PCNs have been used in lacquers and underwater paints and as raw materials for dyes until 1980s.<sup>192, 194</sup> PCNs has most likely been used similarly to PCBs in paints and coatings as corrosion protection for metal constructions such as bridges, towers, ships, pressure pipes,

<sup>191</sup> Secretariat of the Stockholm Convention (2017) Guidance on preparing inventories of pentachlorophenol (PCP) and its salts and esters and on identifying safer alternatives for the phasing out of these chemicals (Draft 2017).

<sup>192</sup> Jakobsson E, Asplund L (2000). Polychlorinated Naphthalenes (CNs). In: J. Paasivirta, ed. The Handbook of Environmental Chemistry, Vol. 3 Anthropogenic Compounds Part K, New Types of Persistent Halogenated Compounds. Berlin, Springer-Verlag.

<sup>193</sup> Popp W, Norpoth K, Vahrenholz C, Hamm S, Balfanz E, Theisen J (1997) Polychlorinated naphthalene exposures and liver function changes. American journal of industrial medicine, 32(4), 413–416.

<sup>194</sup> IPCS (2001) Chlorinated Naphthalenes. Concise International Chemical Assessment Document 34 World Health Organization. Geneva, 2001. ISBN 92-4-153034-0.

water sluices, electricity poles, transformers, tanks (outdoor and indoor) and machinery<sup>195,196,197,198,199</sup> USEPA 2000; USEPA 2013; Wagner et al. 2014). For PCBs it has been described that such additives were mainly used in chloroprene paints and chloroprene lacquers as well as in PVC copolymers (BUWAL 2000). Chloroprene paints containing PCNs or PCBs were also used in underwater paints and lacquers for concrete and brick. They were used as undercoat and as top coat/covering colour (BUWAL 2000). Concentrations ranged from 5 to 35% (BUWAL 2000).

Since both PCBs and PCNs have similar open applications in paints and painted constructions and equipment with PCBs in a larger volume than PCNs, both PCBs and PCNs would be addressed in the inventory of such applications.

### **PCNs (and PCBs) in polymers (cables)**

The use of PCNs as flame retardants in cables and cable sheaths was a major use of PCNs.<sup>192</sup> Other POPs (PCBs, POP-PBDEs) have also been used as flame retardants in cables/cable sheaths.

The major use of PCNs was from 1920s to 1960s and most of these cables from electrical equipment have already entered end of life and have either been disposed to landfills, treated in cable recycling or other end of life treatment and would therefore not require a specific inventory or management activity. Cables in construction of houses or other long term use might still exist. Cables containing PCBs (used in the 1960s/1970s) and POP-PBDEs (produced since the 1970s) are partly still in use. When screening PCNs in cables, also PCBs and POP-PBDEs could be measured.

### **PCNs (and PCBs) in sealants**

The use of PCNs in sealants and putty has been reported until around 2000.<sup>200</sup> For PCBs, sealants/ caulks and putty in buildings and other constructions have been major open applications<sup>201,199</sup> while for PCNs those applications were minor. Typical sealants containing PCBs were polysulfide sealants of different brands (e.g. Thiokol, Thioflex, Vulkseal, Vulkfil, Lasto-meric, 1K, Terostat, PRC and Rubberseal). Due to the similar properties, these sealants may also contain PCNs. Other sealants that contain PCBs and potentially PCNs are polyurethane, acrylic and butyl sealants. PCBs and PCNs have not been used in silicone sealants. Sealants containing PCBs or PCNs have also been used in putty for windows. Sealants in buildings can contain 5 to 30% of PCBs.<sup>202</sup>

<sup>195</sup> Eklund B, Eklund D (2014) Pleasure Boatyard Soils are Often Highly Contaminated. *Environmental Management* 53, 930–946.

<sup>196</sup> ELSA (2016) PCB in der Elbe – Eigenschaften, Vorkommen und Trends sowie Ursachen und Folgen der erhöhten Freisetzung im Jahr 2015. Behörde für Umwelt und Energie Hamburg, Projekt Schadstoffsanierung Elbsedimente.

<sup>197</sup> PCB Elimination Network (2014) PCB Open Application - Identification and Environmentally Sound Management.

<sup>198</sup> Jartun M, Ottesen RT, Steinnes E, Volden T (2009) Painted surfaces--important sources of polychlorinated biphenyls (PCBs) contamination to the urban and marine environment. *Environ Pollut.* 157(1), 295-302.

<sup>199</sup> Wagner U, Schneider E, Watson A, Weber R (2014) Management of PCBs from Open and Closed Applications - Case Study Switzerland. GIZ Global Chemicals Waste Information Platform [http://www.global-chemicals-waste-platform.net/fileadmin/files/doc/Management\\_of\\_PCBs\\_Case\\_Study\\_Switzerland.pdf](http://www.global-chemicals-waste-platform.net/fileadmin/files/doc/Management_of_PCBs_Case_Study_Switzerland.pdf)

<sup>200</sup> Yamashita N, Taniyasu S, Hanari N, Falandysz J (2003) Polychlorinated naphthalene contamination of some recently manufactured industrial products and commercial goods in Japan. *J Environ Sci Health A* 38:1745–1759.

<sup>201</sup> USEPA (2015) PCBs in Building Materials—Questions & Answers. July 28, 2015.

<sup>202</sup> Priha E, Hellman S, Sorvari J (2005) PCB contamination from polysulphide sealants in residential areas-exposure and risk assessment. *Chemosphere* 59, 537-543.



### PCNs in rubber

PCNs have been used in chloroprene rubber until around 2000<sup>200,203</sup>. Such chloroprene rubber has been used in rubber belts, rubber belts for printers and shock absorbing materials.

### PCNs in treated wood

PCNs have been used in wood preservatives in the past. Higher chlorinated PCN mixtures were used in the 1920s to 1970s while lower chlorinated naphthalenes were used until 1987.<sup>192</sup> Treated wood used in construction of buildings might still exist to a share while other wood applications might already have entered end of life.

In addition to PCNs, other POPs have been used in wood treatment such as pentachlorophenol (PCP and PCP-Na), DDT, dieldrin, endosulfan, HCHs/lindane, mirex and PCBs. In an inventory of treated wood, all POPs used for wood impregnation could be addressed and managed.

### PCNs in military applications

Some use of PCNs has been reported for military purposes such as fog ammunition<sup>204</sup> and inert artillery and mortar projectiles with associated pollution on military training sites.<sup>205,206,207</sup>

### PCN applications not considered relevant

Some former uses of PCNs are not considered relevant for inventory purposes since the related products have entered end of life decades ago and are in landfills or have been released to the environment. These include textiles, water proof and flame retarded paper, battery separator and oils in open applications such as lubricant and cutting oils.

### Unintentionally produced PCNs

#### *Unintentional PCNs in the production of chlorinated solvents*

Unintentional POPs are formed in the production of chlorinated solvents where the smaller organochlorine compounds undergo condensation reactions and build-up of aromatic compounds including unintentional POPs.<sup>208</sup> High levels of unintentional POPs like HCB and PCNs are formed in the production of chlorinated solvents such as tetrachloroethylene, trichloroethylene and ethylene dichloride.<sup>209,210,211</sup> In the solvents production, the crude products are distilled and the residues with high boiling points “heavy ends” including the unintentional POPs like PCNs, PCBs and HCBd are separated from the solvents.<sup>208,210</sup>

<sup>203</sup> Yamamoto T, Noma Y, Sakai S (2016) Thermal destruction of wastes containing polychlorinated naphthalenes in an industrial waste incinerator. *Environ Sci Pollut Res* DOI 10.1007/s11356-016-7100-8.

<sup>204</sup> Generalstab Schweizer Armee (1945) Bericht des Chefs des Generalstabes der Armee an den Oberbefehlshaber der Armee über den Aktivdienst 1939-1945. Pp 322-326.

<sup>205</sup> Clausen J, Robb J, Curry D, Korte N (2004) A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA. *Environ Pollut* 129 (1), 13-21.

<sup>206</sup> Hewitt A D, Jenkins T F, Bigl S R, Clausen J L, Craig H, Walsh M E, Martel R, Nieman K (2011) EPA federal facilities forum issue paper: Site characterization for munitions constituents.

<sup>207</sup> Falandysz J (1998) Polychlorinated naphthalenes: an environmental update. *Environ Pollut* 101, 77–90

<sup>208</sup> UNEP (2015b) Formation and release of unintentional POPs from production processes for pesticides and industrial chemicals: Review of new information for reducing or preventing releases and related information gaps. UNEP/POPS/TOOLKIT/BATBEP/2015/2

<sup>209</sup> Mumma CE, Lawless EW (1975) Survey of Industrial Processing Data: Task I - Hexachlorobenzene and Hexachlorobutadiene Pollution from Chlorocarbon Processing. Midwest Research Institute prepared for US Environmental Protection Agency. June 1975. Available online at National Service Center for Environmental Publications (NSCEP).

<sup>210</sup> Zhang L, Yang W, Zhang L, Lib X (2015) Highly chlorinated unintentionally produced POPs generated during the methanol-based production of chlorinated methanes: a case study in China. *Chemosphere* 133, 1–5.

<sup>211</sup> Weber R, Watson A, Malkov M, Costner P, Vijgen J (2011) Unintentionally produced hexachlorobenzene and pentachlorobenzene POPs waste from solvent production – the need to establish emission factors and inventories. *Organohalogen Compounds* 73, 2205-2208. <http://www.dioxin20xx.org/pdfs/2011/5002.pdf>



### ***Unintentional PCNs in the production of chlorinated paraffins***

Chlorinated paraffins are produced by chlorination of C10–C30 n-alkanes from petroleum using molecular chlorine, either of the liquid paraffin or in a solvent. A first assessment of unintentional POPs in chlorinated paraffins detected PCNs (and PCBs) at a concentration of approx. 40 mg/kg.<sup>212</sup>

### ***Unintentional PCNs in the production of chlorine***

High levels of PCNs have been formed during production of chlorine via chloralkali electrolysis when graphite electrodes have been used. PCNs levels were higher than that of PCDF.

### ***Unintentional PCNs in thermal processes***

PCNs are formed together with PCDD/PCDFs in thermal processes such as incineration or metal industries by the same mechanism.<sup>213,214</sup> The total concentration of PCNs in waste incineration are in the same order of magnitude as PCDD/PCDFs with somewhat higher levels of PCNs in the gas phase<sup>215</sup> and similar levels in fly ash.<sup>213</sup>

### **PCNs in waste fractions**

Since PCNs have been produced and used between 1920 to approx. 2000, most products and articles containing PCNs are at in the end of life phase or have already entered end of life the last decades and PCNs have been included a Basel Guideline<sup>216</sup>.

The Basel Convention waste fractions with high risk of PCN contamination such as category Y5, Y 10, Y12, Y45, A1090, A1100; A1190; A3040; A3180; A3180 could be analysed for PCN content. A list of waste fractions potentially containing PCNs are listed in Table A1-2.

<sup>212</sup> Takasuga T, Nakano T, Shibata Y (2012) Unintentional POPs (PCBs, PCBz, PCNs) contamination in articles containing chlorinated paraffins and related impacted chlorinated paraffin products. Presentation, Dioxin 2012, 26-31. August, Cairns/Australien.

<sup>213</sup> Imagawa T, Lee CW (2001) Correlation of polychlorinated naphthalenes with polychlorinated dibenzofurans formed from waste incineration. Chemosphere. 44(6), 1511-1520.

<sup>214</sup> Weber R, Iino F, Imagawa T, Takeuchi M, Sakurai T, Sadakata M (2001) Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: mechanistic aspects and correlation to fluidized bed incinerators. Chemosphere. 44(6), 1429-1438.

<sup>215</sup> Takasuga T, Inoue T, Ohi E, Kumar KS (2004) Formation of Polychlorinated Naphthalenes, Dibenzo-p-Dioxins, Dibenzofurans, Biphenyls, and Organochlorine Pesticides in Thermal Processes and Their Occurrence in Ambient Air. Arch. Environ. Contam. Toxicol. 46, 419–431.

<sup>216</sup> UNEP (2017) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls, polychlorinated terphenyls, polychlorinated naphthalenes or polybrominated biphenyls including hexabromobiphenyl. UNEP/CHW.13/6/Add.4.

**Table A1-2:** Basel Convention waste categories that might contain or be contaminated with PCNs (UNEP 2017)<sup>216</sup>

Basel Conv. Annex category	Category	Type of waste
Annex 1	Y5	Wastes from the manufacture, formulation and use of wood preserving chemicals;
	Y6	Wastes from the production, formulation and use of organic solvents;
	Y8	Waste mineral oils unfit for their originally intended use
	Y9	Waste oils/water, hydrocarbons/water mixtures, emulsions;
	Y10	Waste substances and articles containing or contaminated with PCBs and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs);
	Y11	Waste tarry residues arising from refining, distillation and any pyrolytic treatment
	Y12	Wastes from production, formulation and use of inks, dyes, pigments, paints, lacquers, varnish
	Y13	Wastes from production, formulation and use of resins, latex, plasticizers, glues/adhesives)
	Y18	Residues arising from industrial waste disposal operations;
	Y41	Halogenated organic solvents.
	Y45	Organohalogen compounds other than substances referred to in this Annex (e.g. Y39, Y41, Y42, Y43, Y44)
List A of Annex VIII	A1190	Waste metal cables coated or insulated with plastics containing or contaminated with coal tar, PCBs, lead, cadmium, other organohalogen or Annex I compounds to exhibit Annex III characteristics;
	A1090:	Ashes from the incineration of insulated copper wire;
	A1100:	Dusts/residues from gas cleaning systems of copper smelters;
	A3040	Waste thermal (heat transfer) fluids;
	A3160	Waste halogenated or unhalogenated non-aqueous distillation residues arising from organic solvent recovery operations;
	A3170	Wastes arising from the production of aliphatic halogenated hydrocarbons
	A3180	Wastes, substances and articles containing, consisting of or contaminated with PCBs, PCT, PCNs, PBB, or any other polybrominated analogues of these compounds, at a concentration level of 50 mg/kg* or more;
	A4140	Waste consisting of or containing of specification or outdated chemicals corresp. to Annex I categories and exhibiting Annex III haz. characteristics;
List B of Annex IX	B1040	Scrap assemblies from electrical power generation not contaminated with lubricating oil, PCB or PCT to an extent to render them hazardous;
	B3040	Rubber wastes ((i) Waste and scrap of hard rubber (e.g., ebonite); (ii) Other rubber wastes (excluding such wastes specified elsewhere).

\*The provisional suggested low POP content for PCN is [10 mg/kg or 50 mg/kg]<sup>216</sup>

## Annex 1-F: HCBd in articles and products

The generation and major (former) uses of HCBd is described in the HCBd inventory guidance<sup>217</sup>. Most of production of HCBd has likely stopped. HCBd is generated in a range of industrial processes which can be assessed for the presence of HCBd (and possibly unintentional POPs):

### HCBd in use equipment and stockpiles<sup>216</sup>

The most important HCBd uses for currently used equipment, stockpiles and waste streams in terms of potential releases or concentration are expected to be:<sup>216</sup>

- Transformer, heat exchange and hydraulic fluids;
- Obsolete HCBd insecticide stockpiles and fungicide waste.

### Intentional and unintentional generation of HCBd in the production of tetrachloroethylene, trichloroethylene, and tetrachloromethane

HCBd is unintentionally generated during the production of certain organochlorine solvents, particularly tetrachloroethylene, trichloroethylene, and tetrachloromethane/carbon tetrachloride<sup>218,219</sup> (Lecloux 2004). Although the production of HCBd is banned it might be separated from the raw product and possibly still marketed (see HCBd inventory guidance<sup>217</sup>).

In addition to HCBd, wastes and possibly products from the production of these organochlorine solvents can contain hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs)<sup>210,211,220,221</sup> and lower levels of PCDD/PCDFs<sup>210</sup>.

Samples at organochlorine solvent production sites which might be sampled and analysed for HCBd and unintentional POPs are the raw products, the solvents, the heavy end after distillation of the solvents and other products marketed from these processes.

### HCBd in chlorinated solvents

Chlorinated solvents tetrachloroethylene, trichloroethylene or tetrachloromethane/carbon tetrachloride might be contaminated with HCBd.<sup>222,223</sup> These and possibly other organochlorine solvents and hexachlorocyclopentadiene can be sampled and analysed for HCBd content.

### Unintentional generation of HCBd in the production of other organochlorines

HCBd is unintentionally formed or reported to be possibly formed in other processes from the organochlorine and chlorine industry where levels are likely small to moderate and therefore cannot be separated and recovered for HCBd production/use (see chapter 4.5 of HCBd inventory guidance<sup>217</sup>). These include ethylene dichloride, vinyl chloride monomer, chloroprene

<sup>217</sup> Secretariat of the Stockholm Convention (2017) Guidance on preparing inventories of pentachlorophenol (PCP) and its salts and esters and on identifying safer alternatives for the phasing out of these chemicals (Draft).

<sup>218</sup> Mumma CE, Lawless EW (1975) Survey of Industrial Processing Data: Task I - Hexachlorobenzene and Hexachlorobutadiene Pollution from Chlorocarbon Processing. Midwest Research Institute prepared for US Environmental Protection Agency. June 1975. Available online at National Service Center for Environmental Publications (NSCEP).

<sup>219</sup> Lecloux A (2004) Hexachlorobutadiene – Sources, environmental fate and risk characterization. Science Dossier, EuroChlor.

<sup>220</sup> Dow Chemical. 1990. Waste Analysis Sheet: Heavy Ends from the distillation of Ethylene Dichlorine in Ethylene Dichloride Production. Plaquemine, LA, February 21.

<sup>221</sup> Thornton J (2001) Environmental Impacts of Polyvinyl Chloride Building Materials. A Healthy Building Network Report.

<sup>222</sup> BUA (1991) Hexachlorobutadiene. BUA Report 62. GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA).

<sup>223</sup> Environment Canada 2004. Risk Management Strategy - Update 2004 Hexachlorobutadiene (HCBd).

and possibly allyl chloride and epichlorohydrin<sup>224</sup>. HCBd might also be formed during the production of chlorine.<sup>218</sup> Products and wastes from these industries might contain HCBd at levels above the provisional low POPs content which should be included in the HCBd inventory. Also unintentionally produced POPs might be formed in these processes. Therefore in addition to HCBd<sup>225</sup>, products and wastes from the production of these chemicals can also be analysed for other unintentional POPs.

### **Unintentional production of HCBd in thermal processes<sup>226</sup>**

HCBd is unintentionally formed in some thermal processes. HCBd is unintentionally formed in the production of magnesium.<sup>219,227</sup> HCBd is also generated when hexachloroethane (or other organochlorine) is used for refining of the magnesium or aluminium production<sup>228,229</sup>.

HCBd might also be unintentionally formed in incineration processes in particular when incinerating wastes with high chlorine content such as residues from organochlorine production<sup>230,231</sup>. There is no study which has shown that HCBd is formed and released from municipal waste incinerators. Considering findings from laboratory tests with CuCl<sub>2</sub> and acetylene, HCBd might be formed together with other unintentional POPs in secondary copper smelters.

### **HCBd in ground water and drinking water around organochlorine disposal sites**

Ground water and drinking water close to landfills from the organochlorine industry has been found contaminated by HCBd and other pollutants.<sup>232,233</sup> Health assessment found likely health impact in humans<sup>232</sup> indicating that in addition to ground water and drinking water, human exposure and effects should be monitored and assessed. In addition also leachates from such landfills would be a matrix to sample and analyse for release.

### **HCBd in fish around organochlorine production sites and related disposal sites**

Fish and other biota in surface waters impacted from organochlorine industry and related landfills might have increased levels of HCBd (and other unintentional POPs).<sup>234</sup> In particular

<sup>224</sup> In a dossier for Eurochlor the presence of HCBd in these processes was considered unlikely from a chemical point of view (LeCloux 2004)<sup>219</sup>.

<sup>225</sup> UNEP (2017) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene. UNEP/CHW.13/6/Add.2.

<sup>226</sup> While HCBd is not currently listed in Annex C of the Convention but acknowledged to be formed unintentionally by the POPs Review Committee, Parties interested in the management and reduction of HCBd from thermal sources could assess the release of HCBd from thermal sources and related wastes and stockpiles.

<sup>227</sup> Van der Honing M (2007) Exploration of management options for Hexachlorobutadiene (HCBd) Paper for the 6th meeting of the UNECE CLRTAP Task Force on Persistent Organic Pollutants, Vienna, 4-6 June 2007. SenterNovem, The Netherlands, 2007.

<sup>228</sup> U.S. National Toxicology Program (2011) NTP 12th Report on Carcinogens. Rep Carcinog. 2011;12:iii-499.

<sup>229</sup> Vogelgesang J, et al. (1986) The origin of a contamination of fish from the river Neckar with HCB, octachlorostyrene and pentachlorobenzene: Formation in an industrial process II. The formation of contaminants in the degassing of an aluminium foundry with chlorine. Z Lebensm Unters Forsch. 182, 471-474.

<sup>230</sup> INERIS (2005) Les substances dangereuses prioritaires de la directive cadre sur l'eau. Fiches de données technicoéconomiques, Rapport Ministère de l'Écologie et du Développement Durable.

<sup>231</sup> UNEP (2013) Risk management evaluation on hexachlorobutadiene. Addendum Report of the Persistent Organic Pollutants Review Committee on the work of its ninth meeting. UNEP/POPS/POPRC.9/13/Add.2

<sup>232</sup> Clark CS, Meyer CR, et al. (1982) An environmental health survey of drinking water contamination by leachate from a pesticide waste dump in Hardeman County, Tennessee. Arch Environ Health. 37(1), 9-18.

<sup>233</sup> Forter M (2016) Hexachlorobutadiene in the drinking water of the City of Basel (Switzerland), the Rhine and the chemical landfill „Feldreben“ of BASF, Novartis and Syngenta. Conference proceeding; 13 IHPA Forum, November 03-06, 2015, Zaragoza, Spain.

<sup>234</sup> U.S. Department of Health and Human Services (2006) Health Consultation – Devils Swamp Lake a review of fish data East Baton Rouge parish, Louisiana EPA Facility ID: LAD985202464.

industries producing organochlorine solvents and related landfills and potential releases to surface water and associated accumulation in biota including edible fish would be assessed.

### HCBD in wastes in import and export

Import and export of HCBD-containing wastes may take place for the purpose of environmentally sound disposal in accordance with the Basel Convention procedures for transboundary movement of hazardous wastes. Table 1-3 compiles major Basel Convention waste with may consist, contain or be contaminated with HCBD. A provisional low POP content value for HCBD define a waste as POPs waste and has been set to [1] or [100] mg/kg.<sup>225</sup>

**Table 1-3:** Major Basel Convention waste categories which may consist of or contain HCBD<sup>225,217</sup>

Basel Conv. Annex category	Category	Type of waste
Annex 1	Y4	Wastes from the production, formulation and use of biocides;
	Y6	Wastes from the production, formulation and use of organic solvents;
	Y9	Waste oils/water, hydrocarbons/water mixtures, emulsions;
	Y10	Waste substances and articles containing or contaminated with PCBs and/or polychlorinated terphenyls (PCTs) and/or PBBs;
	Y11	Waste tarry residues arising from refining, distillation and any pyrolytic treatment
	Y18	Residues arising from industrial waste disposal operations;
	Y41	Halogenated organic solvents.
List A of Annex VIII	A3040	Waste thermal (heat transfer) fluids;
	A3160	Waste halogenated or unhalogenated non-aqueous distillation residues arising from organic solvent recovery operations;
	A3170	Wastes arising from the production of aliphatic halogenated hydrocarbons (such as chloromethane, dichloro-ethane, vinyl chloride, vinylidene chloride, allyl chloride and epichlorhydrin);
	A4030	Wastes from the production, formulation and use of biocides and phytopharmaceuticals, including waste pesticides and herbicides which are off-specification, outdated or unfit for their originally intended use;
	A4060	Waste oils/water, hydrocarbons/water mixtures, emulsions;
	A4100	Wastes from industrial pollution control devices for cleaning of industrial off-gases but excluding such wastes specified on list B;
	A4130	Waste packages and containers containing Annex I substances in concentrations sufficient to exhibit Annex III hazard characteristics;
	A4140	Waste consisting of or containing off-specification or outdated chemicals corresponding to Annex I categories and exhibiting Annex III hazard characteristics;
	A4160	Spent activated carbon not included on list.
List B of Annex IX	B1040	Scrap assemblies from electrical power generation not contaminated with lubricating oil, PCB or PCT to an extent to render them hazardous;
	B3040	Rubber wastes ((i) Waste and scrap of hard rubber (e.g., ebonite); (ii) Other rubber wastes (excluding such wastes specified elsewhere).



## Annex 1-G PeCB and other unintentional POPs (HCB, PCDD, PCDF, PCBs and PCNs) as unintentional trace contaminants in products and articles

Pentachlorobenzene (PeCB) and polychlorinated naphthalenes (PCNs) were added to Annex C (unintentional production) at the 4<sup>th</sup> COP (2009) and 5<sup>th</sup> COP (2015) respectively. Similar to HCB, they are also listed as an intentionally produced POP in SC Annex A. Today, the relevance of PeCB and HCB are rather as trace contaminants in products than from intentional production. However, production of PeCB and HCB also still might take place (see below).

Since the different unintentionally formed POPs are normally formed in most processes at the same time, it is reasonable not to solely address PeCB or PCN in suspected chemicals and articles, but to also address and monitor all listed unintentionally produced POPs in screenings of suspected products and articles. The necessity to screen PCDD/PCDF in products has recently been highlighted by discovery of extreme high levels of PCDD/PCDF (522 µg TEQ/kg) in Chinese chloranil with PCDD/PCDF levels 35 times above the provisional low POPs threshold of the Basel Convention for wastes (Liu et al. 2011).<sup>235</sup> The estimated total PCDD/PCDF content of this currently marketed chemical from China alone was estimated to 1044 g TEQ which is about 10% of China's total PCDD/PCDF inventory, but present directly in treated consumer products. PeCB, HCB, and PCBs were also detected in these chemicals in relevant concentration (Liu et al. 2011).

Unintentionally produced POPs present as unintentional trace contaminants in chemicals, mixtures, and articles can be addressed by lists of chemicals, mixtures, and articles which, from past analysis, have been found to contain these chemicals or are suspected to contain unintentionally produced POPs.

### PeCB and HCB as product

Some companies still offer HCB and PeCB although production and marketing is banned under the Convention. Therefore, trade of these chemicals might still take place. Companies offering HCB and PeCB are listed in the Annexes of the POPs Customs Control Guidance<sup>236</sup>.

### PeCB, HCB, and PCDD/PCDF in pesticides and related organochlorine chemicals

Some pesticides are known to contain or form relevant levels of HCB during production and therefore can be suspected also to contain PeCB. These include, for example, PCNB (CAS No 82-68-8), PCP (CAS No 87-86-5), dimethyltetrachloro terephthalate dacthal (CAS No 1861-32-1), chlorothalonil (CAS No 1897-45-6), and dicloram (CAS No 1918-02-1) (Tobin, 1986).<sup>237</sup>

While releases from production in industrial countries have been reduced, production capacity has shifted to developing/transition countries like China, India, and others. Recent screening of contemporary used pesticides in Australia (Holt et al. 2010) and Chloranil in China (Liu et al. 2011) revealed that PCDD/PCDF were present in all tested products and that some products contained high levels of PCDD/PCDF.

In the updated UNEP standardized toolkit for Dioxin and Furan releases (Stockholm Convention 2013), a range of chemicals are listed which are known or suspected to contain PCDD/PCDF. Since unintentionally produced POPs are normally formed in parallel, these chemicals can be suspected to also contain PeCB, HCB, and PCB. This list might therefore be used for monitoring of PeCB and other unintentionally produced POPs in products and articles.

Samples might be gathered from stakeholders or purchased from the market.

<sup>235</sup> Liu W, Tao F, Zhang W, Li S, Zheng M (2011) Contamination and emission factors of PCDD/Fs, unintentional PCBs, HxCBz, PeCB and polychlorophenols in chloranil in China. *Chemosphere* 86, 248-251.

<sup>236</sup> Stockholm Convention (2017) Guidance for the control of the import and export of POPs (Draft).

<sup>237</sup> Tobin P (1986) Known and potential sources of hexachlorobenzene. In: Morris, C.R.; Cabral, J.R.P. Hexachlorobenzene: Proceedings of an International Symposium. Lyon, IARC Sci. Publ. 77, 1-12.



### PeCB, HCB in pigments and tetrachlorophthalic anhydride

Some pigments based on tetrachlorophthalic anhydride contain relatively high levels of HCB. They can also be suspected to contain PeCB and possibly other unintentionally formed POPs. Japan has informed the Conference of Parties (COP4) of the Stockholm Convention of the high HCB content and suggested BAT levels for HCB in these pigments and in tetrachlorophthalic anhydride ([Government of Japan 2006](#)<sup>238</sup> and [2007](#)<sup>239</sup>). Pigments reported to contain HCB could be monitored for PeCB and other unintentionally produced POPs (Table A1-4).

**Table A1-4:** Pigments known to contain HCB, and possibly PeCB or other unintentionally produced POPs

<b>Pigment/chemical</b>	<b>CAS Registry Number</b>
Pigment Yellow 110	5590-18-1
Pigment Yellow 138	30125-47-4
Pigment Green 7 <sup>240</sup>	1328-45-6 and 1328-53-6
Pigment Green 36	14302-13-7
Solvent Red 135	20749-68-2 and 71902-17-5
Tetrachlorophthalic anhydride	117-08-8

### Unintentionally produced POPs in articles

Articles where chemicals and mixtures have been added or included known or suspected to contain unintentionally POPs could then also contain unintentionally produced POPs, for example, the above mentioned pigments are used in a wide range of products such as plastic, bank notes, and paints. Potentially unintentionally POPs containing biocides are used for treatment of wood or leather (e.g. PCP) or in soap and toothpaste (e.g. triclosan).

### PeCB, HCB, HCB, PCNs, PCBs and PCDD/PCDFs in chlorinated solvent production

During production of certain chlorinated solvents, high amounts of unintentional HCB and PeCB can be formed (UNEP 2010).<sup>241</sup> These include tetrachloroethene (CAS: 127-18-4), trichloroethene (CAS: 79-01-6), and tetrachloromethane (CAS: 56-23-5). The largest part of the unintentionally produced POPs is normally separated in the production by a distillation step from the marketed solvent and remain as heavy distillates (Jacob et al. 1986). It has been reported that these deposits also contain PeCB ([UNEP et al. 2010](#)<sup>242</sup>; [Weber et al. 2011](#)<sup>243</sup>). There is a scarcity of data on the content of HCB and PeCB in chlorinated solvents (UNEP 2010<sup>244</sup>).

<sup>238</sup> Government of Japan (2006) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product November 2006. Submission to COP3.

<sup>239</sup> Government of Japan (2007) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product. April 2007. Submission to COP3.

<sup>240</sup> Due to its stability, Pigment Green 7 is used in inks, coatings, and many plastics. In application, it is transparent. The pigment is insoluble and has no tendency to migrate in the material. It is a standard pigment used in printing ink and packaging industry. It is also allowed in cosmetics except those used around the eyes, and is used in some tattoos.

<sup>241</sup> UNEP (2010) Additional consideration of new persistent organic pollutants: pentachlorobenzene. Stockholm Convention document for 6th POP Reviewing Committee meeting ([UNEP/POPS/POPRC.6/INF/21](#)) Geneva 11-15. October 2010.

<sup>242</sup> UNEP, OCHA, and EU Commission (2010) A Joint United Nations – European Commission Environmental Emergency Response Mission: Technical Scoping Mission Kalush Area, Ukraine March 2010.

<sup>243</sup> Weber R, Watson A, Malkov M, Costner P, Vijgen J (2011) Unintentionally produced hexachlorobenzene and pentachlorobenzene POPs waste from solvent production – the need to establish emission factors and inventories. [Organohalogen Compounds 73, 2205-2208](#).

<sup>244</sup> UNEP (2010) Additional consideration of new persistent organic pollutants: pentachlorobenzene. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/21) Geneva 11-15. October 2010.

Therefore, screening of PeCB, HCB, and possibly other unintentionally formed POPs in chlorinated solvents could be considered.

### Unintentional POPs in biosolids/sewage sludge

Sewage sludge and related biosolids are sinks for unintentionally produced POPs (PCDD/PCDF, PCB, HCB, and PeCB). In some countries, regulation limits exist for POPs in respect to the application on agricultural areas and pasture areas to prevent the contamination of food. Biosolids and organic fertilizers are also traded at the international level and control of POPs levels could be addressed with respect to imports, exports, and trade.

In a survey of sewage sludges in Germany, levels of PeCB and HCB were relatively low (below 10 ng/g) and significantly lower compared to their brominated analogues hexabromobenzene and pentabromobenzene detected at an average concentration of 330 ng/g and 45 ng/g respectively ([Kuch et al. 2005](#)<sup>245</sup>).

While formerly the use of PCP was the main contamination source of PCDD/PCDF in sewage sludge (Zennegg et al. 2013<sup>246</sup>), today elevated levels of PCDD/PCDF in sewage sludges are mainly associated with industries such as the textile industry (Fuente et al. 2007<sup>247</sup>).

### Unintentionally produced POPs (PCDD/PCDFs, PeCB, HCB, PCBs) in food and feed

Food and feed in particular can be contaminated with PCDD/PCDF and other unintentionally produced POPs in connection with historic releases of PCDD/PCDF, intentionally and unintentionally PCBs and other unintentionally produced POPs from industries, contaminated pesticides, or application of contaminated sludge.<sup>248,249</sup> This includes, for example, fish from lakes and rivers or the sea with former PCDD/PCDF, PCBs or other unintentionally produced POPs input.<sup>250</sup> Floodplains of such rivers can also be impacted by PCDD/PCDF and other unintentionally produced POPs with contamination of grazing cattle and related milk and meat.<sup>251</sup> Furthermore, also relevant contamination are eggs and milk from areas where formerly PCDD/PCDF, PCBs or other unintentionally produced POPs contamination has occurred.

If a Party decides to include food and feed into the monitoring of unintentionally produced POPs-containing articles and products, the development of the monitoring concept would be linked to the development of the inventory of PCDD/PCDF, PCBs and other unintentional POPs contaminated sites. A first priority selection of samples can be made based on such an inventory. Monitoring could also include an assessment of the feed market.<sup>252</sup> Furthermore, a monitoring concept could also address imported food and feed.<sup>253</sup>

<sup>245</sup> Kuch B, Schneider C, Metzger JW, Weber R (2005) Hexabromobenzene and Pentabromophenol in German Sewage Sludge – Indication of Significant Commercial Use. [Organohalogen Compounds 67, 434-437](#).

<sup>246</sup> Zennegg M1, Munoz M, Schmid P, Gerecke AC (2013) Temporal trends of persistent organic pollutants in digested sewage sludge (1993-2012). *Environ Int.* 60, 202-208.

<sup>247</sup> Fuentes MJ, Font R, Gomez-Rico MF, Molto J (2007) Multivariate statistical analysis of PCDD/FS in sewage sludges from different areas of the Valencian Community (Spain). *Chemosphere* 67, 1423–1433.

<sup>248</sup> UNEP Stockholm Convention (2012) *ibidem*, Weber et al. (2008) Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. *Env Sci Pollut Res.* 15, 363-393.

<sup>249</sup> Birch GF, Harrington C, Symons RK, Hunt JW (2007) The source and distribution of PCDDs and PCDFs in sediments of Port Jackson, Australia. *Marine Pollution Bulletin* 54, 295-308.

<sup>250</sup> Assmuth T, Jalonen P (2005) Risks and management of dioxin-like compounds in Baltic Sea fish: An integrated assessment. [TemaNord 2005:568](#)

<sup>251</sup> Schulz AJ, Wiesmueller T, et al. (2005) Dioxin concentration in cows' milk in dependence on feed and soil contamination. *Proc. Soc. Nutr. Physiol.*, 14, 52; Schulz AJ, Wiesmueller T, et al. (2005) Dioxin concentration in milk and tissues of cows and sheep related to feed and soil contamination. *J. Anim. Physiol. Anim. Nutr.* 89, 72-78; Kamphues et al. (2011) *Organohalogen Compd.* 73, 2040-2041.

<sup>252</sup> Weber R, Watson A (2011) Assessment of the PCDD/PCDF Fingerprint of the Dioxin Food Scandal from Bio-Diesel in Germany and Possible PCDD/F Sources. [Organohalogen Compounds 73, 400-403](#).

<sup>253</sup> Hussain A, Dashti B, Gevaio B, Al-Wadi M, Brouwer A, Behnisch PA (2011) First Surveillance monitoring results of feed and food samples from markets in Kuwait from international origin for PCDD/PCDF/PCB-TEQ by DR CALUX. [Organohalogen Compounds 73, 2000-2003](#).

## ANNEX 2 Examples for instrumental analysis

Acknowledgement: The analytical conditions and chromatograms were provided by Prof. Dr. Dr. Takumi Takasuga (Shimadzu Techno Research, Kyoto, Japan).

### Annex 2-A: GC/MS analysis of PBDE (instrumental setting and chromatogram)

#### PBDEs GC/MS conditions (example)

An example of instrumental setting for the GC/MS analysis of PBDEs are given in Table A2-1 and the exact masses of native and <sup>13</sup>C-labeled HBB in Table A2-2.

A chromatogram of PBDEs from GC/MS analysis is shown in Figure A2-1.

**Table A2-1:** GC/MS conditions for PBDE

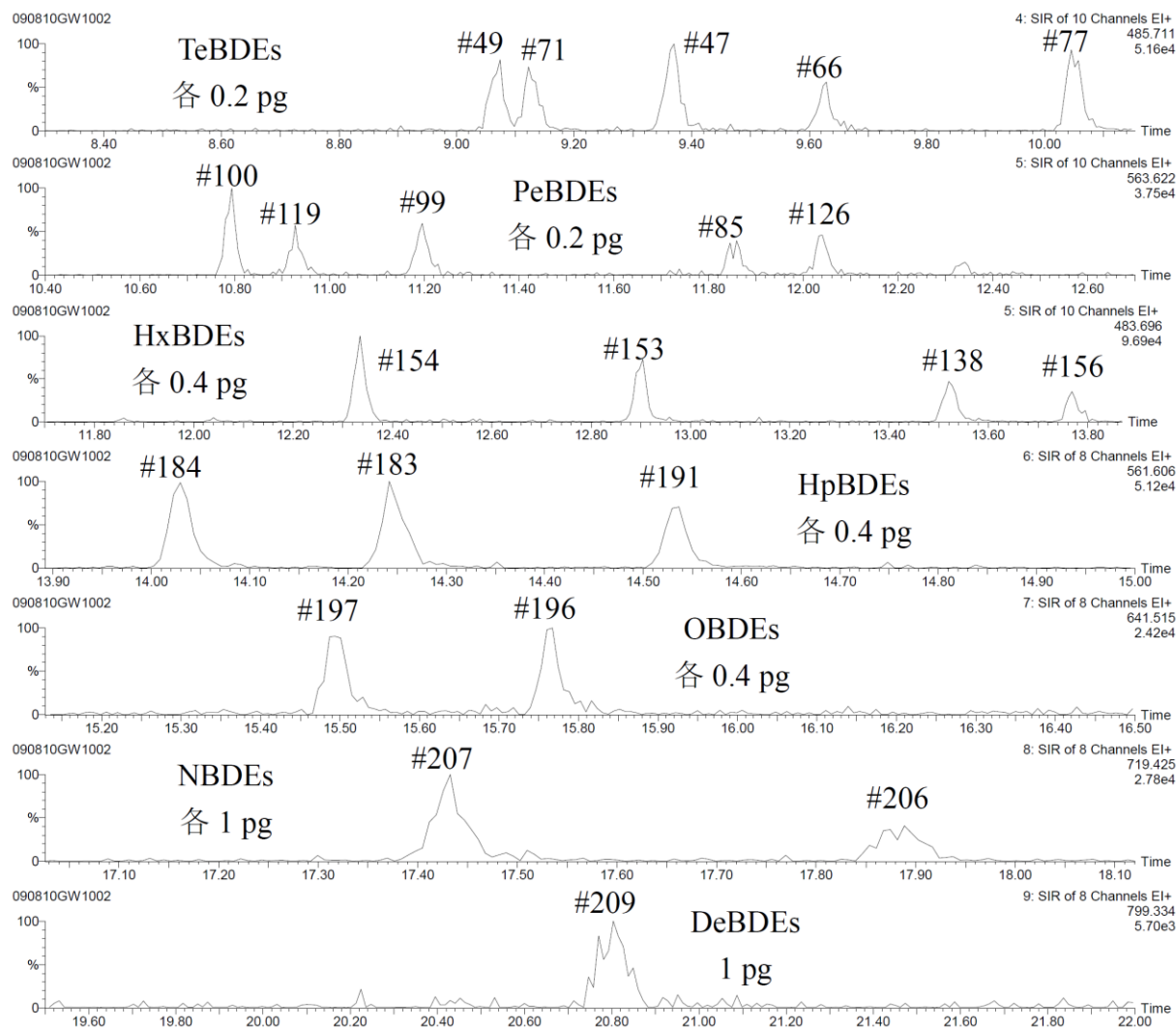
Instrument	LRMS or HRMS
Column	DB-5MS or ENV-5MS 15 m × 0.25 mm I.D. (0.1 μm) (5% Phenyl Polysilphenylene-siloxane)
GC program	120 °C (1 min) – 20 °C/min – 200 °C – 10 °C/min – 300 °C (10 min)
Inj.	On Column
Guard col.	Deactivated capillary 0.5 m × 0.53 mm I.D.
Inj. Temp.	120 °C (0.1 min) – 100 °C /min – 300 °C (15 min)
Inj. Volume	2 μL
Carrier gas	He (1.0 mL/min)
Ionization	EI
Electron Voltage	30~40 eV
Trap Current	500 μA
Accelerated Voltage	8 kV
Interface temp.	300 °C
Ion source temp.	300 °C
Detection	SRM (e.g. SIM)
Resolution	High resolution or low resolution

## PBDE masses and mass windows

The accurate masses of native and  $^{13}\text{C}$ -labelled PBDE homologues are listed in Table A2-2

**Table A2-2:** Masses of detected ions ( $m/z$ 's) for PBDE (HRMS masses; for LRMS reduced digits)

Compounds within GC time windows	Quantification	Confirmation
Tetrabromodiphenylether	485.7112	483.7132
Pentabromodiphenylether	563.6216	565.6197
Tetrabromo[ $^{13}\text{C}_{12}$ ]diphenylether	497.7513	495.7534
Perfluorokerosene	492.9697	
Pentabromodiphenylether	565.6197	563.6216
Hexabromodiphenylether (M-2Br)	483.6955	481.6975
Heptabromodiphenylether (M-2Br)	561.6060	563.6040
Pentabromo[ $^{13}\text{C}_{12}$ ]diphenylether	577.6598	575.6618
Hexabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	495.7357	493.7377
Heptabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	573.6462	575.6442
Perfluorokerosene	530.9664	
Hexabromodiphenylether (M-2Br)	483.6955	481.6975
Heptabromodiphenylether (M-2Br)	561.6060	563.6040
Heptabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	573.6462	575.6442
Perfluorokerosene	566.9665	
Octabromodiphenylether (M-2Br)	641.5145	639.5165
Octabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	653.5546	651.5567
Perfluorokerosene	642.9601	
Nonabromodiphenylether (M-2Br)	719.4250	721.4230
Nonabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	731.4651	733.4631
Perfluorokerosene	730.9537	
Decabromodiphenylether (M-2Br)	799.3335	797.3355
Decabromo[ $^{13}\text{C}_{12}$ ]diphenylether(M-2Br)	811.3737	809.3757
Perfluorokerosene	804.9505	

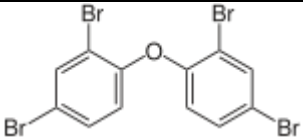
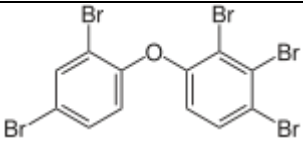
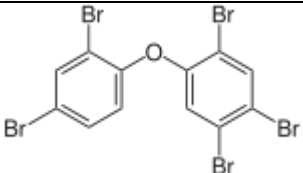
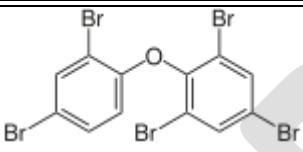
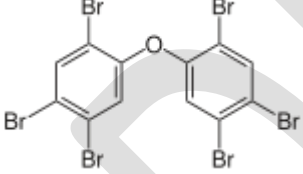
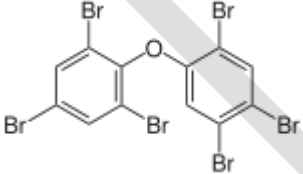


**Figure A2-1:** Chromatogram of tetraBDE to decaBDE (Please note that only tetraBDE, pentaBDE, hexaBDE and heptaBDE are listed as POPs)

### Major POP-PBDE congeners in commercial mixtures

Table A2-3 and A2-4 list the major POP-PBDE in c-PentaBDE and c-OctaBDE present in articles where these mixtures have been applied (La Guardia et al. 2006)<sup>254</sup>

**Table A2-3:** Major POP-PBDEs in commercial PentaBDE (La Guardia et al. 2006)

Composition of commercial PentaBDE			
Structure	Congener	Name	Fraction
	BDE-47	2,2',4,4'-tetra-bromodiphenyl ether	38–42 %
	BDE-85	2,2',3,4,4'-penta-bromodiphenyl ether	2.2–3.0 %
	BDE-99	2,2',4,4',5-penta-bromodiphenyl ether	45–49 %
	BDE-100	2,2',4,4',6-penta-bromodiphenyl ether	7.8–13 %
	BDE-153	2,2',4,4',5,5'-hexa-bromodiphenyl ether	5.3–5.4 %
	BDE-154	2,2',4,4',5,6'-hexa-bromodiphenyl ether	2.7–4.5 %

*Please note: Other congeners than mentioned above are only traces in concentration in commercial mixtures*

<sup>254</sup> La Guardia MJ, Hale RC, Harvey E (2006) Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures, Environ. Sci. Technol. 40, 6247–6254.



**Table A2-4:** Major POP-PBDEs and other PBDE congeners in c-OctaBDE in treated articles<sup>254</sup>

Structure	Congener	Name	Fraction
	BDE-153	2,2',4,4',5,5'-hexa-bromodiphenyl ether	0.15–8.7 %
	BDE-154	2,2',4,4',5,6'-hexa-bromodiphenyl ether	0.04–1.1 %
	BDE-171	2,2',3,3',4,4',6-hepta-bromodiphenyl ether	0.17–1.8 %
	BDE-180	2,2',3,4,4',5,5'-hepta-bromodiphenyl ether	n.d.–1.7 %
	BDE-183	2,2',3,4,4',5,6-hepta-bromodiphenyl ether	13–42 %
	BDE-196*	2,2',3,3',4,4',5,6'-octa-bromodiphenyl ether	3.1–10.5 %
	BDE-197*	2,2',3,3',4,4',6,6'-octa-bromodiphenyl ether	11–22 %
	BDE-203*	2,2',3,4,4',5,5',6-octa-bromodiphenyl ether	4.4–8.1 %

\* Congeners not considered as POPs under the Stockholm Convention.

Please note: Other congeners than mentioned above are only in trace concentrations

## Annex 2-B: GC/MS analysis of HBB (instrumental setting and chromatogram)

### HBB GC/MS conditions (example)

An example of instrumental setting for the GC/MS analysis of HBB are given in Table A2-5 and the exact masses of native and  $^{13}\text{C}$ -labeled HBB in Table A2-6.

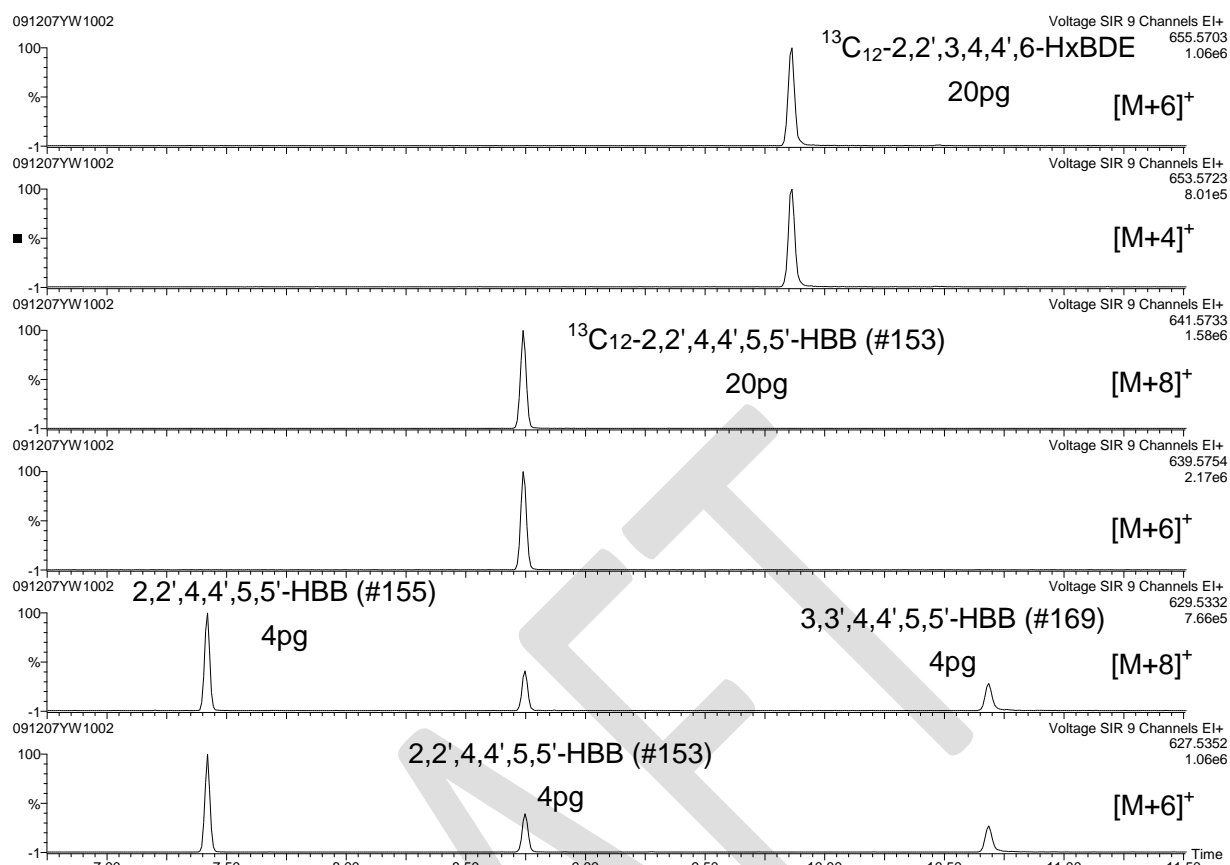
A chromatogram of HBB from GC/MS analysis is shown in Figure A2-2 and A2-3.

**Table A2-5:** GC/MS conditions HBB (example)

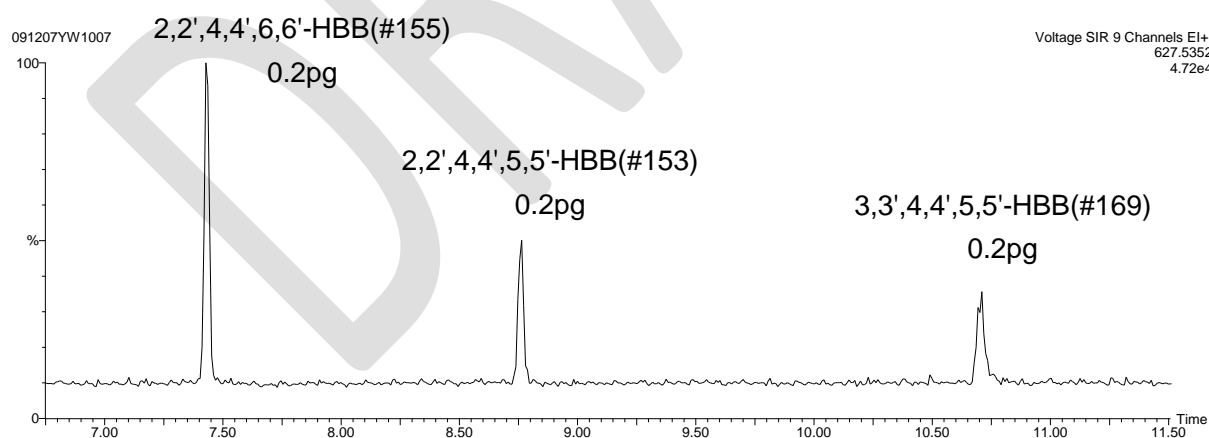
Instrument	Autospec Ultima (Waters/Micromass) GC:HP 6890 (Agilent)
Column	ENV-5MS 15 m × 0.25 mm I.D. (0.1 μm) (Kanto chemical) (5% Phenyl Polysilphenylene-siloxane)
GC prog.	120 °C (1 min) – 20 °C /min – 200 °C (0 min) – 10 °C /min – 300 °C (8 min)
Inj.	On Column
Guard col.	Deactivated capillary 0.5 m × 0.53 mm I.D.
Inj. Temp.	120 °C (0.1 min) – 100 °C /min – 300 °C (15 min)
Inj. Volume	2 μL
Carrier gas	He (1.0 mL/min)
Ionization	EI
Electron Voltage	30~40 eV
Trap Current	500 μA
Accelerated Voltage	8 kV
Interface temp.	300°C
Ion souece temp.	300°C
Detection	SRM (e.g. SIM)
Resolution	M/ΔM > 10000 (10% Valley)

**Table A2-6:** Masses of detected ions ( $m/z$ 's) for HBB

	Quant.	Confirm.
Hexabromobiphenyl	627.5352	625.5372
Hexabromo[ $^{13}\text{C}_{12}$ ]biphenyl	639.5754	637.5775
Hexabromo[ $^{13}\text{C}_{12}$ ]diphenylether	655.5703	653.5723
Perfluorokerosene	642.9600	



**Figure A2-2:** Chromatogram of native HBB congeners and <sup>13</sup>C<sub>12</sub>-HBB



**Figure A2-3:** Chromatogram of native HBB congeners

## Annex 2-C: GC/MS analysis of PCP (instrumental setting and chromatogram)

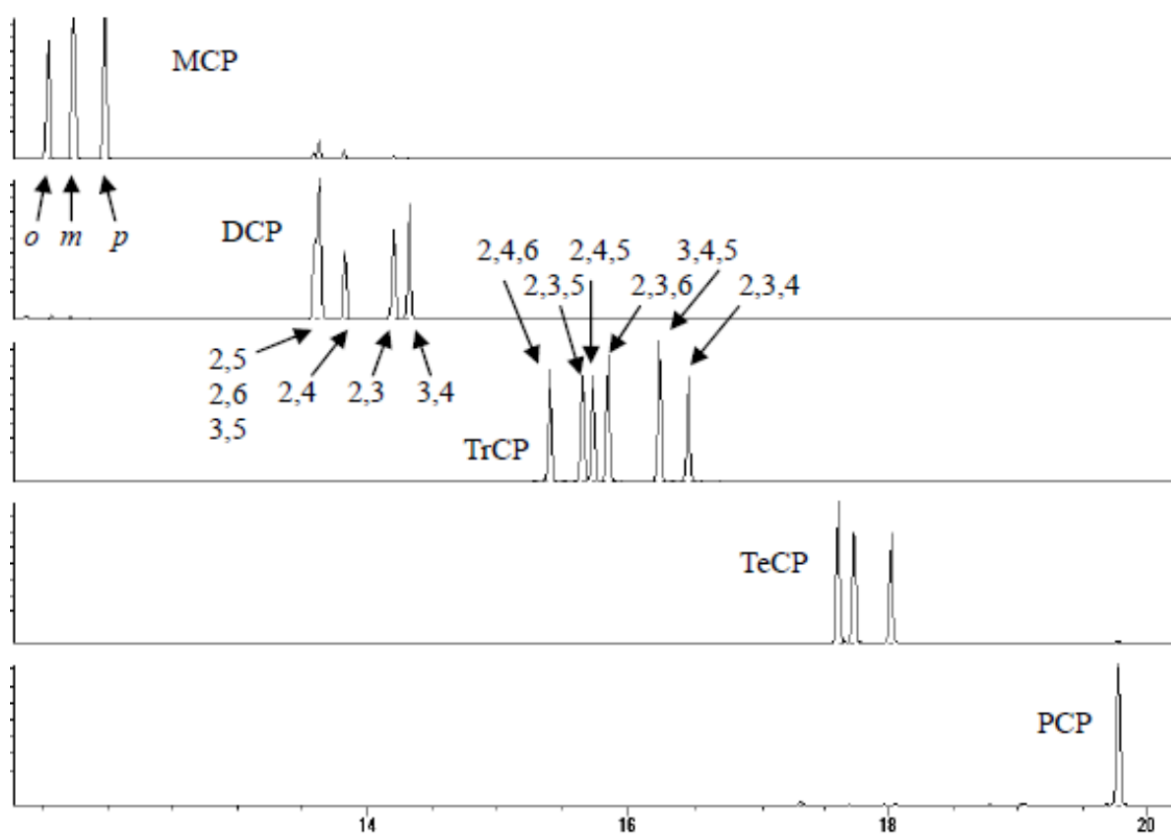
### GC/MS conditions for PCP analysis (example)

An example of instrumental setting for the GC/MS analysis of PCP and the masses of the TMS derivative of native and  $^{13}\text{C}$ -labeled PCP is given in Table A2-7.

A chromatogram of PBDEs from GC/MS analysis is shown in Figure A2-4.

**Table A2-7:** PCP GC/MS conditions (example)

GC condition	
Instrument	GC
GC column	Restek Rtx-5MS 30 m×0.25 mm×0.25 $\mu\text{m}$
Column Temp.	40°C (2 min) $\rightarrow$ 10°C /min $\rightarrow$ 290°C (2 min)
Injection	split less
Injector Temp.	250°C
Injection volume	1 $\mu\text{L}$
MS condition	
Instrument	LRMS or HRMS
Ionization	EI
Interface Temp.	230°C
Ion source Temp.	230°C
PCP-TMS	m/z 323; 325
$^{13}\text{C}_6$ -PCP-TMS	m/z 329



**Figure A2-4:** Chromatogram of PCP and other chlorinated phenols (not listed in the convention); (Chloropenols TMS derivatization. GC column ; Rtx-5MS 30 m)

## Annex 2-D: GC/MS analysis of PCNs (instrumental setting; chromatogram)

### GC/MS conditions for PCNs (example)

An example of instrumental setting for the GC/MS analysis of PCNs is given in Table A2-8 and the exact masses of native and  $^{13}\text{C}$ -labeled PCNs in Table A2-9.

A chromatogram of PCN homologues from GC/MS analysis is shown in Figure A2-5.

**Table A2-8:** PCP GC/MS conditions (example)

GC column	DB-5MS (Agilent Technologies/J&W) fused silica capillary column ID 0.32 mm, length 60 m, thickness 0.25 $\mu\text{m}$
Oven Temp.	90°C (2 min hold) - (20°C/min) $\rightarrow$ 160°C - (3°C/min) $\rightarrow$ 245°C - (5°C/min) $\rightarrow$ 310°C (2 min hold)
Injection	On-column or Split less
Injector Temp. (On-column)	90°C (1 min hold) - (100°C/min) $\rightarrow$ 300°C
Injection volume	1~2 $\mu\text{L}$
HRMS condition	Autospec Ultima (Waters/Micromass)
Ionization	El
Ionization voltage	35 V (35~70 V)
Ionization current	500 $\mu\text{A}$
Accelerating voltage	8 kV
Ion source Temp.	290~300 °C
Interface Temp.	290~300 °C
MS resolution	10 000

**Table A2-9:** Masses of detected ions ( $m/z$ 's) and isotope ratio for PCNs

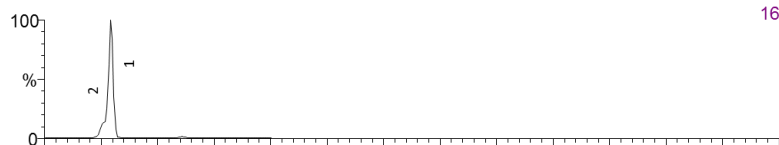
	CL degree	$\text{M}^+$	$(\text{M}+2)^+$	$(\text{M}+4)^+$
Native PCN	MoCNs (not listed)	162.0237(100)	164.0208(32.6)	
	DiCNs	195.9847(100)	197.9818(64.5)	
	TrCNs	229.9457(100)	231.9428(96.5)	
	TeCNs	263.9067(77.8)	265.9038(100)	
	PeCNs		299.8648(100)	301.8619(64.3)
	HxCNs		333.8258(100)	335.8229(80.3)
	HpCNs		367.7869(100)	369.7839(96.3)
	OcCN		401.7479(89.1)	403.7450(100)
Internal Standard for PCN	$^{13}\text{C}_{10}$ -DiCN	206.0183(100)	208.0152(64.0)	
	$^{13}\text{C}_{10}$ -TeCNs	273.9402(78.2)	275.9373(100)	
	$^{13}\text{C}_{10}$ -PeCNs		309.8983(100)	311.8954(64.0)
	$^{13}\text{C}_{10}$ -HxCNs		343.8593(100)	345.8564(80.0)
	$^{13}\text{C}_{10}$ -HpCN		377.8204(100)	379.8174(95.9)
	$^{13}\text{C}_{10}$ -OcCN		411.7814(89.4)	413.7785(100)
	$^{13}\text{C}_{12}$ -DiCB*, **	234.0406(100)	236.0376(65.6)	
	$^{13}\text{C}_{12}$ -TrCB*	268.0016(100)	269.9986(98.0)	
	$^{13}\text{C}_{12}$ -TeCB**	301.9626(78.2)	303.9597(100)	
	$^{13}\text{C}_{12}$ -PeCB*		337.9207(100)	339.9177(65.3)
	$^{13}\text{C}_{12}$ -HxCB*		371.8817(100)	373.8788(81.5)
	$^{13}\text{C}_{12}$ -OxCB*		439.8038(87.8)	441.8008(100)

Up to now, not sufficient of  $^{13}\text{C}_{10}$ -PCN for internal standard, so alternatively used  $^{13}\text{C}_{12}$ -PCB



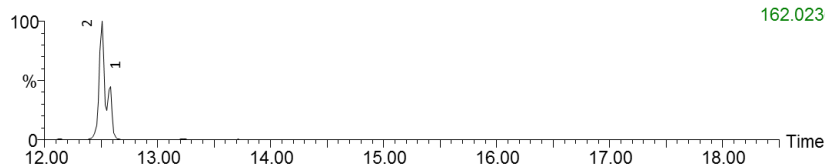
## MoCNs

Halowax Mix



162.0236

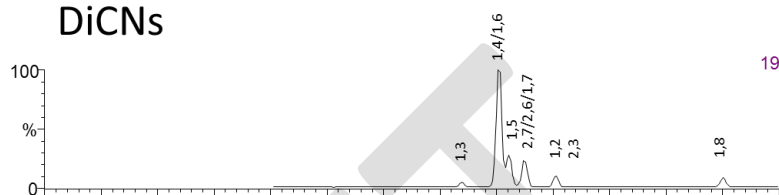
Incineration Sample



162.0236

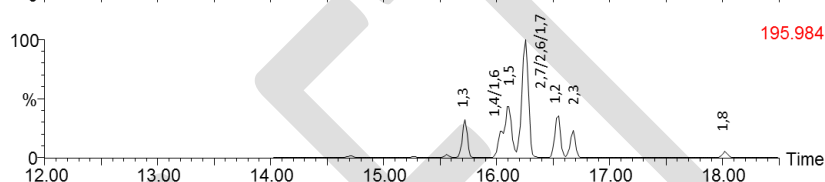
## DiCNs

Halowax Mix



195.9847

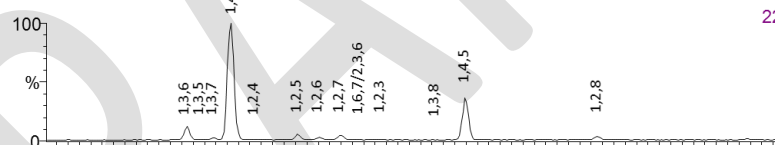
Incineration Sample



195.9847

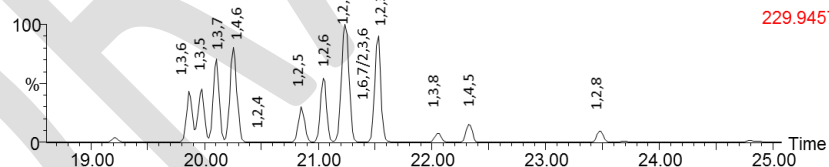
## TrCNs

Halowax Mix



229.9457

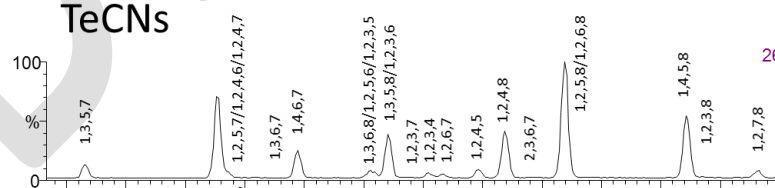
Incineration Sample



229.9457

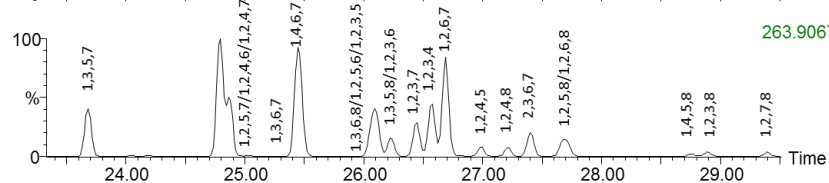
## TeCNs

Halowax Mix

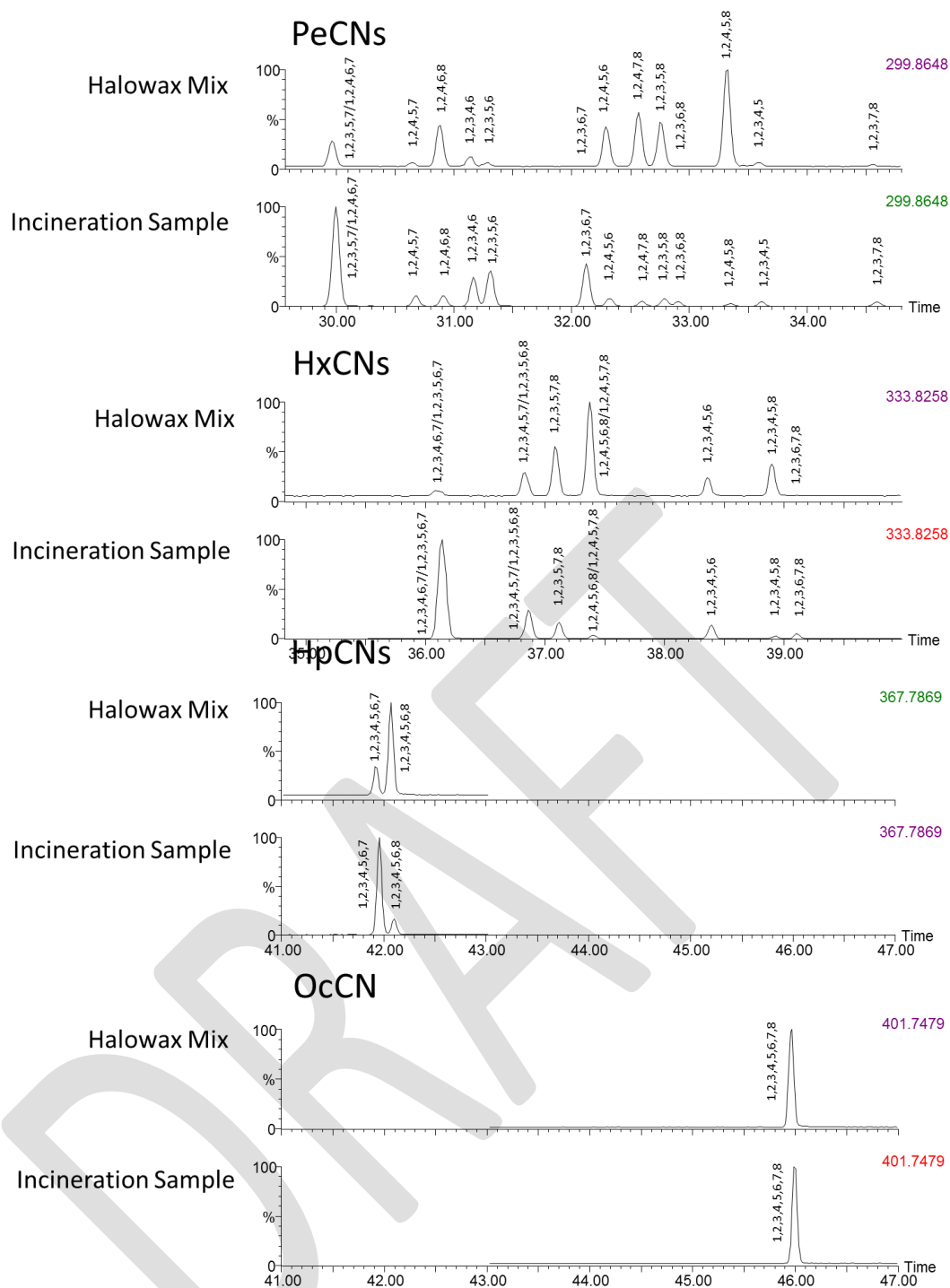


263.9067

Incineration Sample



263.9067



※Halowax Mix : Halowax 1000,1001,1013,1014,1031,1051,1099 mixture

Incineration sample : flue gas sample

**Figure A2-5:** Chromatogram of PCN congeners from technical mixtures and waste incineration<sup>255</sup>

<sup>255</sup>Noma Y, Yamamoto T, Sakai S (2004) Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the Halowax series. *Environ Sci Technol.* 38, 1675-80. Takasuga T, Inoue T, Ohi E, Senthil Kumar K (2004) Formation of Polychlorinated Naphthalenes, Dibenzo-p-Dioxins, Dibenzofurans, Biphenyls, and Organochlorine Pesticides in Thermal Processes and Their Occurrence in Ambient Air. *Arch. Environ. Contam. Toxicol.* 46, 419-431.

## Annex 2-E: GC/MS analysis of HCBd (instrumental setting; chromatogram)

### GC/MS conditions for HCBd (example)

An example of instrumental setting for the GC/MS analysis of PCNs is given in Table A2-8 and the exact masses of native and  $^{13}\text{C}$ -labeled HCBd in Table A2-10.

A chromatogram of HCBd from GC/MS analysis is shown in Figure A2-6.

**Table A2-9:** HCBd GC/MS conditions (example)

GC condition	
Instrument	HP 6890 (HEWLETT PACKARD)
GC column	DB-5 (5%-phenyl-95%-dimethylsiloxane) (J&W) 30m x 0.25mm I.D. (0.25 $\mu\text{m}$ )
Column Temp.	50°C (1 min) - 5°C /min - 130°C - 20°C /min-190°C
Injection	On-column
Injector Temp. (On-column)	50°C (0.1 min)-100°C /min-300°C (15 min)
Carrier gas	He (1 mL/min)
Injection volume	2 $\mu\text{L}$
Interface temperature	300°C
Ion source temp.	300°C
MS condition	LRMS or HRMS
Ionization current	300 $\mu\text{A}$
Ionization	EI
Ionization voltage	35 eV
Trap Current	600 $\mu\text{A}$
Accelerated Voltage	8 kV
Ion source Temp.	300 °C
Interface Temp.	290~300 °C
Detection mode	SIM

**Table A2-10:** Masses of detected ions for Hexachloro-1,3-butadiene,  $^{13}\text{C}_4$ - Hexachloro-1,3-butadiene and  $^{13}\text{C}_6$ -Fluoranthene

		Quant.	Confirm
		$[\text{M}-\text{Cl}]^+$	$[\text{M}-\text{Cl}]^{+2}$
Target substance	Hexachloro-1,3-butadiene	222.8443	224.8413
		$[\text{M}-\text{Cl}]^{+4}$	$[\text{M}-\text{Cl}]^{+6}$
Surrogate material	$^{13}\text{C}_4$ - Hexachloro-1,3-butadiene	230.8518	232.8488
Internal standard substance	$^{13}\text{C}_6$ -Fluoranthene	208.0984	

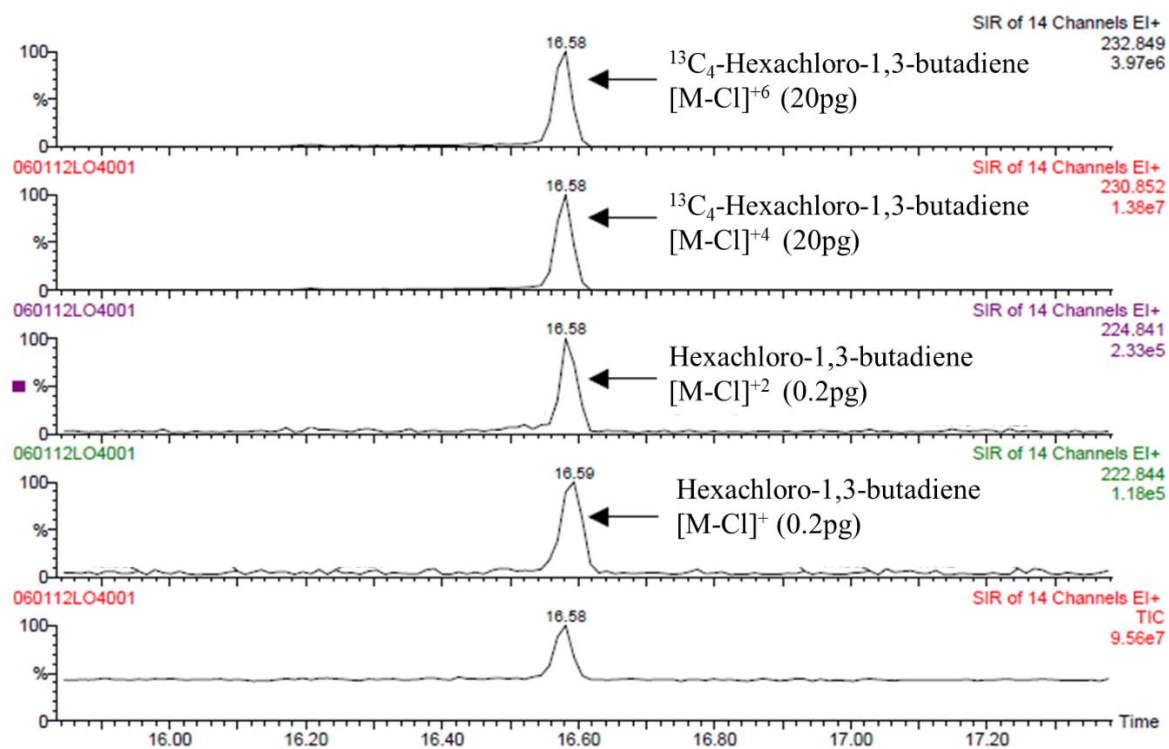


Figure A2-6: Chromatogram of native and  $^{13}\text{C}$ -labeled HCBD

## Annex 2-F: GC/MS analysis of PeCB (instrumental setting; chromatogram)

### GC/MS conditions for PeCB and POPs pesticides (example)

An example of instrumental setting for the GC/MS analysis of PeCB within POPs pesticide analysis is given in Table A2-11 and the exact masses of native and  $^{13}\text{C}$ -labelled HCB in Table A2-12.

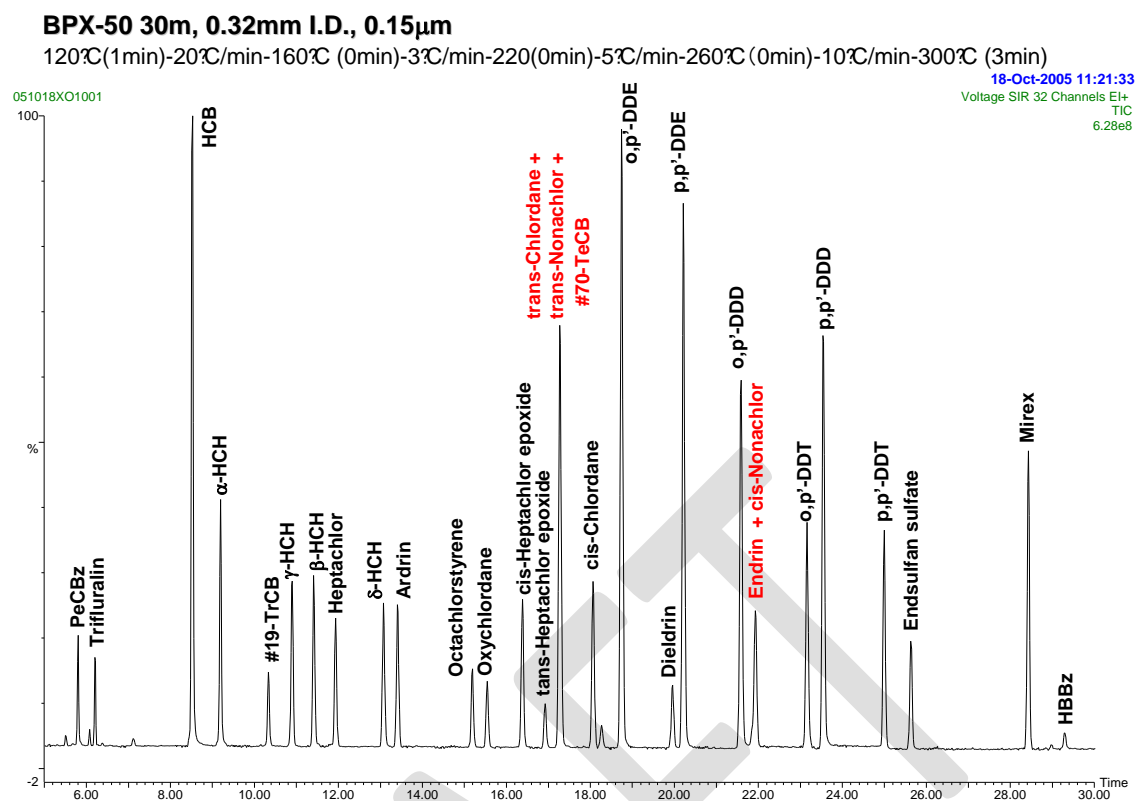
A chromatogram of HCB from GC/MS analysis is shown in Figure A2-7.

**Table A2-11:** HCB GC/MS conditions (example)

MS Instrument	LRMS or HRMS
GC	HP 6890 (Agilent)
Column	DB-17HT 30 m x 0.32 mm I.D. (0.15 $\mu\text{m}$ ) (Agilent Technologies/J&W)
GC prog.	120°C (1 min)-20°C /min-160°C (0 min)-3°C /min- -220°C (0 min)-10°C/min-300°C (3 min)
Inj.	On Column
Guard col.	Deactivated capillary 0.5 m x 0.53 mm I.D.
Inj. Temp.	120°C (0.1 min)-100°C /min-300°C (15 min)
Inj. Volume	2 $\mu\text{L}$
Carrier gas	He (1.0 mL/min)
Ionization	EI
Electron Voltage	30~40eV
Trap Current	500 $\mu\text{A}$
Accelerated Voltage	8 kV
Interface temp.	300°C
Ion source temp.	300°C
Detection	SRM (e.g. SIM)
Resolution	$M/\Delta M > 10,000$ (10% Valley)

**Table A2-12:** Masses of detected ions (m/z) for native and  $^{13}\text{C}$ -labelled PeCB and HCB

	Quantification	Confirmation
PeCB	249.8492	251.8462
$^{13}\text{C}_6$ -PeCB	255.8693	257.8663
HCB	283.8102	285.8072
$^{13}\text{C}_6$ -HCB	289.8303	291.8273



**Figure A2-7:** Chromatogram of PeCB, HCB and POPs pesticides (Column BPX-50; 30 m)



## Annex 2-G: LC-MS/MS analysis of PFOS (instrumental setting; chromatogram)

### LC-MS/MS conditions for PFOS and related chemicals and selected PFAS (example)

An example of instrumental setting for the LC-MS/MS analysis of for PFOS and related chemicals and selected PFAS is given in Table A2-13 and PFOS, PFOS related chemicals and other PFCs included in state-of-the-art monitoring in Table A2-14.

A chromatogram of PFOS from LC-MS/MS analysis is shown in Figure A2-8.

**Table A2-13:** HCBd GC/MS conditions (example)

Instrument	: LC-MS/MS
column	: Inersil ODS-SP (15 cm×2.1 mm ID、3 μm) GL Science
phase A	: 10 mM Ammonium acetate
phase B	: Acetonitrile
gradient	: 0-1min A : 65% B : 35% 1-5min A : 65→50% B : 35→50% 5-15min A : 50% B : 50% 15-18 min A : 50→10% B : 50→90% 18-25 min A : 10% B : 90% 25-25.1 min A : 10→65% B : 90→35% 25.1-35 min A : 65% B : 35%
Flow rate	: 0.2 mL/min
Col. Temp.	: 40 °C
Inj. volume	: 10 μL
<b>MS conditions</b>	
Instrument	: API 3200 (Applied Biosystems)
Ionization	: ESI negative
Monitor ions ( <i>m/z</i> )	: PFOS 498.7→79.9 (quant.) 498.7→98.9 (confirm.) PFOA 412.7→368.8 (quant.) 412.7→169.0 (confirm.) <sup>13</sup> C <sub>4</sub> -PFOS 502.9→79.9 <sup>13</sup> C <sub>4</sub> -PFOA 416.9→372.0

**Table A2-14:** PFOS and related chemicals and other PFCs included in state-of-the-art monitoring. (*Please note: Red marked substances are PFOS and related chemicals*)

Abbreviation	Full name	CAS #	Detection method
<b>Fluorooctane sulfonamides/ sulfonamidoethanols</b>			
<b>PFOSA*</b>	<b>Perfluorooctane sulphonamide</b>	<b>754-91-6</b>	<b>LC-MS</b>
<b>N-Me-FOSA*</b>	<b>N-Methyl-heptadecafluorooctane sulphonamide</b>	<b>31506-32-8</b>	<b>LC-MS</b>
<b>N-Et-FOSA</b>	<b>N-Ethyl-heptadecafluorooctane sulphonamide</b>	<b>4151-50-2</b>	<b>LC-MS</b>
<b>N-Me-FOSE*</b>	<b>N-Methyl-heptadecafluorooctane sulfonamidoethanol</b>	<b>24448-09-7</b>	<b>LC-MS</b>
<b>N-Et-FOSE*</b>	<b>N-Ethyl-heptadecafluorooctane sulfonamidoethanol</b>	<b>1691-99-2</b>	<b>LC-MS</b>
<b>Fluortelomer alcohols</b>			
4:2 FTOH	4:2 Fluortelomer alcohol	2043-47-2	GC-MS or LC-MS
6:2 FTOH	6:2 Fluortelomer alcohol	647-42-7	GC-MS or LC-MS
8:2 FTOH	8:2 Fluortelomer alcohol	678-39-7	GC-MS or LC-MS
10:2 FTOH	10:2 Fluortelomer alcohol	865-86-1	GC-MS or LC-MS
<b>Fluortelomer sulfonates</b>			
6:2 FTS	6:2 Fluortelomer sulfonate	27619-97-2	LC-MS
8:2 FTS	8:2 Fluortelomer sulfonate	39108-34-4	LC-MS
<b>Fluortelomer carboxylates</b>			
6:2 FTUCA	6:2 Fluortelomer unsaturated carboxylate	$C_8H_2F_{12}O_2^*$	LC-MS
8:2 FTUCA	8:2 Fluortelomer unsaturated carboxylate	70887-84-2	LC-MS
<b>Perfluoro sulfonates</b>			
PFBS	Perfluorobutane sulfonate	375-73-5	LC-MS
PFHxS	Perfluorohexane sulfonate	432-50-7	LC-MS
<b>PFOS*</b>	<b>Perfluorooctane sulfonate</b>	<b>1763-23-1</b>	<b>LC-MS</b>
PFDCS	Perfluorodecane sulfonate	335-77-3	LC-MS
<b>Perfluoro carboxylates</b>			
PFBA	Perfluorobutanoate	375-22-4	LC-MS
PFPA	Perfluoropentanoate	2706-90-3	LC-MS
PFHxA	Perfluorohexanoate	307-24-4	LC-MS
PFHpA	Perfluoroheptanoate	375-85-9	LC-MS
PFOA	Perfluorooctanoate	335-67-1	LC-MS
PFNA	Perfluorononanoate	375-95-1	LC-MS

PFDcA	Perfluorodecanoate	335-76-2	LC-MS
PFUnA	Perfluoroundecanoate	2058-94-8	LC-MS
PFDcA	Perfluorododecanoate	307-55-1	LC-MS
PFTTrA	Perfluorotetradecanoate	376-06-7	LC-MS
<b>Polyfluoro alkyl phosphate esters (PAPs)</b>			
4:2 monoPAPs	4:2 mono alkylated phosphate ester		LC-MS
6:2 monoPAPs	6:2 mono alkylated phosphate ester		LC-MS
8:2 monoPAPs	8:2 mono alkylated phosphate ester		LC-MS
10:2 monoPAPs	10:2 mono alkylated phosphate ester		LC-MS
4:2/4:2 diPAPs	4:2/4:2 dialkylated mercapto ether phosphate diester		LC-MS
4:2/6:2 diPAPs	4:2/6:2 dialkylated mercapto ether phosphate diester		LC-MS
6:2/6:2 diPAPs	6:2/6:2 dialkylated phosphate diester		LC-MS
6:2/8:2 diPAPs	6:2/8:2 dialkylated phosphate diester		LC-MS
8:2/8:2 diPAPs	8:2/8:2 dialkylated phosphate diester		LC-MS
8:2/10:2 diPAPs	8:2/10:2 dialkylated phosphate diester		LC-MS
10:2/10:2 diPAPs	10:2/10:2 dialkylated phosphate diester		LC-MS
10:2/12:2 diPAPs	10:2/12:2 dialkylated phosphate diester		LC-MS
12:2/12:2 diPAPs	12:2/12:2 dialkylated phosphate diester		LC-MS
<b>Fluorotelomer Mercapto alkyl phosphate diesters FTMAPs (S-diPAPs)</b>			
6:2/6:2 FTMAPs	6:2/6:2 dialkylated mercapto ether phosphate diester		LC-MS
6:2/8:2 FTMAPs	6:2/8:2 dialkylated mercapto ether phosphate diester		LC-MS
8:2/8:2 FTMAPs	8:2/8:2 dialkylated mercapto ether phosphate diester		LC-MS
8:2/10:2 FTMAPs	8:2/10:2 dialkylated mercapto ether phosphate diester		LC-MS
10:2/10:2 FTMAPs	10:2/10:2 dialkylated mercapto ether phosphate diester		LC-MS
10:2/12:2 FTMAPs	10:2/12:2 dialkylated mercapto ether phosphate diester		LC-MS
12:2/12:2 FTMAPs	12:2/12:2 dialkylated mercapto ether phosphate diester		LC-MS

\*No CAS number available

## PFOS標準品 0.5 ng/mL

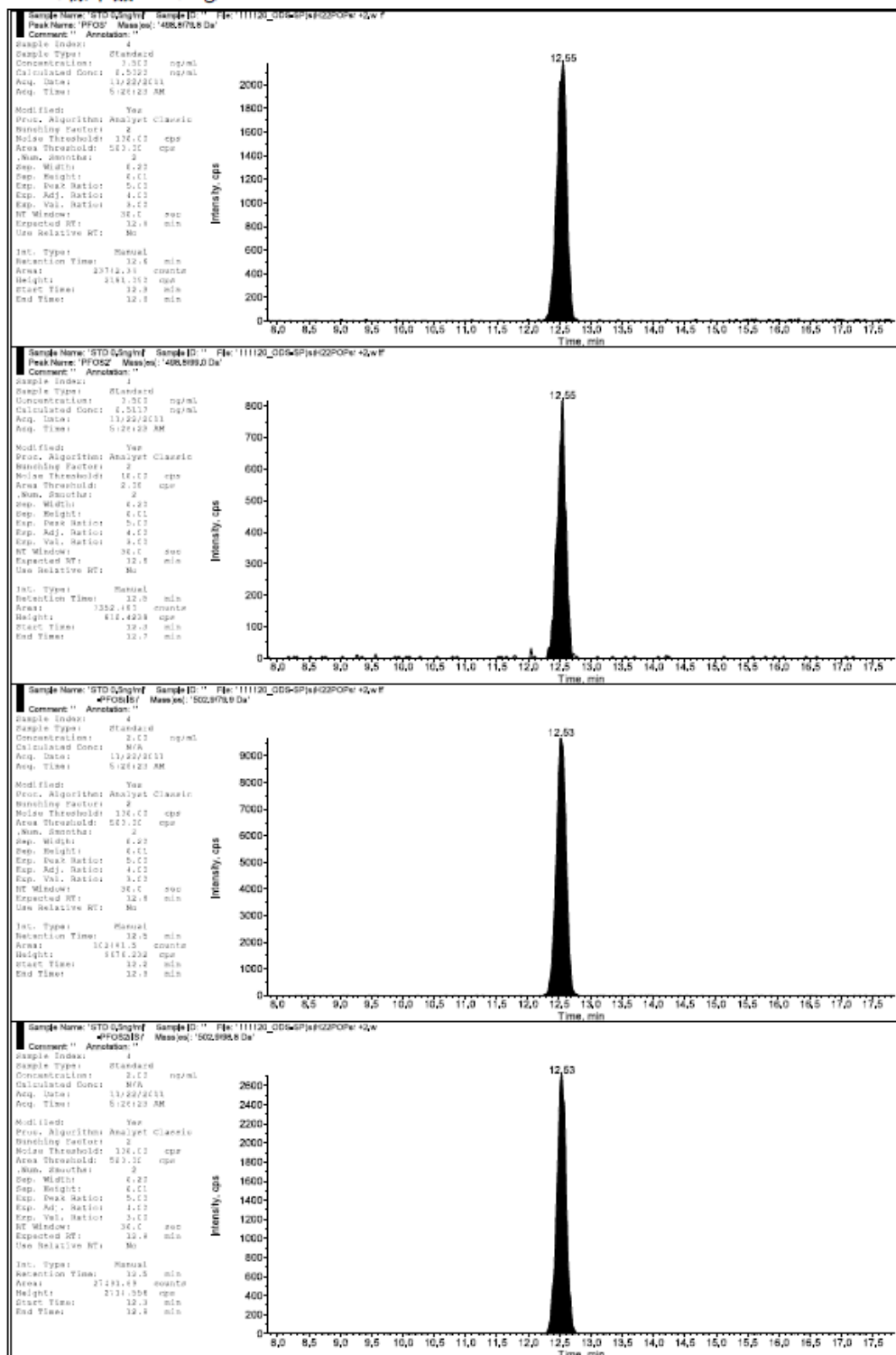


Figure A2-8: Chromatogram of PFOS on Inersil ODS-SP column

## Annex 2-H: HPLC-MS analysis of HBCD (instrumental setting; chromatogram)

### HPLC-MS conditions for HBCD

An example of instrumental setting for the HPLC-MS/MS analysis of HBCD including native and  $^{13}\text{C}$ -labeled masses is given in Table A2-15.

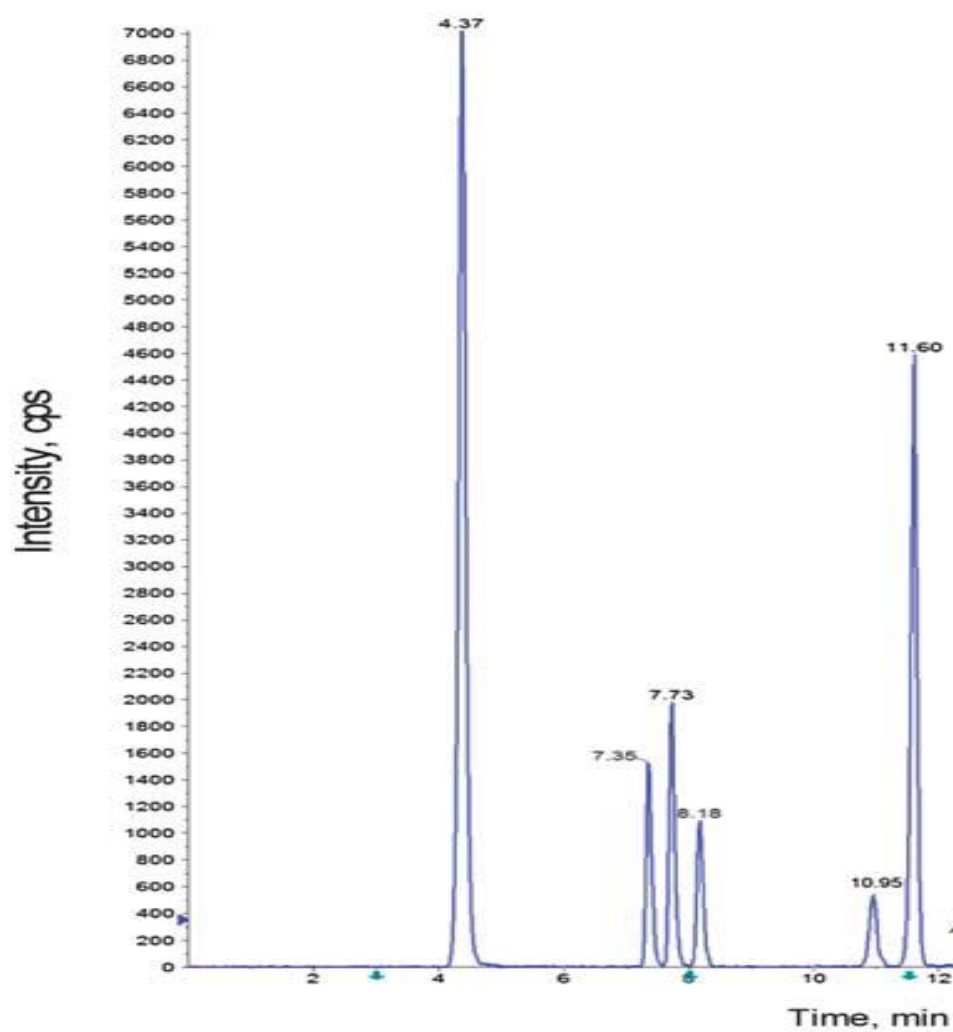
A chromatogram of HBCD from HPLC-MS/MS analysis is shown in Figure A2-9.

**Table A2-15:** HPLC-APCI-MS/MS conditions for HBCD analysis (example)<sup>256</sup>

LC-instrument	: HPLC system
column	: Zorbax Eclipse C18 analytical column (4.6 × 150 mm, 3 mm)
phase A	: 5% of MeOH in ultrapure water
phase B	: mixture of ACN : MeOH (70% : 30%)
gradient	: 0-8 min: 100% A, 0% B 8-8.1 min: A : 100→0% and B : 0→100% 8.1-22.4 min: 0% A and 100% B
Flow rate	: 0.4 – 1.6 mL/min
Col. Temp.	: 40 °C
Inj. volume	: 10 µL
<b>MS conditions</b>	
Instrument	: LC MS/MS
Ionization	: APCI negative ion mode
Monitor ions ( <i>m/z</i> )	: HBCD 639.8 → 78.8 (Quant.) HBCD 639.8 → 80.8 (confirm) $^{13}\text{C}_{12}$ -HBCD 652.1 → 78.8

<sup>256</sup> Al-Odaini NA, Yim UH, et al. (2013) Isotopic dilution determination of emerging flame retardants in marine sediments by HPLC-APCI-MS/MS. Anal. Methods 5, 1771-1777.

## a) Standard



**Figure A2-9:** Chromatogram of HBCD of the total multiple reaction monitoring (MRM) of standards, with the 3 HBCD isomers eluting at 7.35, 7.73 and 8.18 min.



## ANNEX 3 Case studies

### Annex 3-A Case studies of PFOS/PFC screening in products and articles

#### Monitoring project of PFOS/PFCs in consumer products in Norway and Sweden

The Norwegian Pollution Control Authority (SFT) has commissioned a survey carried out by Swerea IVF (Sweden) together with Norwegian Institute for Air Research (NILU) that aimed to identify and quantify possible sources of PFC in Norway in industrial manufacturing and applications used by the Norwegian population in daily life (Herzke et al. 2009)<sup>257</sup>

The study included waterproofing agents (5), paint/inks (5), impregnated products: paper, textiles, leather and carpets (2/2/2/2), non-stick ware (6), electronics (5) and firefighting agents (5).

PFOS, which has been banned in Norway since 2007, was detected in 47% of samples in low concentrations and only in 4 of the 34 analysed products the amounts were close to or exceeding the regulation.<sup>258</sup> These products were all within the leather or carpet product groups: The two leather samples had the highest concentrations of PFCs: Office furniture leather; (pool of 3) and black shoe, leather, showed PFOS levels of 38 and 21  $\mu\text{g}/\text{m}^2$ , exceeding the EU regulation of 1  $\mu\text{g}/\text{m}^2$ . Carpets were around the regulation of 1  $\mu\text{g}/\text{m}^2$ . The relatively low levels detected indicate that PFOS were not applied as major performance chemical but rather as by-product or contaminant of other PFCs or treatment procedure. Only five of the 34 analysed industrial materials and consumer products contained none of the analysed 29 polyfluorinated substances.

Specific feature of the Norwegian study on screening PFOS/PFCs in consumer products:

- Sample candidates were identified in different ways:
  - by having or giving certain properties that are common for perfluorinated chemicals (e.g. water repellent, stain resistant, anti-grease, non-stick, surfactant), by their previous known high concentration of PFCs (Teflon table cloth, AFFF, water proofing agents) or
  - by information from literature that production of these articles may include perfluorinated chemicals (epoxy resin board, semiconductor fabrication etc.).

A number of product types were identified as potential PFC containing groups and several samples were collected in each group distributed as

- Good analytical coverage: 29 different PFCs were analysed in all collected samples
- Regional approach: Cooperation of Norway and Sweden.
- Data published in a report in the public domain with product names

#### Monitoring of PFOS/PFCs in selected consumer products<sup>259</sup>

Twenty-nine samples of household products were analysed for PFOS and other long-chain and short chain per- and polyfluorinated substances at the Norwegian Institute for Air Research.

All in all the findings did not reveal very high levels of per- and polyfluorinated substances in these particular products. Some substances were only found a few times and then only just above the level of detection (PFBS, PFOS, 6:2 FTS, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA and PFTeA). PFOS was also only found in two products. The PFASs found the most often was 8:2 FTOH, 6:2 FTOH, PFOA, PFBA, PFHpA and PFHxA. However for the latter three

<sup>257</sup> Herzke D, Posner S, Olsson E (2009) Survey, screening and analyses of PFCs in consumer products. TA-2578/2009; Swerea IVF Project report 09/47. <http://www.klif.no/publikasjoner/2578/ta2578.pdf>

<sup>258</sup> Regulation EC No 552/2009 of 22 June 2009 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XVII, p.53.

<sup>259</sup> Blom C, Hanssen L Analysis of per- and polyfluorinated substances in articles. <http://norden.diva-portal.org/smash/get/diva2:808634/FULLTEXT04.pdf>

the levels were mainly very low. Only PFOA, 8:2 FTOH and 6:2 FTOH were found in amounts at or above 1  $\mu\text{g}/\text{m}^2$  or 10 mg/kg or mg/L. The study concluded that for further studies a screening of total fluorinated organics should be conducted for consumer products as a first step.

### Monitoring baking and muffin papers<sup>260</sup>

As a contribution to the European Perfood project (<http://www.perfood.eu>), 154 paper-based food contact materials were collected and screened for fluorinated contaminants (Schlummer et al. 2011)<sup>260</sup>. As screening methods sliding spark spectroscopy, wave length dispersive x-ray fluorescence and HS-GC-EPED were applied. 47 fluorine-positive samples were identified and subjected to a detailed analysis for PFOS and other perfluorinated sulfonates (PFSA), fluorotelomer alcohols (FTOH), and perfluorinated carboxylates (PFCA). Samples were fortified with isotope-labelled standards of PFSA, FTOH, and PFCA, and extracted with methanol by pressurized liquid extraction (PLE, ASE 200, Dionex, Germany). In order to avoid cross contaminations, the PLE apparatus was equipped with Teflon-free tubes and carefully checked for blanks. The methanol extracts were split into two equal aliquots. One aliquot was subjected to GC-(CI)-MS (TSQ 7000, Thermo) analysis using methane for chemical ionisation. The other aliquot was cleaned by SPE (Oasis WAX) and measured by LC-(ESI)-MS/MS (LC Quattro, Waters). For both analytical approaches quantification was based on an isotope dilution method.

In this study, PFOS and other perfluorinated sulfonates (PFSA) were not detected in any sample at levels above 1 ng/g. Instead 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were identified in all fluorine positive samples at levels ranging from 9 to 39500 ng/g, whereas 4:2 FTOH were only quantified in about 25% of the samples (maximum value 54 ng/g). Concentrations of PFCA were considerably lower and ranged from LOD (<1) to 619 ng/g PFOA, LOD (<1) to 1500 ng/g PFNA, and LOD (<1) to 390 ng/g PFDA.

This strongly indicates a switch from FOSE-based coatings for paper to FTOH containing macromolecules in industrial practise. Three patterns of PFCA congeners could be distinguished and may indicate to at least three different mother compounds, i.e. fluorine based paper coatings:

Pattern A: dominated by more or less equal amounts of PFOA, PFDA and Perfluorododecanoic acid (PFDoA),

Pattern B: dominated by PFOA and PFNA followed by PFHpA and PFDA.

Pattern C: clearly dominated by PFHxA.

In this first screening studies performed in 2009/2010, most baking and muffin papers were fluorine positive and had significant FTOH and PFCA levels. However, in a second screening in 2010/11 a series of baking and muffin papers were re-analysed. And this time, most samples were fluorine negative in the screening (detection limit approx. 0.1%), meaning that most of the investigated brand marks had changed for the European market their coating in recent years towards non-organofluorine coatings and already some years before have moved away from PFOS precursor based coatings.

### Monitoring of paper packaging for food (Denmark)<sup>261</sup>

PFOS and related chemicals in food packaging are of particular concern due to possible direct human exposure. In an (on-going) survey for the Danish Food Administration approximately 85 samples were taken by food inspectors in food packaging businesses (samples with no previous contact with food) and by DTU-Food in retail stores (samples in contact with foods). Three subsamples of 0.2 dm<sup>2</sup> each were combined in 60 ml 50% ethanol/water and extracted

<sup>260</sup> Schlummer M, Gruber L, Fengler R, Fiedler D, Wolz G (2011) How Poly- And Perfluoroalkyl Substances (PFAS) May Enter Our Food From Food Contact Materials (FCM). [Perfood Newsletter, Issue 2](#): November 2011

<sup>261</sup> Danish Veterinary and Food Administration (2012) Danish Technical University Report (not published).

for 24 hrs at 60 °C. The extracts/migrates were filtered through 0.2 µm nylon/PP filters and analysed by an UHPLC-ESI<sup>-</sup>-MS/MS (Waters Quattro Ultima) method in single reaction monitoring (SRM also called SIR) mode for the compounds. An Acquity C<sub>18</sub> CSH column (1.7 µm\*2.1 mm\*150 mm, Waters) was used with a 35 min gradient program, with MeOH/water (+NH<sub>4</sub>OH) mobile phase, Trier 2011 - JCA).

In the SIR mode only the deprotonated precursor ion was transmitted, in order to maintain high enough sensitivity while analysing for many compound on this instrument, which only has 20 Hz data sampling frequency. In the MRM methods two MRM transitions were used, but the method was then split up into three separate methods to maintain a high enough sensitivity of particularly the polyfluorinated compounds (FTOHs, PAPs): 1) Even PFCAs+PFSA+PFOSA+FTMAPs, 2) Un-even PFCAs+FTOHs, 3) monoPAPs and diPAPs. <sup>13</sup>C internal standards included 6:2, 8:2 monoPAPs, and 6:2/6:2, 8:2/8:2 diPAPs, 8H-7:1 FTOH and 9H-PFNA. The internal standard corrected well, except for very water soluble PFCs, possibly due to ion suppression by co-eluting salts. The previous d<sub>4</sub>-6:2/6:2 diPAPs was found to contain considerable amounts of d<sub>2</sub>-6:2 monoPAPs, formed either by hydrolysis from storage in water/alcohol or from impurities. Consequently the monoPAPs and diPAPs standards were not mixed. Loss of analytes was a big problem, and working solution only kept for < 1 week. Only four samples contained PFSA, and only two of these contained PFOS but in low levels (< 10 ppb). The other samples contained FTOH based PFCs in 57 % of the samples. However by an MRM method, the early eluting ions of 4:2 monoPAPs and PFBA were found to have interferences from the matrix. The study confirmed a previous study from the Danish, Canadian and Swedish markets sampled in 2009, where fluorinated compounds were present in 60% of the paper and board samples (Trier 2011), but the levels in the samples from 2010-2011 had generally decreased. Also this study revealed/conformed with the pattern of detected PFCs that industry already have shifted away from PFOS-derived coatings to diPAPs and now towards FTOH containing coatings. PFCA impurities/breakdown products were often seen in the paper extracts/migrates.

### **Non-analytical screening of PFOS/PFCs on the Danish market<sup>262</sup>**

In a first steps of monitoring of PFOS and related chemicals in a country approaches such as import statistics, product registers, company survey and audits should be considered and used and based on this outcome then additional instrumental screening and analysis would be conducted. The Danish Ministry of Environment (2008) published a documented survey in this respect for Denmark. The main purpose of this project was to estimate the use of PFOS and other PFCs in consumer products in Denmark.

Approaches of the Danish market survey of PFOS/PFCs on the national market were:

- Compilation of information from the Danish Product Register.
- Information from different companies such as producers, importers, suppliers and stores. Producers of fluorinated substances have been identified by Internet survey.
- The most important companies within the most relevant sectors were contacted by phone (not by questionnaires). This approach only gave sparse information (either companies did not know the chemical content of their products or they did not want to give information about the use of fluorinated substances (the survey was performed by a consultancy and not by a relevant authority).
- Stores and companies marketing and selling consumer products with a content of fluorinated substances have been identified initially by identifying the different products that contain fluorinated substances, and then secondly identifying the sectors in which the products are sold or produced.

<sup>262</sup> Danish Ministry of Environment (2008) Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. Survey of Chemical Substances in Consumer Products, No. 99, 2008.

- Information found on the Internet search about the content of fluorinated substances in different products was combined with statistics of sales of products in Denmark in order to estimate the use of fluorinated substances in Denmark in different product categories.

### **Monitoring of ground and drinking water in the United States<sup>263</sup>**

Drinking water contamination with PFOS (and PFOA currently assessed in the POPRC) poses risks to humans and animals. Between 2013–2015 the U.S. Environmental Protection Agency (USEPA) analysed national drinking water for PFOS and other PFAS concentrations within the third Unregulated Contaminant Monitoring Rule (UCMR3) program.<sup>263</sup>

The study found that drinking water supplies for 6 million U.S. residents exceed US EPA's lifetime health advisory (70 ng/L) for PFOS + PFOA<sup>263</sup> (drinking water is regulated for the sum of PFOS and PFOA).

It was found that the number of industrial sites that manufacture or use these compounds, the number of military fire training areas, and the number of wastewater treatment plants are all significant predictors of PFOS and other PFAS detection frequencies and concentrations in public water supplies. Among samples with detectable PFAS levels, each additional military site within a watershed's eight digit hydrologic unit is associated with a 35% increase in PFOS. The number of civilian airports with personnel trained in the use of aqueous film-forming foams is significantly associated with the detection of PFOS (and other PFASs) above the minimal reporting level.<sup>263</sup>

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<sup>263</sup> Hu XC, Andrews DQ, Lindstrom AB et al.(2016) Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ Sci Technol Lett.* 3(10):344-350.

### Annex 3-B Case studies of PBDEs screening in products, articles and wastes

A few countries/institutes or NGOs have performed screening of PBDE in articles and wastes. These case studies already give a good insight into POP-PBDE contamination of several material/recycling flows. The case studies are shortly described below with links to the reports/publications mentioned in footnote with respective web-link.

#### Monitoring of PBDEs in WEEE plastic in EU<sup>264</sup>

The largest and most relevant substance flow of POP-PBDEs and BFR containing materials are plastic fractions from WEEE recycling. The Swiss national material testing institute EMPA developed a standardized methodology for sampling of WEEE plastic for a survey of RoHS regulated substances in WEEE plastic in Europe including c-OctaBDE (Wäger et al. 2010)<sup>264</sup>. The report on the study can be downloaded at EMPA's E-waste (WEEE) information Web-page (<http://ewasteguide.info/>).

Specific features of EMPA's case study<sup>264</sup> on PBDEs and other RoHS relevant substance screening in WEEE plastics are:

- In the study a sampling methodology and a sampling protocol has been developed and is described in detail of Annex 1 and Annex 2 of the EMPA study (Wäger et al. 2010)<sup>264</sup>. This sampling strategy and protocol can be applied (in a modified way) in other countries and regions having shredder plants for processing of WEEE.
- The study gives a broad overview on the current POP-PBDEs content of the polymer fractions of WEEE categories in Europe.
- The study further gives an overview on other critical RoHS relevant pollutants which might be relevant today for other regions too.

#### Determination of POPs-PBDEs and BFRs in WEEE plastics in Nigeria<sup>265,266</sup>

The largest POP-PBDEs share within EEE/WEEE are casings of Cathod Ray Tubes (CRTs) (see *POP-PBDEs Inventory Guidance*). In a monitoring study of POP-PBDEs in Nigeria the two major CRT categories (TVs and computers) were monitored. In this case study 382 single housings of computer and TV Cathode Ray Tubes (CRTs) were sampled at WEEE storage sites in Nigeria<sup>265,266</sup>. Furthermore the recycling of the plastic (large share is ABS) of these appliances is of particular interest from an economic perspective.

382 single housings of computer and TV Cathode Ray Tubes (CRTs) were sampled at WEEE storage sites in Nigeria. These two electronic appliances contain the largest share of POP-PBDEs in EEE/WEEE (POP-PBDEs Inventory Guidance). Furthermore the recycling of the plastic (large share is ABS) of these appliances is of particular interest from an economic perspective.

The samples were specifically selected from waste storages, electronics workshops, roadsides, dumpsites and dismantling sites. The labels on the TVs and computer monitor plastic housings were examined for information on the manufacturer, brand, model, serial number, year and origin of production. Mainly for TV samples, the year of production was found printed on the inside of the plastic casings. The information was immediately recorded and about 250 cm<sup>2</sup> sizes were cut from each sample. Dismantling and cutting were done with simple tools (Figure A4-1). A hole was made on the cut samples through which a metal tag (Figure A4-2) was

<sup>264</sup> Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. [Final Report September 17, 2010](#).

<sup>265</sup> Sindiku O, Babayemi JO, Osibanjo O, Schlummer M, Schluep M, Weber R (2012) Assessing POP-PBDEs and BFRs in E-waste polymers in Nigeria. [Organohalogen Compounds 74, 1320-1323](#).

<sup>266</sup> Sindiku O, Babayemi J, Osibanjo O, Schlummer M, Schluep M, Watson A, Weber R (2014) Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in E-waste polymers in Nigeria. *Environ Sci Pollut Res Int*. DOI: 10.1007/s11356-014-3266-0



attached with the aid of a safety pin (Figure A4-3). These were transferred to the workshop where 40 mm X 40 mm squares were cut (Figure A4-4), and the cut squares packaged in labelled drug envelopes (Figure A4-5) for further analytical screening and analysis and stored for further analysis at a dark place, in order to avoid degradation processes.

The ranges of the year of production were 1987-2006 for computers, and 1981-2004 for TVs. This time span is considered being the most relevant for the use of POP-PBDEs as their use is thought to have been stopped in about 2004.

The numbers of samples with the regions of origin (production or assembly) are shown in Table A-3. A total of 382 samples were collected - 224 Computers and 158 TV sets. For computer samples, the highest proportion originated from Asia (100), followed by America (74), and then Europe (50). Most of the TV samples were produced in Europe (100), followed by Asia (58), and none from America. This broadly reflects presence of these e-wastes in Nigeria. Second hand TVs are not imported from the US as the systems are not compatible.



**Figure A3-1a:** Sampling tools



**Figure A3-1b:** Labelling tags



**Fig. A3-1c:** Labelled field sample



**Fig. A3-1d:** Cut squares



**Fig. A3-1e:** packaged samples

**Table A3-1:** Number of samples from each region of production/assembly

Region	Computer	TVs	Total
Europe	50	100	150
Asia	100	58	158
America	74	0	74
<b>Total</b>	<b>224</b>	<b>158</b>	<b>382</b>

Small parts of these sub-samples were subjected to a screening with EDXRGF aiming at the semi-quantification of bromine, chlorine but also of inorganic compounds listed in the RoHS directive. Bromine positive samples were then selected for GC/ECD and GC/MS analysis.

Extraction was performed by a dissolution/precipitation approach, since most casings were built by styrene based polymers which at least partly dissolve in classic extraction solvents (e.g. acetone, acetone/cyclohexane, ethyl acetate, THF, toluene, etc.). Dissolution was performed by THF and precipitation by *n*-heptane (see methodology described above).

In case of high bromine levels, GC-ECD provides typical fingerprint of technically applied BFRs. However, in case of lower bromine concentrations (below 1000 ppm) and unclear ECD results the aliquots of the sample extracts were fortified with <sup>13</sup>C-labelled internal standards and further subjected to GC/MS analysis in the EI-mode. By this approach an emission factor for c-OctaBDE in the two key (TV casings and computer monitors) were derived.

Finally, the type and amount of BFR have been measured for 382 computers and products.



Specific features of the case study on BFR screening and PBDE in WEEE plastic are:

- In the study a sampling methodology of CRT polymers for countries having no shredder plants (and where the above mentioned EMPA approach is difficult to apply) have been developed.
- Bromine screening was applied and POP-PBDEs content assessed for the different main importing regions (North America, Asia, and Europe).
- Product specific information (producer, product name, production year, region of origin) on POP-PBDEs/BFRs content in the CRTs products specific.
- With the generated data set POP-PBDEs impact factors for plastic of TV CRTs (6.9 kg c-OctaBDE/tonne TV CRT plastic) and computer CRTs (0.5 kg c-OctaBDE/tonne PC CRT plastic) in Nigerian. Based on the EEE/WEEE inventory of Nigeria<sup>267</sup> these impact factors have been used for developing the POP-PBDE inventory for Nigerian EEE/WEEE.

### Monitoring of BFRs in polymers of electronics on Swiss market<sup>268</sup>

The Swiss relevant authorities monitored in 2000 consumer products the presence of brominated flame retardants including electrical devices, building materials and lighting equipment ([Bantelmann et al. 2010](#)<sup>268</sup>). The aim of the survey was to evaluate the compliance of commercial articles with the provisions of the Swiss restrictions on BFRs: In Switzerland, the placing on the market and use of PBBs, c-PentaBDE, and c-OctaBDE as substances on its own, as well as in preparations with contents of each of these BFRs equal to or exceeding 0.1% by mass is prohibited. Placing on the market – but not the use – of articles that contain these substances in concentrations equal to or exceeding 0.1% by mass is banned as well.

Only 2 from the approximately 2000 samples contained c-OctaBDE above the 0.1% RoHS threshold.

Specific features of the case study on PBDEs and other RoHS relevant substances in WEEE plastic are:

- The study is a comprehensive market survey with a three step approach to monitor brominated flame retardants in contemporary products
  - Screening of BFRs in products
  - Analysis of the bromine positive samples for prohibited POP-PBDEs and common used flame retardants
  - Scanning of bromine positive samples where the BFR were not those commonly used for new brominated flame (Zennegg et al. 2011)<sup>269</sup>
- The study gives an insight on BFRs used in electronic products imported to the European market. The study shows that the POP-PBDE content in current products on the Swiss (and therefore European) market is small.
  - Only 2 from the approximately 2000 samples contained c-OctaBDE above the 0.1% RoHS threshold.
  - 17 samples contained DecaBDE above the RoHS threshold of 0.1%
- The study further gives an overview on other critical RoHS relevant pollutants which is relevant today for many other regions with RoHS like legislation.

<sup>267</sup> Ogungbuyi O, Nnorom IC, Osibanjo O, Schluep M (2012) Nigeria e-Waste Country Assessment. Basel Convention Coordinating Centre for Africa (BCCC-Nigeria) and Swiss EMPA, Ibadan, Nigeria and St. Gallen, Switzerland May 2012.

<sup>268</sup> Bantelmann E, Ammann A et al. (2010) Brominated flame retardants in products: Results of the Swiss market survey 2008. BFR 2010, April 7-9, Kyoto, Japan <http://www.bfr2010.com/abstract-download/2010/90004.pdf>.

<sup>269</sup> Zennegg M (2011) Identification of "Novel" Brominated flame retardants in new products of the Swiss market. [Organohalogen Compounds 73, 1238-1241](#).

The results of the third screening level of unknown BFRs in the samples by EMPA revealed that some of these samples contained e.g. hexabromobenzene or pentabromobenzene where the chlorinated analogues (HCB & PeCB) are prohibited by the Stockholm Convention.

### **Monitoring of POP-PBDEs and other BFRs in plastics in consumer products<sup>270</sup>**

A three-tiered testing strategy comparing results from non-destructive testing (X-ray fluorescence (XRF)) (n =1714), a surface wipe test (n=137) and destructive chemical analysis (n=48) was undertaken to systematically identify BFRs in a wide range of consumer products<sup>270</sup>. XRF rapidly identified bromine in 92% of products later confirmed to contain BFRs. Surface wipes of products identified tetrabromobisphenol A (TBBPA), c-octaBDE congeners and BDE-209 with relatively high accuracy (>75%) when confirmed by destructive chemical analysis. A relationship between the amounts of BFRs detected in surface wipes and subsequent destructive testing shows promise in predicting not only the types of BFRs present but also estimating the concentrations<sup>270</sup>.

### **Monitoring POP-PBDEs in carpet rebond from recycled PUR foam<sup>271</sup>**

PUR foam is recycled to carpet rebond in some regions in particular North America (see *Guidelines on BAT and BEP for the recycling and waste disposal of articles containing PBDEs listed under the Stockholm Convention*).

A [monitoring project](#) of POP-PBDEs in carpet rebond was performed with XRF for bromine screening and 26 samples were analysed for PBDEs by GC/MS analysis ([DiGangi et al. 2011](#))<sup>271</sup>.

Specific features of the case study on PBDEs and screening of carpet rebond:

- The study combines bromine screening methodology with confirmation analysis (as suggested in this guidance document).
- The study sampled in different world regions covering industrial and developing countries.
- The study addresses a product category manufactured from recycling materials possibly impacted by POP-PBDE-containing materials.
- The study was planned and performed from an NGO working on POPs ([www.IPEN.org](http://www.IPEN.org)) and results were published including the company names with high/low impacted products that consumers could assess company performance and possibly ask a company when purchasing similar products.

### **Monitoring of POP-PBDEs and other flame retardants in baby products<sup>272</sup>**

PUR foam samples collected from 101 commonly used US baby products were monitored for POP-PBDEs and other flame retardants ([Stapleton et al. 2011](#))<sup>272</sup>. From these products:

- Five samples contained POP-PBDE congeners commonly associated with c-PentaBDE, suggesting that such products are still in-use in sensitive use areas although production of c-PentaBDE is considered to have stopped in 2004<sup>273</sup>.
- 80% of the PUR foam baby products contained an identifiable flame retardant additive, and all but one of these was either chlorinated or brominated compounds.

<sup>270</sup> Gallen C, Banks A, Brandsma S, Baduel C, Thai P, Eaglesham G, Heffernan A, Leonards P, Bainton P, Mueller JF. (2014) Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in the plastics of consumer products. *Sci Total Environ.* 491-492:255-265.

<sup>271</sup> DiGangi J, Strakova J, Watson A (2011) A Survey of PBDES in Recycled Carpet Padding. [Organohalogen Compounds 73, 2067-2070](#).

<sup>272</sup> Stapleton MH, Klosterhaus S, et. al. (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. [Env. Sci. Technol.](#) 45. 5323-5331.

<sup>273</sup> With some uncertainties for the c-PentaBDE production in China which might have stopped later.

- The most common flame retardant detected was tris(1,3-dichloroisopropyl) phosphate (TDCPP; detection frequency 36%), followed by polybrominated aromatic compounds typically found in the Firemaster550 commercial mixture (detection frequency 17%).

Specific features of the case study on BFRs/PBDEs and CFR screening in PUR baby products:

- The study combined bromine screening methodology with confirmation analysis (as suggested in this guidance document). A portable X-ray fluorescence (XRF) analyser was used to estimate the bromine and chlorine content of the foams. A significant correlation was observed for bromine with quantitative analysis of BFRs; however, there was no significant relationship observed for chlorine and CFRs.
- For the first time a wide range of polyurethane baby products were sampled, screened and analysed for POP-PBDEs and other flame retardants.
- Based on exposure estimates conducted by the US Consumer Product Safety Commission, the study predict that infants may receive greater exposure to TDCPP from these products compared to the average child or adult from upholstered furniture, all of which are higher than acceptable daily intake levels of TDCPP set by the US Consumer Product Safety Commission.
- The study revealed that flammability standard<sup>274</sup> in a country can result in high levels of flame retardant in sensitive products with critical exposure to vulnerable groups like infants.

#### **Monitoring of PBDE, HBCD and other FRs in consumer/children products<sup>275</sup>**

In 2012-2013, the Washington State Department of Ecology assessed the presence of PBDEs, HBCDD and other flame retardant in general consumer and children's products. 169 products from 30 retailers in Washington State were collected between August 2012 and August 2013. Product types included seat cushions, mattresses, upholstered furniture for children, electronics, clothing, and baby carriers.

The majority of samples tested (94%) did not contain PBDEs above a reporting limit of 100 parts per million (ppm), which supports the conclusion that manufacturers have moved away from using PBDEs in products available to Washington State consumers. Alternative flame retardants are still being used.<sup>275</sup>

Numerous products were found to contain chlorinated phosphate flame retardants, in particular tris(1,3-dichloro-2-propyl) phosphate (TDCPP) but also tris(2-chloroethyl) phosphate (TCEP) and tris(1-chloro-2-propyl) phosphate (TDPP), and the non-halogenated phosphate triphenyl phosphate (TPP). The majority of these samples were foam and many were children's products. A subset of samples were tested for TBBPA, HBCD, and a newer flame retardant mixture called Antiblaze® V6 (V6). All three flame retardants were found in some of the samples analyzed.<sup>275</sup> Overall a number of samples were found to contain a flame retardant identified as a chemical of high concern to children (CHCC) above the reporting limit established in the Children's Safe Product Act.<sup>275</sup>

#### **Monitoring of POP-PBDEs in children toys<sup>276</sup>**

A Chinese research group assessed the presence of PBDEs and other BFRs (including PBBs, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE)) in children's toys purchased from South China (Chen et al. 2009)<sup>276</sup>. In all samples PBDE or other BFRs were detected. The median BFR concentrations in the hard plastic toys were notably

<sup>274</sup> Baby products containing PUR foam must meet California state furniture flammability standards, which likely affects the use of flame retardants in baby products throughout the U.S and possibly North America.

<sup>275</sup> Washington State Department of Ecology (2014) Flame Retardants in General Consumer and Children's Products. <https://fortress.wa.gov/ecy/publications/publications/1404021.pdf>

<sup>276</sup> Chen S-J, Ma Y-J, et al. (2009) Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure & Risk Assessment. *Environ Sci Technol* 43, 4200- 4206.

higher than values in other toys. The PBDE concentrations were below the threshold limit (1000 ppm) required by the European Commission's Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) directives in all of the toys, except for one hard plastic toy with a total PBDE concentration of 5344 ppm. The BFR profiles in the toys were consistent with the patterns of their current production and consumption in China, where PBDEs, specifically decaBDE product, were the dominant BFR, followed by the emerging DBDPE. The relatively high concentrations of octa- and nonaBDEs in the foam toys may suggest the decomposition of highly brominated BDEs during the manufacturing processes of the toys.

Specific feature of the study analysing POP-PBDEs and other BFRs in toys:

- This was the first study to examine the concentrations of PBDEs and other BFRs in toys, and the potential exposures to children.
- Revealed the broad use of recycled WEEE plastic in sensitive use areas like children toys.
- The study highlighted that because of extended periods of play, mouthing behaviour, and frequent hand-to-mouth contact, toys may pose a significant pathway of BFR exposure in children.
- Together with a second study of the group on PBDE/BFR screening in household goods<sup>277</sup>, the research reveals that the recycling of WEEE plastics seems largely uncontrolled in some regions.

### **Monitoring of POP-PBDEs in waste streams in the Netherlands<sup>278</sup>**

The Dutch authorities investigated how waste materials that possibly contain POP-PBDEs are sorted, separated, disposed of, recycled, landfilled, incinerated and/or exported in the Netherlands. The relevant information was collected from interviews with key actors in the waste sector and from reports and scientific literature. POP-PBDEs have been used mainly in the electronics and the automotive sectors. For both End-of-Life vehicles (ELVs) and WEEE there are national organizations coordinating the collection and processing. These waste flows are therefore relatively well documented. Many companies are involved in collection, sorting and the first processing steps, while only a few companies perform the actual separation of plastics which may contain POP-PBDEs. Only part of these separated plastics can be traced to companies producing recycled plastics which are ready to use in new products. In which new products these plastics are subsequently used is even harder to trace, as most of this production is not done in the Netherlands.

Sampling of materials for PBDEs analysis was performed in waste products, in shredded materials and in new products. The focus of waste sampling was on plastic waste products which were likely to contain POP-PBDEs, such as the automotive and electronic waste stream materials (especially polyurethane and acrylonitrile butadiene styrene). Samples were taken of new plastic products sold in the Netherlands (such as toys and household/office items), and manufactured using recycled plastic.

A cost-effective, fast 'direct probe' screening method that has been newly developed at IVM was applied to quickly determine the presence or absence of POP-PBDEs. The method can be used to screen samples for POP-PBDEs, so that the more laborious solvent extraction procedures are only done when quantifiable amounts are present.

In general, POP-PBDEs were found in very few single automotive parts (when found, the car part was from the USA) or WEEE items. Seats of American cars were shown to be a POP-

<sup>277</sup> Chen S-J, Ma Y-J, et al. (2010) Measurement and human exposure assessment of brominated flame retardants in household products from South China. *J. Hazard. Mater.* 176, 979-984.

<sup>278</sup> Leslie H.A, Leonards PEG, Brandsma SH Jonkers N (2013) POP STREAM POP-BDE waste streams in the Netherlands: analysis and inventory. (available at the Basel Convention Website).

PBDE hot spot in the ELV sector, with up to 25,000 µg/g in polyurethane foam of a Pontiac car seat (mostly c-PentaBDE congeners).

Combining the measured concentrations with information collected from the sectors, mass flows of these flame retardants were calculated and mapped through Dutch waste streams. Based on the mass flow analysis, 22% of the POP-PBDEs in WEEE is expected to end up in recycled plastics. In the automotive sector, 14% of the POP-PBDEs is expected to end up in plastics recycling, while an additional 19% is expected to end up in second-hand parts (reuse).

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### Annex 3-C Case studies of HBCD screening in products and articles

A few countries or institutes have performed screening of HBCD in articles and wastes. These case studies already give a good insight into HBCD contamination of several material/recycling flows. The case studies are shortly described below with links to the reports/publications mentioned in footnote with respective web-links where available.

#### Monitoring of HBCD, PBDE and PBDD/PBDF in vehicles<sup>279</sup>

A total of 40 End-of-Life Vehicles (ELVs) manufactured during 1993 and 2004 were investigated at an ELV-dismantling plant in Japan. For comparison, 5 currently-used vehicles manufactured during 2008 to 2012 were also included in the study. Interior materials/components including dashboard, door trim panel, automotive headliner, car seat fabric, seat polyurethane foam (PUF), plastic parts of car seats, floor covering, floor mat, and soundproof material were collected from each vehicle. In a first step, a screening survey of bromine in each material/component was conducted by using a handheld X-ray fluorescence (XRF) analyzer with RoHS/WEEE mode and analytical time was set at 30 seconds. The materials/components containing more than 0.1% by weight of bromine were selected for further chemical analysis. They were crushed into homogeneous small pieces and then pulverized to a fine powder with a freezer mill prior to the ultrasonic extraction with toluene.<sup>279</sup>

The XRF survey showed that 32 out of 515 materials/components investigated (6.2% of the total) contained more than 0.1% by weight of bromine. These samples were further analysed for PBDEs and HBCD. Subsequent analysis by mass spectrometry confirmed that 16 samples were treated with either the technical PBDEs or HBCDs; this result indicates the use of alternative BFRs in the rest of 11 samples. The congener and isomer profiles of PBDEs indicated that 12 samples including 9 seat fabric samples were DecaBDE treated materials. Only a set of seat fabric and PUF collected from a foreign car (ELV-10) were found to be treated with the PentaBDE technical mixture. High HBCD contents were found in only 2 floor covering samples (none of seat fabric).<sup>279</sup>

#### Monitoring of HBCD in EPS and XPS packaging and food contact materials<sup>280</sup>

Rani et al. (2014)<sup>280</sup> determined the concentration of HBCD in 34 polystyrene products including EPS and XPS in an Asian country. They used high pressure liquid chromatography-tandem mass spectrometry (HPLC-MS) for determining HBCD. In some food related EPS articles relatively high concentration of HBCD was detected including an ice box (960,000 ng/g) and disposable tray (8430 ng/g) used in fish market. HBCD was also detected in buoy used in aquaculture (53500 ng/g). Overall the study showed that HBCD is/has been used to some extent in PS packaging including food packaging and that PS including HBCD is recycled to some extent including packing and other products.

#### Monitoring of HBCD in Buoy in aquafarms and related oysters<sup>281</sup>

A Korean group detected elevated levels of HBCD in all tested buoy samples used in aquaculture farms. The concentrations of HBCDs in EPS buoys were in the range of 28-249 µg/g with the median concentration of 91 µg/g. The HBCD contents among EPS buoys showed a large variation, even within one buoy.<sup>281</sup>

<sup>279</sup> Kajiwara N, Takigami H, Kose T, Suzuki G, Sakai S. (2014). Brominated flame retardants and related substances in the interior materials and cabin dusts of end-of-life vehicles collected in Japan. *Organohalogen Compounds* 76, 1022-1025. <http://www.dioxin20xx.org/pdfs/2014/1015.pdf>

<sup>280</sup> Rani M, Shim WJ, Han GM, Jang M, Song YK, Hong SH. (2014). Hexabromocyclododecane in polystyrene based consumer products: an evidence of unregulated use. *Chemosphere*. 110, 111-119.

<sup>281</sup> Hong SH, Jang M, Rani M, Han GM, Song YK, Shim WJ. (2013). Expanded polystyrene (EPS) buoy as a possible source of hexabromocyclododecanes (HBCDs) in the marine environment. *Organohalogen Compd* 75, 882-885. <http://www.dioxin20xx.org/pdfs/2013/3211.pdf>



To obtain preliminary information about the impact of EPS buoys on farmed oysters, the concentration levels and profiles of HBCD isomers were measured in oyster samples collected from aquaculture farms and natural coasts. Two times higher concentration of HBCDs as measured in farmed oyster than in wild oyster. The level of HBCDs in farmed oyster is higher than those from the coastal areas of Korea, Japan, China, Malaysia, Vietnam, Indonesia, France, and Norway. Also the sediments in the aquafarms had higher HBCD levels compared to other sediments in literature<sup>281</sup>.

The study concluded that the presence of HBCDs in aquaculture buoy demonstrate the lack of proper control for the use of HBCDs in manufacturing polystyrene products.<sup>281</sup>

### **Rapid distinction between EPS/XPS containing HBCD and brominated polymeric alternatives<sup>282</sup>**

Schlummer et al. (2015)<sup>282</sup> developed a screening method for identifying HBCD containing EPS/XPS and the foams containing the brominated polymeric alternative. The test principle is based on the fact that PolyFR (a brominated polymeric macromolecule) is not extractable whereas HBCD (a low molecular weight substance) is extractable. Following rapid extraction of HBCD the brominated flame retardant is identified and quantified via bromine analysis using a handheld X-ray fluorescence instrument. The method was applied to 27 expanded and extruded polystyrene foam samples (foams and extruded polystyrene foam raw materials), which were provided without any information about the applied flame retardant. The presence of HBCD was confirmed for all HBCD-positive samples in the test.

A robustness test revealed a high degree of correctness and a high repeatability for the test system: samples containing HBCD and HBCD-free samples were identified correctly with relative standard deviations of quantitative results below 14%. Moreover, X-ray fluorescence spectroscopy test results agree well with HBCD determinations performed in a laboratory with a gas chromatography-flame ionisation detector.<sup>282</sup>

### **Monitoring of HBCD in textile<sup>283,284</sup>**

Kajiwarra et al. (2008<sup>283</sup>, 2009<sup>284</sup>) screened curtains and other textiles on the Japanese market with a handheld X-ray fluorescence (XRF) analyser for bromine content. Ten bromine containing textiles (mainly curtains) were used in this study. All reported extracted textiles contained HBCD in percentage range. This indicates that HBCD was a major brominated flame retardant used on textiles in this country and possible region.

Furthermore the study evaluated the extraction efficiency, reproducibility, and the possibility of isomerization of HBCD diastereomers with different methods of extraction including Soxhlet, ultrasonic, and soaking extractions with toluene and dichloromethane (DCM).

### **Monitoring of HBCD in WEEE plastic in EU<sup>285</sup>**

HBCD has also been used as a minor use BFR in high impact polystyrene (HIPS) in electronics (UNEP 2010<sup>286</sup>). Therefore HIPS plastic casings or parts and WEEE plastic fractions from recycling might contain HBCD. The Swiss national material testing institute (EMPA) developed a

<sup>282</sup>Schlummer M, Vogelsang J, Fiedler D, Gruber L, Wolz G (2015) Rapid identification of polystyrene foam wastes containing hexabromocyclododecane or its alternative polymeric brominated flame retardant by X-ray fluorescence spectroscopy. *Waste Management & Research*, doi: 10.1177/0734242X15589783

<sup>283</sup>Kajiwarra N, Sueoka M, Ohiwa T, Takigami H (2008) Determination of flame-retardant hexabromocyclododecane diastereomers in textiles. *Organohalogen Compounds* 70, 1414-1417. <http://www.dioxin20xx.org/pdfs/2008/08-569.pdf>

<sup>284</sup>Kajiwarra N, Sueoka M, Ohiwa T, Takigami H. (2009) Determination of flame-retardant hexabromocyclododecane diastereomers in textiles. *Chemosphere* 74, 1485-1489.

<sup>285</sup>Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. [Final Report September 17, 2010.](#)

<sup>286</sup>UNEP (2010), Risk profile on hexabromocyclododecane. UNEP/POPS/POPRC.6/13/Add.2.

standardized methodology for sampling of WEEE plastic for a survey of RoHS regulated substances in WEEE plastic in Europe including c-OctaBDE (Wäger et al. 2010)<sup>285</sup>.

In this study which investigated individually plastic the major WEEE categories however did not detect any HBCD in the related mixed WEEE plastic from different European countries with a detection limit for HBCD of 0.2 g/kg plastic (200 ppm) (Wäger et al. 2010)<sup>285</sup>. Therefore detection limit in this study for HBCD was relatively high. However, it seems that the average HBCD concentration in European WEEE plastic is below this concentration. Since a large share of European WEEE plastic stem from Asia this also indicate that the average concentration in WEEE plastic from Asia might in average be below 200 ppm.

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### Annex 3-D Case studies of PCP screening in products and articles

Some institutes have performed screening of PCP in articles, products and wastes. These case studies give an initial insight into PCP contamination of products and materials. The case studies are shortly described below with links to the reports/publications mentioned in footnote with respective web-links where available.

#### **Screening of PCP and other POPs in wooden artwork<sup>287</sup>**

In East Germany PCP, DDT and HCH has been extensively used as wood preservative including art works. The applicability of energy-dispersive  $\mu$ -XRF spectrometry for the monitoring of chlorine-containing wood preservatives in art objects was tested. Since largely these three chlorinated POPs has been used for treatment and since HCH was largely evaporated over time, the detection of high chlorine content was specific for DDT or PCP. The use of  $\mu$ -XRF technique combines the advantages of high spatial resolution (about 100  $\mu$ m spot size), needed in studies of penetration profiles of cut sections, and the ability to analyse larger areas in a relatively short time.<sup>287</sup> The degree of surface decontamination was determined non-destructively for the wooden scenery parts of a 'Theatrum Sacrum' from the cloister church of Neuzelle (Brandenburg, Germany).<sup>287</sup>

#### **Screening of PCP and other POPs in wooden museum artwork and remediation<sup>288</sup>**

In the second half of the 20th century, many wooden museum artwork were massively treated with POPs pesticides (such as DDT, PCP or lindane) to protect them against insect and mould infestation. Today, some of these toxic pesticides such as DDT have effloresced on the objects surfaces forming a white layer of crystals or they are emitted into the indoor air of storage rooms or exhibitions. In order to prevent the conservators as well as the visitors from health risks, it is inevitable to decontaminate these objects. Two projects were conducted in Switzerland to evaluate suitable decontamination methods and to investigate their influence on the wooden microstructure. In a first step, the pesticides distribution was investigated by GC/MS and  $\mu$ -XRF on wooden dummies. In a second step, the penetration behaviour of the pesticides was investigated by GC/MS and  $\mu$ -XRF and, additionally, the distribution in the wood microstructure was determined by  $\mu$ -XRF. In a third step, the efficiency of the two above mentioned decontamination methods was tested by GC/MS and  $\mu$ -XRF. This method can be used for screening of PCP and

#### **Screening of POP and other pesticides and pollutants in textiles in a museum<sup>289</sup>**

The presence of POPs and other organochlorine pesticides in air of rooms and storage cabinets in the textiles collection of the German Historical Museum in Berlin where discovered by GC/MS analysis.<sup>289</sup> To estimate the extent of pollution of the objects and the risks these toxins pose to both collections and museum staff, a field study with a portable XRF spectrometer was conducted with an attempt of a reliable quantitative analysis. The screening showed that the majority of the objects in the textiles collection at the Museum have been treated with different POPs and other pesticides at various points in the past. In addition to chlorine as indication to PCP and other POPs, other potentially hazardous elements such as lead, arsenic, and mercury were found in the majority of textiles.<sup>289</sup> It was concluded that such knowledge is a crucial prerequisite to proper risk prediction.

<sup>287</sup> Bartoll J, Unger A, Püschner K, Stege H (2003) Micro-XRF investigations of chlorinecontaining wood preservatives in art objects, *Studies in Conservation* 48, 195–202.

<sup>288</sup> Wörle M, Hubert V, et al. (2012) Evaluation of decontamination methods of pesticide contaminated wooden objects in museum collections: Efficiency of the treatments and influence on the wooden structure. *Journal of Cultural Heritage* 13, S209–S215.

<sup>289</sup> Krug S, Hahn O (2014) Portable X-ray fluorescence analysis of pesticides in the textile collection at the German Historical Museum, Berlin. *Studies in Conservation* 59, 355–366.

### Monitoring PCP and PCDD/F in Guar Gum<sup>290</sup>

Guar gum is an edible thickening agent extracted from guar beans. Food grade guar gum powder is authorized as food additive and used as a thickening, emulsifying, binding and gelling additive in a very wide range of foodstuffs. Industrial grade guar gum powder is used in various non-food sectors. India produces approximately 80 % of the world's total production of guar beans. In July 2007, a contamination by PCP and PCDD/Fs in guar gum originating from India was found. Contamination levels of PCDD/Fs and PCP in certain batches of guar gum were very high (up to a range of 100 mg/kg PCP and nearly 1000 ng WHO-PCDD/F-TEQ /kg product). To ensure a uniform approach within the EU, the Commission's services derived the following reference points of action for unacceptably high levels of dioxins and pentachlorophenol in guar gum:

- Pentachlorophenol: Any level of pentachlorophenol in guar gum exceeding 0.01 mg/kg taking into account the measurement uncertainty is considered as un-acceptable.
- Dioxins: Levels of dioxins (PCDD/F) in guar gum should be lower than 0.75 pg WHO-PCDD/F-TEQ/g product (or 0.75 ng WHO-PCDD/F-TEQ /kg product). Levels higher than 0.75 pg WHO-PCDD/FTEQ/g product are considered as unacceptably contaminated with dioxins.

A proficiency test on the determination of PCP, PCDD/Fs and PCBs in guar gum was organized with more than 50 laboratories. For the determination of the PCDD/F contamination from PCP the GC-HRMS results were compared with CALUX bio-assay showing for the PCDD/F congeners present from PCP a ca. 2 time higher dioxin-toxicity for the bio-assay test compared to the instrumental analysis with GC-HRMS.

### PCP treated wood in cattle stables and PCDD/PCDF contamination in wood and meat

In a screening study in USA beef, all contaminated beef samples (with levels above 4 ng TEQ/kg fat) could be related to exposure from treated PCP<sup>291</sup>. Fries et al.<sup>292</sup> analysed the PCP and PCDD/PCDF levels in the wood samples of these stables (Table A3-2) and found a good correlation between PCP levels and PCDD/PCDF concentration (Figure A3-2; Table A3-2).<sup>292</sup> PCDD/PCDF levels in wood with elevated PCP concentration (1580 to 8540 mg/kg wood) had levels between 27,200 and 315,000 ng TEQ/kg wood and therefore were all above the Basel Convention provisional low POPs content level of 15,000 ng TEQ/kg<sup>292</sup> (Table A3-2). PCDD/PCDF levels in wood with intermediate PCP concentration (110 to 875 mg/kg wood) were up to 52,600 ng TEQ/kg and therefore also considerably above the Basel Convention provisional low POPs content level<sup>292</sup> (Table A3-2). This demonstrates the relevance of PCDD/PCDF contamination in PCP treated wood and the need for environmentally sound management of PCP treated wood.

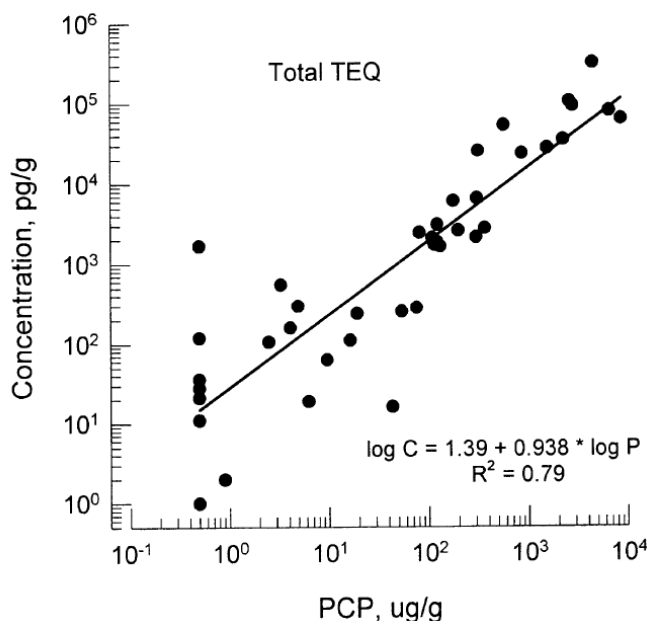
**Table A3-2:** Concentrations of pentachlorophenol (PCP) and total PCDD/PCDF expressed as toxic equivalents (TEQs) in wood samples (Fries et al. 2002)<sup>292</sup>

PCP level	Amount of samples	PCP concentration (mg/kg wood)	PCDD/PCDF level (µg TEQ/t)
PCP <LQ	6	<LQ	11–1685
PCP low	12	2.5–82.4	16–2425
PCP intermediate	13	110–875	1,600–52,600
PCP high	7	1580–8540	27,000–315,000

<sup>290</sup> Kotz A, Malisch R et al (2009) Proficiency test on the determination of PCDD/Fs and PCP in guar gum and follow-up analyses. *Organohalogen Compounds* 71, 2137-2142. <http://dioxin20xx.org/pdfs/2009/09-437.pdf>

<sup>291</sup> Huwe JK, Davison K, Feil VJ, Larsen G, Lorentzen M, Zaylskie R, Tiernan TO (2004) Levels of polychlorinated dibenzo-p-dioxins and dibenzofurans in cattle raised at agricultural research facilities across the USA and the influence of pentachlorophenol-treated wood. *Food Additives and Contaminants* 21, 182-194.

<sup>292</sup> Fries GF, Feil VJ, Zaylskie RG, Bialek KM, Rice CP (2002) Treated wood in livestock facilities: relationship among residues of pentachlorophenol, dioxins, and furans in wood and beef. *Environm. Pollution*, 116, 301-307.



**Figure A3-3:** Concentrations of PCDD/PCDF (TEQ) in wood of beef stables as functions of concentrations of PCP (Fries et al. 2002)<sup>292</sup>

#### **PCP treated wood as feed additive and PCDD/PCDF contamination in wood and meat**

PCP treated wood was added as saw mill dust as additive in the animal feed mixture containing choline chloride. The associated PCDD/PCDF contamination in the PCP treated saw mill dust resulted in high levels of PCDD/PCDF in chicken above EU-regulation limit values.<sup>293</sup>

<sup>293</sup> Llerena JJ1, Abad E, Caixach J, Rivera J. (2003) An episode of dioxin contamination in feedingstuff: the choline chloride case. *Chemosphere*. 53(6), 679-683.

### Annex 3-E Case studies of PCN screening in products and materials

A few countries or institutes have performed screening of PCN in articles, products and wastes. These case studies give an initial insight into PCN contamination of several a few products and materials. The case studies are shortly described below with links to the reports/publications mentioned in footnote with respective web-links where available.

#### Analysis of illegally imported technical PCNs<sup>294</sup>

Technical polychlorinated naphthalene formulation were illegally imported from the United Kingdom to Japan and were assessed for detailed content and congener profile.<sup>294</sup> The PCN composition was compared to known technical Halowax mixtures (Halowax 1000, 1001 and 1031). Principal component analysis (PCA) and Cluster Analysis of PCN of congeners with isomer-specific assessment of homologue groups and ratio of different homologue classes showed that the composition of the unknown mixture was similar to Halowax 1001. However the detailed principal component analysis and cluster analysis demonstrated that the illegally imported PCN were not identical with Halowax 1001.<sup>294</sup> Also the chlorine content of the imported PCN formulation was determined (50–52%). Based on the chlorine content and congener and homologue distribution it was concluded that the illegally imported PCN mixture could be a stockpiled Seekay wax R93.<sup>294</sup>

#### Analysis of PCNs in PCBs<sup>295,296</sup>

Yamashita et al.<sup>295</sup> investigated a wide range of technical PCB mixtures for PCN content. The investigated PCB mixtures included Aroclors 1016, 1232, 1248, 1254, 1260, 1262, Kanechlors 300, 400, 500, and 600 (KC-300, KC-400, KC-500 and KC-600), Clophens A40 and T64, Phenoclors 3,4,5, and 6 (DP3, DP4, DPS and DP6), Sovol, and Chlorofen. The PCN levels in commercial PCB formulation were in a range of 39 to 730 mg/kg.<sup>295</sup>

Recently Huang et al.<sup>296</sup> analysed the major Chinese PCB formulation (PCB3) and detected relatively high PCN levels (1307 mg/kg)<sup>296</sup>.

#### Monitoring of PCNs in Neoprene FB rubber<sup>297</sup>

Feral aerosol adhesive bombs (AAB) and bombs (negative control) made of PCN free Neoprene FB and supplied by another manufacturer, were purchased from the market in March 2002 in Japan. Some other sampled commercial goods (containing the feral Neoprene FB and also the feral raw rubber materials) were sampled. The imported technical PCNs mixture, the feral Neoprene FB and the feral rubber coated sheet were dissolved in methylene chloride and toluene and next subjected for clean-up procedure. The adhesive materials contained in the aerosol adhesive bombs were obtained after a slow decompression step and released out of the bomb content. After clean-up the samples were analysed by GC-HRMS.

#### Analysis of PCN and other UOPs in by-product of chloromethane production<sup>298</sup>

<sup>294</sup> Falandysz J, Chudzynski K, Takekuma M, Yamamoto T, Noma Y, Hanari N, Yamashita N (2008) Multivariate analysis of identity of imported technical CN formulation. *J. Environm. Sci. Health Part A*, 43, 1381–1390.

<sup>295</sup> Yamashita N, Kannan K, Imagawa T, Miyazaki A, Giesy J P (2000) Concentrations and Profiles of Polychlorinated Naphthalene Congeners in Eighteen Technical PCB Preparations. *Environ. Sci. Technol.* 34, 4236-4241..

<sup>296</sup> Huang J, Yu G, Yamauchi M, Matsumura T, Yamazaki N, Weber R. (2014) Congener-specific analysis of polychlorinated naphthalenes (PCNs) in the major Chinese technical PCB formulation from a stored Chinese electrical capacitor. *Environ Sci Pollut Res Int.* 2015 Oct;22(19):14471-14477.

<sup>297</sup> Yamashita N, Taniyasu S, Hanari N, Falandysz J (2003) Polychlorinated naphthalene contamination of some recently manufactured industrial products and commercial goods in Japan. *J Environ Sci Health A* 38:1745–1759.



High levels of unintentional PCNs and other POPs (HCB, HCBd) and are formed in the production of chlorinated solvents such as tetrachloroethylene, trichloroethylene and ethylene dichloride. The production of unintentionally produced POPs during the methanol based production of chlorinated methanes were investigated in China. High levels of octachloronaphthalene and other PCNs and other highly chlorinated compounds such as decachlorobiphenyl, octachlorostyrene, hexachloro-cyclopentadiene, hexachlorobutadiene, hexachlorobenzene, and pentachloro-benzene were found in the carbon tetrachloride by-product of the methanol-based production of chlorinated methanes.<sup>301</sup> The total emission amounts during the production of chlorinated methanes in China of PCNs in 2010 was estimated to 427 kg.<sup>298</sup> Furthermore large amounts hexachloro-cyclopentadiene, hexachlorobutadiene, polychlorinated benzenes, polychlorinated naphthalenes, octachlorostyrene, and polychlorinated biphenyls release were estimated to be 10080, 7350, 5210, 212, and 167 kg, respectively.<sup>301</sup> Also PCDD/PCDFs were detected in the by-product. The total dioxin-like TEQ from chlorinated methane production in China in 2010 were estimated for PCNs to 563 g TEQ and for PCDD/PCDFs to 32.8 g TEQ respectively.<sup>298</sup>

### **Monitoring of PCNs in rubber and different waste fractions<sup>299</sup>**

Monitoring of PCN were conducted in 21 rubber belts and 1 Neoprene FB rubber and a range of waste fractions (rubber products, refuse derived fuel (RDF), automobile shredder residue (ASR) and fly ashes). PCNs patterns were compared to 7 different Halowax formulations. PCNs were detected at different levels. The highest level were found in the Neoprene FB rubber

<sup>298</sup> Zhang L, Yang W, Zhang L, Li X (2015) Highly chlorinated unintentionally produced persistent organic pollutants generated during the methanol-based production of chlorinated methanes: A case study in China. *Chemosphere* 133, 1-5.

<sup>299</sup> Yamamoto T, Noma Y, Hirai Y, Nose K, Sakai S (2005) Congener-specific analysis of Polychlorinated Naphthalenes in the waste samples. *Organohalogen Compounds* 67, 708-711. <http://www.dioxin20xx.org/pdfs/2005/05-453.pdf>

### Annex 3-F Case studies of HCBd screening in products and materials

A few countries or institutes have performed screening of HCBd in articles, products and wastes. These case studies give an initial insight into HCBd contamination of some products and materials. The case studies are briefly described below with links to the reports/publications mentioned in footnote with respective web-links where available.

#### Monitoring of HCBd (and HCB) in industrial processes<sup>300</sup>

The USEPA developed an inventory of HCBd (and HCB) in the production of organochlorines and elemental chlorine for 1972 which may serve as a useful case study for countries having organochlorine solvent and other organochlorine production processes. The study assessed and estimated the total quantity of HCBd and HCB contained in U.S. industrial wastes, by-products, and products in 1972 from major production processes of organochlorine solvents (tetrachloro methane/carbon tetrachloride, perchloroethylene, trichloroethylene), Vinylchloride/EDC, organochlorine pesticides (Dacthal, mirex, pentachloronitrobenzene, atrazine, simazine) and a range of other processes and products. The study also compiled information on HCBd formation and release in the production of chlorine (Mumma and Lawless 1975). Data on processes and production volumes were compiled together with data on contamination levels of related production processes. The compilation revealed that in 1972 between 3276 and 6539 tonnes of HCBd and between 1093 and 2198 tonnes of HCB were contained in U.S. industrial wastes, by-products, and products (Table A3-3).<sup>300</sup>

**Table A3-3:** Estimated total quantity of HCBd and HCB contained in U.S. industrial wastes, by-products, and products in 1972 (Mumma and Lawless 1975)<sup>300</sup>

	HCBd in tonnes (in 000 lb)		HCB tonnes (in 000 lb)	
	High	Low	High	Low
Tetrachloroethylene	3,902 (8,670)	1,953 (4,340)	1,575 (3,500)	787 (1,750)
Trichloroethylene	1,350 (3,000)	675 (1,500)	202.5 (450)	103.5 (230)
Tetrachloromethane/Carbon tetrachloride <small>Error! Bookmark not defined.</small>	1,255.5 (2,790)	630 (1,400)	180 (400)	90 (200)
Chlorine production	32 (70)	18 (40)	175.5 (390)	72 (160)
Dacthal	0	0	45 / 100	36 (80)
Vinyl chloride	0	0	12.15 (27)	0
Atrazine, simazine	0	0	4.05 (9)	2.25 (5)
Pentachloronitrobenzene	0	0	2.7 / 6	1.35 (3)
Mirex	0	0	0.9 / 2	0.45 (1)
<b>Total</b>	<b>6,538.5 (14,530)</b>	<b>3,276 (7,280)</b>	<b>2,198 (4,884)</b>	<b>1,093 (2,429)</b>

#### Analysis of HCBd and other UOPs in by-product of chloromethane production<sup>301</sup>

The production of unintentionally produced POPs during the methanol based production of a chlorinated methane production were investigated in China. High concentrations of hexachlorobutadiene and other highly chlorinated compounds such as decachlorobiphenyl, octachloronaphthalene, octachlorostyrene, hexachlorocyclopentadiene, hexachlorobenzene,

<sup>300</sup> Mumma CE, Lawless EW (1975) Survey of Industrial Processing Data: Task I - Hexachlorobenzene and Hexachlorobutadiene Pollution from Chlorocarbon Processing. Midwest Research Institute prepared for US Environmental Protection Agency. June 1975. Available online at National Service Center for Environmental Publications (NSCEP).

<sup>301</sup> Zhang L, Yang W, Zhang L, Lib X (2015) Highly chlorinated unintentionally produced POPs generated during the methanol-based production of chlorinated methanes: a case study in China. Chemosphere 133, 1–5.

and pentachlorobenzene were found in the carbon tetrachloride by-product of the methanol-based production of chlorinated methanes.<sup>301</sup> The total emission amounts during the production of chlorinated methanes in China of hexachlorobutadiene in 2010 was estimated to 7350 kg.<sup>301</sup> Furthermore large amounts hexachlorocyclopentadiene, polychlorinated benzenes, polychlorinated naphthalenes, octachlorostyrene, and polychlorinated biphenyls release were estimated to be 10080, 5210, 427, 212, and 167 kg, respectively.<sup>301</sup> Also PCDD/PCDFs were detected in the by-product.<sup>301</sup>

### **Analysis of HCBd in drinking water close to organochlorine landfills in the US<sup>302</sup>**

Ground water that was used as a source of potable water by residents of a small community became contaminated by leachate from a 300,000 barrel pesticide waste dump. High levels of HCBd and carbon tetrachloride was detected in the drinking water.<sup>302</sup> An environmental health survey of the residents and an apparent control group was conducted to determine if any adverse health effects resulting from exposure to the toxic compounds, many of which were hepatotoxins, could be detected. The initial hepatic profile testing revealed elevated concentrations of the serum enzymes, alkaline phosphatase and serum glutamic oxaloacetic transaminase, in residents who had used the contaminated water.<sup>302</sup> Six individuals in the exposed group had slight hepatomegaly compared to one individual in the intermediate exposure group and none in the controls. The biochemical and clinical observations are suggestive of a transitory liver injury probably related to exposure to the contaminated drinking water.<sup>302</sup>

### **Analysis of HCBd in drinking water close to organochlorine landfills in Switzerland<sup>303</sup>**

In 2006, Greenpeace Switzerland analysed this drinking water by GC/MS screening and found a range of chemicals including HCBd and tetrachlorobutadiene.<sup>303</sup> Greenpeace considers that the chlorinated butadienes and other pollutants in the drinking water most likely stem from the neighbouring chemical landfill because chlorinated butadienes as well as other pollutants detected in the drinking water had previously been detected in the wastes of this chemical landfill and the surrounding groundwater.<sup>303</sup> Also the water supplier "Hardwasser AG" had already detected HCBd and tetrachlorobutadiene in the drinking water in 1980 and 2005 without publishing the results.<sup>303</sup> After the Greenpeace analysis and due to the suspicion of genotoxic effects of the chlorinated butadiene, the national authorities determined a limit value for drinking water of 75 ng/l<sup>304</sup> and the authorities forced the drinking water supply company to treat the drinking water.<sup>303</sup>

### **Analysis of HCBd in fish around landfills from organochlorine production<sup>305,306</sup>**

In 2004, the USEPA proposed the Devil's Swamp Lake site in Baton Rouge, Louisiana, to the National Priorities List (NPL). Fish has been measured for contamination finding high levels of HCBd, HCB and PCBs. As part of prudent public health practices, the Louisiana Department of Health and Hospitals/Office of Public Health/Section of Environmental Epidemiology has reviewed catfish and largemouth bass data from the Devil's Swamp Lake site. It was concluded that future exposures are likely (fishing club and barbeque activities) and ingestion of fish pose a threat to human health. A health advisory suggesting limiting fish consumption was issued.<sup>306</sup>

<sup>302</sup> Clark CS, Meyer CR, et al. (1982) An environmental health survey of drinking water contamination by leachate from a pesticide waste dump in Hardeman County, Tennessee. Arch Environ Health. 37(1), 9-18.

<sup>303</sup> Forter M (2016) Hexachlorobutadiene in the drinking water of the City of Basel (Switzerland), the Rhine and the chemical landfill „Feldreben“ of BASF, Novartis and Syngenta. Conference proceeding; 13 IHPA Forum, November 03-06, 2015, Zaragoza, Spain.

<sup>304</sup> Swiss Federal Office of Public Health (2010) Toxikologische Beurteilung von polychlorierten Butadienen im Trinkwasser. Faktenblatt, Bern, 27.4.2010.

<sup>305</sup> U.S. EPA (2004) HRS Documentation Record Devil's Swamp Lake (LAD981155872). EPA Region 6 (214) 665-7436 Superfund Site Assessment Section (6H-MA).

<sup>306</sup> U.S. Department of Health and Human Services (2006) Health Consultation – Devils Swamp Lake a review of fish data East Baton Rouge parish, Louisiana EPA Facility ID: LAD985202464.

## Annex 3-G Case studies of PeCB, HCB and PCDD/F in articles and products

### Screening of unintentionally POPs in chloranil<sup>307</sup>

Unintentionally POPs including PeCB, HCB and PCDD/PCDF have recently been screened in chloranil samples from Chinese producers. Extremely high levels of PCDD/PCDF (522 µg TEQ/kg) were detected in one chloranil product and therefore with PCDD/PCDF levels 35 times above the low POPs threshold (15 µg TEQ/kg) of the Basel Convention for wastes. The estimated total PCDD/PCDF content of this currently marketed chemical from China alone was 1044 g TEQ, which is about 10% of China's total PCDD/PCDF inventory, but present directly in treated consumer products. PeCB, HCB, and PCBs were also detected in these chemicals in relevant concentrations (Liu et al., 2011).

### Monitoring of HCB in pigments<sup>308,309</sup>

The Japanese government have submitted two reports on HCB in Tetrachlorophthalic acid (TCPA, tetrachloro-1,2-benzenedicarboxylic acid)<sup>310</sup> and related pigments (e.g. Pigment Yellow 110 (CAS Registry Number 5590-18-1), Pigment Yellow 138 (CAS Registry Number 30125-47-4), Solvent Red 135; Solvent Red 162; (CAS Registry Number 20749-68-2 and 71902-17-5)) to the COP4 ([Government of Japan 2006](#) and [2007](#)). These case studies can be seen from product coverage as state of art approach of monitoring unintentionally POPs in products. The limitation of the study is that no PeCB or PCDD/PCDF has been reported. Unintentionally HCB levels for TCPA were found up to 3,000 ppm and the suggested BAT levels for TCPA and pigments were in ppm range (up to 200 ppm).

Specific features of the reports:

- Comprehensive dataset on HCB in TCPA and key related pigments.
- Background information on production processes and cleaning steps for the products and related achievable HCB levels.
- Suggestion on BAT approach for minimizing HCB with suggested BAT/BEP levels.

### Monitoring of HCB, PCB, PCDD/PCDF in chlorinated paraffins<sup>311</sup>

A first detailed assessment of unintentional POPs in chlorinated paraffins revealed that also chlorinated paraffins can contain high levels of PCBs and PCNs as well as PCDFs. Three samples of technical grade CPs from an East Asian country (with legislation in place limiting PCDD/PCDF in chemicals and products) were analyzed, had lower-bound PCDD/PCDF concentrations that ranged from 133 to 545 µg TEQ/t.<sup>311</sup>

LCCPs produced from an East Asian country were found to have total PCB concentrations ranging from 140,000 to 210,000 ng/g, with a mean of 165,000 ng/g, as well as HCB concentrations ranging from 6,100 to 8,900 ng/g, with a mean of 7,733 ng/g. Considerable lower levels of PCB (40 ng/g) and HCB (7 ng/g) were detected in a CP sample from an East Asian country with legislation in place limiting unintentional POPs in chemicals and products.<sup>311</sup>

<sup>307</sup> Liu W, Tao F, Zhang W, Li S, Zheng M, (2012) Contamination and emission factors of PCDD/Fs, unintentional PCBs, HxCBz, PeCB and polychlorophenols in chloranil in China. *Chemosphere* 86, 248-251.

<sup>308</sup> Government of Japan (2006) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in TCPA and Solvent Red 135. November 2006.

<sup>309</sup> Government of Japan (2007) Assessment Committee on BAT Levels for Reduction of a Specified Chemical as a Contaminant By-product: Report on BAT Levels concerning By-product HCB in Other Pigments Derived from TCPA and Phthalocyanine.

<sup>310</sup> The dimethyl ester of tetrachlorophthalic acid is used as an herbicide, Dachtal.

<sup>311</sup> Takasuga T, Nakano T, Shibata Y (2012) Unintentional POPs (PCBs, PCBz, PCNs) contamination in articles containing chlorinated paraffins and related impacted chlorinated paraffin products. Presentation, Dioxin 2012, 26-31. August, Cairns/Australien.

### Monitoring of pesticides for unintentionally POPs<sup>312,313</sup>

In a Chinese study five pentachloronitrobenzene (PCNB) pesticide products (including 2 raw pesticide products and 3 formulations) were analysed for unintentionally POPs including HCB, PeCB, PCBs and PCDD/PCDF. All investigated unintentionally POPs were detected in all formulations. For some formulation the TEQ contribution from PCB were higher compared to total PCDD/PCDF TEQ contribution.

In another study current used pesticides in Australia were screened for unintentionally POPs PCDD/PCDF. PCDD/PCDF were detected in all pesticide formulation with high levels in pentachloronitrobenzene (PCNB) (Holt et al. 2010<sup>313</sup>, Huang et al. 2015<sup>312</sup>). PeCB and HCB were not screened in this study but it was mentioned that PCNB degrades to PeCB in the environment (approx. 3%) and that this is the largest source of unintentionally PeCB s higher than all other sources combined (UNEP 2010<sup>314</sup>).

### Review on new information on unintentional POPs in chemicals<sup>315</sup>

The UNEP BAT/BEP group published a review on new information on the formation and release of unintentional POPs from production processes for pesticides and industrial chemicals were compiled for reducing or preventing releases and related information gaps. The document is a first attempt to gather monitoring information on relevant individual processes of chemical production with respect to the formation and presence of unintentional POPs. One aim was to help to assess and improve these processes where BAT/BEP is not yet applied and to help in developing better inventories of unintentional POPs in these processes and chemicals.<sup>315</sup> Information gaps for individual chemicals have been included<sup>315</sup> which can stipulate monitoring and screening of unintentional POPs in chemicals.

<sup>312</sup> Huang J, Gao J, et al. (2015) Unintentional formed PCDDs, PCDFs, and DL-PCBs as impurities in Chinese pentachloronitrobenzene products. *Environ Sci Pollut Res Int.* 22, 14462-14470.

<sup>313</sup> Holt E, Weber R, Stevenson G, Gaus C (2010) Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/Fs) Impurities in Pesticides: A Neglected Source of Contemporary Relevance. *Environ. Sci. Technol.* 44, 5409–5415.

<sup>314</sup> UNEP (2010) Additional consideration of new persistent organic pollutants: pentachlorobenzene. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/21) Geneva 11-15. October 2010.

<sup>315</sup> UNEP (2015) Formation and release of unintentional POPs from production processes for pesticides and industrial chemicals: Review of new information for reducing or preventing releases and related information gaps. UNEP/POPS/TOOLKIT/BATBEP/2015/2