Draft guidance on sampling, screening and analysis of persistent organic pollutants in products and recycling

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Secretariat of the Basel, Rotterdam and Stockholm
Conventions

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List of Abbreviations and Acronyms

ABS	Acrylonitrile-Butadiene-Styrene
ACN	Acetonitrile
AIST	National Institute of Advanced Industrial Science and Technology, Japan
ASE	Accelerated Solvent Extraction
ASR	Automobile Shredder Residues
BAT	Best Available Techniques
BEP	Best Environmental Practices
BFR	Brominated Flame Retardant
CAS	Chemical Abstract Service
CHCC	Chemical of high concern to children (Washington State)
CEN	European Committee for Standardization
CIC	Combustion Ion Chromatography
CiP	Chemicals in Products
CLs	Concentration limits
CME	Cellulose mixed ester
c-OctaBDE	Commercial Octabromodiphenyl ether
c-PentaBDE	Commercial Pentabromodiphenyl ether
c-DecaBDE	Commercial Decabromodiphenyl ether
COP	Conference Of Parties
CRT	Cathode Ray Tube
DART	Direct Analysis in Real Time
DecaBDE	Decabromodiphenyl ether
DIN	Deutsches Institut für Normung
EC JRC	European Commission Joint Research Center
ECD	Electron Capture Detector
ECHA	European Chemicals Agency
ECNI	Electron capture negative ionization
EEE	Electrical and Electronic Equipment
EI-MS	Electron Impact Mass Spectrometry
EPED	Echelle-Plasma-Emission-Detector
EPS	Expanded Polystyrene
FCs	Functional concentrations
FPF	Flexible Polyurethane Foam
FR	Flame Retardant
GLP	Good Laboratory Practice
HBB	Hexabromobiphenyl
HBBz	Hexabromobenzene
HBCD(D) [1]	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HIPS	High Impact Polystyrene
HPLC	High performance liquid chromatography

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[1] The abbreviation of Hexabromocyclododecane in the Convention is HBCD while in most scientific literature HBCDD is used.

HRMS	High resolution mass spectrometry
IEC	International Electrotechnical Commission
IS	Internal standard
ISO	International Organization for Standardization
JICA	Japan International Cooperation Agency
LC	Liquid chromatography
LCCPs	Long-Chain Chlorinated Paraffins
LIBS	Laser-Induced Breakdown Spectrometry
LOD	Limit of detection
LRMS	Low Resolution Mass Spectrometry
LCqMS	Liquid Chromatography Quadrupole Mass Spectrometry
MAE	Microwave-Assisted Extraction
MCCPs	Medium-Chain Chlorinated Paraffins
MEKC	Micellar electrokinetic capillary chromatography
MeOH	Methanol
MTBE	Methyl Tert-Butyl Ether
NCI	Negative Chemical Ionization
NIR	Near Infrared
PAPs	Polyfluorinated Alkyl Phosphate Esters
PBB	Polybrominated Biphenyl
PBDEs	Polybrominated Diphenyl Ethers
PBDD/PBDF	Polybrominated Dibenzo-*p*-dioxins and Polybrominated Dibenzofurans
PBT	Polybutylene Terephthalate
PC	Polycarbonate
PCBs	Polychlorinated Biphenyls
PCDD/PCDFs	Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans
PCNs	Polychlorinated naphthalenes
PCP	Pentachlorophenol and its salts and esters
PET	Polyethylene Terephthalate
PeBBz	Pentabromobenzene
PeCB	Pentachlorobenzene
PFASs	Per- and Polyfluorinated Alkylated Substances
PFCs	Per-and Polyfluorinated Chemicals/Compounds
PFDA	Perfluorodecanoic cid; Perfluorodecanoate
PFDoA	Perfluorododecanoic acid; Perfluorododecanoate
PFHpA	Perfluoroheptanoic acid; Perfluoroheptanoate
PFHxA	Perfluorohexanoic acid; Perfluorohexanoate
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid; Perfluorononanoate
PFOA	Perfluorooctanoic acid; Perfluorooctanoate
PFOS	Perfluorooctane sulfonic acid; Perfluorooctane sulfonate
PFOSF	Perfluorooctane sulfonyl fluoride
PIGE	Particle-Induced Gamma Ray Emission
PLE	Pressurised Liquid Extraction
POPRC	Persistent Organic Pollutants Review Committee
POPs	Persistent Organic Pollutants

PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene,
PVDF	Polyvinyldifluoride
PUR	Polyurethane
PXDD/PXDF	Polybrominated-chlorinated Dibenzo-*p*-dioxins and Dibenzofurans
QA/QC	Quality Assurance and Quality Control
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (in EU)
RoHS	Restriction of the use of certain Hazardous Substances in electrical and electronic equipment (in EU and other countries)
SAICM	Strategic Approach for International Chemicals Management
SCCPs	Short-Chain Chlorinated Paraffins
SC	Stockholm Convention
SIM	Selected Ion Monitoring
SPE	Solid Phase Extraction
TBBPA	Tetrabromobisphenol A
TCPA	Tetrachlorophthalic acid
THF	Tetrahydrofuran
TCEP	Tris(2-chloroethyl) phosphate
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate
TDPP	Tris(1-chloro-2-propyl) phosphate
TOF	Time of Flight
TPP	Triphenyl phosphate
TOP-Assay	Total Oxidisable Precursor Assay
UAE	Ultrasonic-assisted extraction
UNEP	United Nations Environmental Programme
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 produced POPs

Between 2009 and 2019 eighteen additional substances were listed in the Stockholm Convention as persistent organic pollutants (POPs). Several of these POPs have been used in various products and are therefore still in use and in recycling streams. Some of these POPs are still produced and used due to exemptions and can even be present in new products such as perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and related compounds, polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), pentachlorophenol (PCP), and short-chain chlorinated paraffins (SCCPs). All these POPs are in a wide variety of products and recycling streams (see Annex 1).

A set of guidance has been developed to assist Parties to meet their obligations concerning the POPs listed between 2009 and 2019. For example, the guidance for developing respective inventories[2,3,4,5,6] and the guidance for applying best available techniques and best environment practices (BAT/BEP) [7,8] which give also an overview of (former) uses of these substances and their relevance for the current presence of POPs in products, waste and recycling.

Among the additionally listed POPs in the Stockholm Convention, hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), and polychlorinated naphthalenes (PCNs) were listed in Annex C and can be present as unintentional by-product in a range of chemicals and other products (see Annex 1-E and Annex 1-G and Chapter 8).

Intentional production of PCNs[9], PBDEs listed in 2009 and PeCB have stopped for more than a decade and therefore these substances are now contained only in products in use and in some recycling streams and related products manufactured from these materials. HBCD, DecaBDE, PCP, PFOS and PFOA and related compounds are still produced and used and therefore possibly also used in a range of new products and processes where specific exemptions and acceptable purposes have been granted by the Convention (see Annex 1-A). Furthermore, POPs might still be produced or used by Parties that have not yet ratified the amendments of the Stockholm Convention or by non-Parties.

POPs used in products are also included in large 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 (PUR) foams, synthetic carpets, certain furniture, textiles, recycled wood and paper.

PBDEs listed in 2009 (tetraBDE to heptaBDE restricting commercial PentaBDE and commercial OctaBDE) are listed with a time-limited exemption allowing the recycling of wastes containing these substances and their subsequent use in products until 2030. Therefore, a guidance for recycling and disposal of PBDEs has been developed.[7] This guidance considers the recommendations adopted by the decision SC-5/5 of the Conference of the Parties of the Stockholm Convention on separation of materials containing PBDEs from recycling

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[2] UNEP (2015) Guidance for the inventory of perfluorooctane sulfonic acid (PFOS) and related chemicals listed under the Stockholm Convention on POPs (Draft).

[3] UNEP (2015) Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs (Draft). UNEP (2019) Preliminary draft guidance on preparing inventories of decaBDE. UNEP/POPS/COP.9/INF/18

[4] UNEP (2017) Guidance for the inventory of Hexabromocyclododecane (HBCD) (Draft March 2017).

[5] Secretariat of the Stockholm Convention (2017b) Draft guidance on preparing inventories of polychlorinated naphthalenes. UNEP/POPS/COP.8/INF/19

[6] UNEP (2017) Draft guidance on preparing inventories of hexachlorobutadiene UNEP/POPS/COP.8/INF/18

[7] UNEP (2017) 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 POPs (Draft).

[8] UNEP (2021) Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and their related substances listed under the Stockholm Convention on Persistent Organic Pollutants. Draft March 2021.

[9] PCNs have an exemption as intermediate for the production PFNs but there is no registration for this exemption.

streams, as outlined in annex to decision POPRC-6/2. This requires the monitoring of these recycling streams, including products from recycled materials, for PBDEs content, to ensure their environmentally sound management (UNEP 2017).[7]

In case of PFOS, PFOA and related compounds, DecaBDE or HBCD, recycling is not allowed, hence, products at their end-of-life have to be managed in an environmentally sound manner (ESM). Also, this may require monitoring products potentially contaminated with DecaBDE, HBCD or with PFOS, PFOA and related compounds.

Furthermore, for developing inventories of these additionally listed POPs, monitoring of POP content in products, recycling streams and wastes might be useful. The Stockholm Convention POP inventory guidance documents include a tiered approach that all Parties can develop their own national inventories to the level they are capable of 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 products is their relevance for human exposure. POPs in products are closely linked to human exposure. While for legacy POPs, such as pesticides, the major exposure comes from food, a major exposure for industrial POPs comes from products.[10,11,12,13] For SCCP, household kitchen products, like kitchen blenders and baking ovens, have been highlighted as a relevant exposure path.[14,15] For PBDEs a major exposure stem from chemicals in consumer goods like furniture, vehicles or specific PUR foam products.[16,17] Even toys made out of recycled plastic can lead to relevant exposure of children.[10,11] Also, the recycling of PBDE containing PUR foam resulted in high blood levels in recyclers and carpet installers.[18] The external cost for PBDE exposure has been estimated to $12.6 billion for Europe[19] and 266 billion for the US.[20] Tracking POPs in products and recycling to reduce human exposure is another major reason for monitoring POPs in products and recycling. Furthermore, the export of industrial POPs in products to developing countries is of same or rather higher relevance than the long-range transport of POPs by air or water and needs a better assessment and control.[21]

1.2 Purpose and objective of this guidance

This document provides guidance on monitoring (sampling, screening and analysis) of industrial and unintentional POPs in products in use and in recycling streams for POPs listed from 2009 to 2019. This guidance

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[10] Ionas AC, Ulevicus J, et. al (2016) Children's exposure to polybrominated diphenyl ethers (PBDEs) through mouthing toys. Environ Int. 87, 101-107.

[11] 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.

[12] de Boer J, et al. (2016) Flame retardants: Dust - And not food - Might be the risk. Chemosphere. 150, 461-464.

[13] 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.

[14] Yuan B., Strid A., Ola P., De Wit C.A., Nystrom J Bergman A (2017) Chlorinated paraffins leaking from hand blenders can lead to significant human exposures. Environ. Int. 109, 73-80, https://doi.org/10.1016/j.envint.2017.09.014.

[15] C. Gallistl, J. Sprengel, W. Vetter (2018) High levels of medium-chain chlorinated paraffins and PBDEs on the inside of several household baking oven doors, Sci. Total Environ. 615, 1019-1027, https://doi.org/10.1016/j.scitotenv.2017.09.112.

[16] Carignan CC, Heiger-Bernays W, et al. (2013) Flame Retardant Exposure among Collegiate U.S. Gymnasts. Environ. Sci. Technol., 47 (23), 13848–13856.

[17] 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

[18] 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.

[19] 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.

[20] 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.

[21] 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.

does only address POP pesticides to the extent that they were used in wood, leather and textile treatment in particular pentachlorophenol (PCP).

The guidance document intends to assist Parties in their effort of monitoring POPs in products and recycling and to support the development and improvement of inventories on industrial POPs and unintentional POPs. Here, for some specific inventory questions, a Tier III inventory component including screening and instrumental analysis might be useful or might be needed.

Therefore, guidance is provided:

- On products possibly containing newly listed POPs (in particular for POPs listed between 2009 and 2019) (see Annex 1);
- On recycling streams possibly containing newly listed POPs (listed 2009-2019)
- For developing strategies for monitoring POPs in 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 in use and through recycled materials.

This guidance document complements the activities and guidance materials of the Global Monitoring Plan (GMP)[22], which focuses on the matrices for effectiveness evaluation of the Stockholm Convention (air, human milk/blood and water). For these, the GMP provides guidance and standard operating procedures.[23] Currently, the GMP does not address POPs in products[24] and in the second GMP report of POPs[25], POPs in products or recycling are not addressed.

This guidance can also provide some support for addressing the Strategic Approach for International Chemicals Management (SAICM) Emerging Policy Issues of Chemicals in Products (CiP) as POPs are concerned. Also, the guidance can support the SAICM issue of concern of all per-/poly fluorinated alkylated substances (PFASs).

Please 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 relevant POPs, listed between 2009 and 2019, in products and recycling streams with practical information and case studies on sampling and screening and basic information on extraction and analysis of samples. Where applicable, this guidance refers to international standards developed for the analysis of POPs. However, for a range of POPs in products, no international standard for sampling or 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 products also links closely to the monitoring of POPs in end-of-life products and wastes and the recycling of materials. In the frame of the Basel Convention a set of Technical Guidelines on the

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[22] https://www.unep.org/explore-topics/chemicals-waste/what-we-do/persistent-organic-pollutants/global-monitoring

[23] https://www.unep.org/explore-topics/chemicals-waste/what-we-do/persistent-organic-pollutants/guidance-and-standard?_ga=2.4326963.1025376130.1615222267-352097559.1596638234

[24] UNEP (2015) Guidance on the global monitoring plan for persistent organic pollutants. UNEP/POPS/COP.7/INF/39

[25] UNEP (2017) Second global monitoring report. UNEP/POPS/COP.8/INF/38

environmentally sound management of waste consisting of, containing or contaminated with POPs have been developed. These guidelines can also provide additional information on sampling, analytical and monitoring aspects of POPs in wastes and environmentally sound disposal methods.

1.4 POPs considered and related products

This guidance focusses on industrial and unintentional POPs with the main topic of screening and monitoring them in products and recycling. Industrial POPs considered are:

- Perfluorooctane sulfonate (PFOS) and related compounds (Chapter 3),
- Perfluorooctanoic acid (PFOA) and related compounds (Chapter 3),
- Polybrominated diphenyl ethers (PBDEs) (Chapter 4),
- Hexabromocyclododecane (HBCD) (Chapter 4),
- Hexabrominated biphenyls (HBB) (Chapter 4),
- Pentachlorophenol (PCP), its salts and esters (Chapter 5)
- Polychlorinated naphthalenes (PCNs) (Chapter 6),
- Short-chain chlorinated paraffins (SCCPs) (Chapter 7).

Furthermore, all unintentional POPs in products, with an emphasis on the recently listed POPs in Annex C (HCBD, PeCB, and PCNs), are addressed in Chapter 8. Since unintentional POPs are often formed in the same processes, initially listed unintentionally produced POPs in products are also mentioned and addressed in this document, as appropriate.

Major products and other materials and recyclates, which may contain industrial POPs or unintentional POPs, are described in Annex 1.

Where available, case studies on screening and monitoring of new POPs in products and materials in recycling are referenced and/or provided in Annex 2.

1.5 Approach to combine screening strategies with confirmation analysis

This 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 product groups with regards to their possible POP content (e.g., polystyrene foam and PUR foams for bromine as indication of HBCD and PBDE contents respectively, or carpets for fluorine as indication for PFOS, PFOA and related compounds). A pre-screening of samples helps to minimise time and costs for confirmation analysis, which requires extraction and appropriate clean-up steps and often sophisticated and costly instrumental analysis, which in turn 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 3). Where available, the guidance links to case studies (Annex 2) where sampling and analytical procedures are often described.

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

Studies on POPs in products and recycling 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 products that are possibly impacted by POPs, it can be appropriate to aim for a regional concept of monitoring POPs in products or recycling and avoid repetition in countries with associated waste of resources. Such regional studies might be coordinated by a Stockholm/Basel Convention Regional Centre or other institutions working at national, 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, costs and results could be shared and that regional studies can address the relevant products of different countries with a similar product portfolio and a similar recycling situation 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 PBDEs impacted articles or a region might have a factory producing or using PFOS or PFOA with impact on food/feed from this region).

1.7 Approach for presenting case studies

Where available, best practice case studies for key products or recycling streams possibly containing individual POPs are referenced in the respective chapters and described in Annex 2**.** 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 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 products and materials in recycling are already available and what information is missing. With this kind of 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 the available knowledge, a decision may be made on whether an additional study on selected POPs in products is needed, as well as the possibility of any additional chemical to include in such a study, e.g., SAICM emerging policy issues like PFASs or endocrine disrupting chemicals (EDCs).[26]

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 compounds were no longer detected in coated paper but other PFASs[27] (see Annex 2-A).

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

[27] Schaider LA, Balan SA, Blum A, Andrews DQ, Strynar MJ, Dickinson ME, Lunderberg DM, Lang JR, Peaslee GF. Fluorinated Compounds in U.S. Fast Food Packaging. Environ Sci Technol Lett. 2017;4(3):105-111.

2 General considerations and cross-cutting issues

2.1 Capacity building

Laboratory personnel needs to be trained on different analytical procedures and methodologies for POP monitoring and also on quality assurance and quality control (QA/QC). UNEP has within its activities related to the Global Monitoring Plan for POPs (GMP) a program on capacity building for POP analysis (mainly for governmental laboratories), which could be considered. The programme is implemented in cooperation with the University of Amsterdam (The Netherlands) and the Örebro University (Sweden). Furthermore, capacity building on POP analysis is offered by the Japan International Cooperation Agency (JICA) or in summer schools (e.g., by RECETOX, a Stockholm Convention Regional Centre in central Europe, 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.[28] Furthermore, learning options available through the Internet (E-learning or Webinars) could be explored and assessed.

2.2 Quality assurance and quality control (QA/QC) considerations

2.2.1 General 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 a section 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 from 2009 to 2019 should be considered:

- cleaned laboratory equipment, material, and chemicals to be used to avoid contamination from background;
- known and documented laboratory blank levels for the POPs measured;
- system ensuring that effectiveness of the measurements and procedures are 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, 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;
- use of Certified Reference Materials (CRMs)[29];
- tests to be carried out to evaluate the precision (repeatability and reproducibility), the limits of detection (LODs) and of 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.

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[28] E.g., Wenclawiak, 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.

[29] The use of CRMs is often difficult to comply because of the scarcity of CRMs. In addition, when CRMs exist, the concentrations are often much higher than those found in real samples

2.2.2 Accreditation of laboratories

To develop their own analytical methodologies, laboratories should consider accreditation schemes such as ISO 17025. By this, laboratories can carry out their analyses under accredited conditions with reliable results. As part of their accreditation, the ISO/IEC 17025 standard requires the following tools to be implemented, to demonstrate their competence in operating analytical and calibration services:

- Use of robust and validated analytical methods, where available, international standards.
- Use of (CRMs), if available.
- Participate in Inter-Laboratory Trials (ILT), Proficiency Tests (PT).
- Determination of uncertainties of the results.

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 products, 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 the RoHS compliance has been developed and was published in 2015.[30] A regional/international technical specification for extractable PFOS in articles and its analysis has been developed in 2010 (NPR-CEN/TS 15968) but has not been validated to a standard yet. Furthermore, no analytical procedure (standard) is available for most of the 160 listed PFOS related compounds including in particular the non-extractable PFOS precursors.

Also, no ISO, CEN, or EPA standard are available for unintentional POPs like HCBs, PeCB or PCDD/PCDF for the extraction from products like pigments or dyes. 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 materials. Only recently an ISO standard has been developed for PCBs in pigment and extenders (ISO 787-28:2019).[31]

The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of respective products and mention their limitations for products;
- Describe some standard methodologies used by laboratories experienced in the analysis of POPs contained in certain products or recycling streams;
- Describe case studies with links to publications and 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 Certified reference materials and interlaboratory studies

2.4.1 Certified reference materials

New laboratories, starting POP analysis in products, are encouraged to utilize certified reference materials (CRMs), if available, to confirm the analytical certainty of the target substance. Table 2-1 shows a list of CRMs for POP-BFRs in polymers that are currently available.

Another available CMR for POPs is e.g. PCB in waste mineral oil (BCR-420).

There are however no CMRs for PFOS and PFOA in products.

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[30] 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)

[31] ISO 787-28:2019 General methods of tests for pigments and extenders — Part 28: Determination of total content of polychlorinated biphenyls (PCB) by dissolution, cleanup and GC-MS.

Table 2-1. Some polymer certified reference materials for POP-BFR analysis

Compounds	CRM	Polymer type	Manufacturer
PBDEs	JSAC 0641	Polyester resin	The Japan Society for Analytical Chemistry
PBDEs	JSAC 0642	Polyester resin	
DecaBDE	NMIJ CRM 8108-b	Polystyrene	AIST, Japan
DecaBDE	NMIJ CRM 8110-a		AIST, Japan
PBDEs	ERM-EC590	Polyethylene (LDPE)	EC JRC, EU
PBDEs	ERM-EC591	Polypropylene (PP)	EC JRC, EU
HBCD	113-03-009		

2.4.2 Interlaboratory studies

Interlaboratory assessment for POP analysis is an important approach to demonstrate the quality and reliability of a laboratory. Within the global monitoring plan (GMP) interlaboratory assessment has been conducted for different POPs groups for environmental matrices like sediments and air sample extract.[32] Such interlaboratory assessment have not been conducted yet for POPs in products and materials within the GMP or other UN activity. However, there is an ongoing international interlaboratory study for the determination of POP-BFRs in plastic waste conducted by the National Institute for Environmental Studies (NIES), Japan. In this study, standard solutions, plastic extracts, and plastic pieces were distributed during 2019–2020 along with a protocol of a simple method to determine their contents. Currently, also an interlaboratory comparing

2.5 Step by step approach

To determine the occurrence and quantities of POPs in different products, 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, PFOA and related compounds in other materials, such as industrial materials used downstream in a product chain, consumer products, chemical formulas and industrial blends arriving at the boarders and possibly identified by the customs or other relevant authorities.

2.5.1 Step 1: Survey of products and recycling streams containing POPs

Before collecting samples, a survey should be conducted to determine the presence of products that possibly contain or have been contaminated with POPs. Furthermore, recycling flows contaminated by POPs with associated risk of contaminating new products should be assessed for the presence of POPs in recyclates. Sample candidates can be identified from the list provided in Annex 1 for the specific POPs. 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. This might include industries producing or using the chemicals or products or competent authorities responsible for supervision of industries or the consumer market or the customs.

2.5.2 Step 2: Sample collection

2.5.2.1 Standard sampling procedures and protocol

Standard sampling procedures should be established and agreed upon before the start of a 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

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[32] Fiedler, H; van der Veen, I.; de Boer, J. (2020) Global interlaboratory assessments of perfluoroalkyl substances under the Stockholm Convention on POPs. Trends in Analytical Chemistry DOI10.1016/j.trac.2019.03.023.

for the respective POPs or otherwise accredited for performing an adequate analysis of the respective sample and selected POPs.

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

- Type of sample;
- Location and date of sampling;
- Any relevant information on the sample (e.g., year of manufacture, country of manufacture, polymer type).
- Take a picture of each sample
- If the products consist of multiple components, specify which component was sampled.

2.5.2.2 Representative sampling from recyclates and mixed waste containing POPs

Considering the need to move to a circular economy, waste becomes the resource and different methods are established to produce recyclates. The correct sampling of POPs in waste (e.g. plastics, other polymers, rubber or textiles) takes into account the interrelated following issues [33]:

- the distribution of the concentrations of POP substances in waste;
- the statistical questions of the determination of the size of a representative sample;
- the chemical characterization of particles and samples by field and laboratory methods.

Additional complexity stems from the fact that the relevant field methods measure the total element concentration (e.g. bromine or fluorine) and not substances, and the sorting methods for plastic are based on measurement of solid or atomic density. This is particularly pertinent to POP-regulated BFRs in plastic which have been progressively substituted by other brominated and dense substances in new products for a long time and plastic waste thus contains both POP-BFRs and non-regulated BFRs. Therefore, there is no direct relationship between bromine on the one hand and concentration of POP-regulated BFRs on the other [34]. The same is true for fluorine and listed PFASs and non-regulated PFAS.

In mixed plastic waste e.g. from e-waste or end of life vehicles, the distribution of concentrations of additives are skewed by large values and are never Gaussian (normal). The 99th – 99.9th centile fractions of particles ranked by increasing concentration are typically much more concentrated than in classical normal distributions. The median (the concentration of the 50th centile of particles ranked by increasing concentration) is 10-20 times smaller than the mean concentration, while they are equal in a normal distribution. These populations are best described by taking into account all of the following concentrations: median, mean and the last centiles. The confidence interval of the mean (typically the double or the triple of the standard deviation) does not enclose the 95th or 99th centile of the population as is the case with a normal distribution, because the standard deviation is higher than 2 or 3 times the mean. The distribution of concentrations decreases with time, due to substitution of regulated substances by others.

The high centiles which account for a large part of the POP content in waste must be present in a representative sample and any sub-samples to reliably determine the content of the relevant POP substances. The sample, which is a smaller portion of a batch, must therefore contain enough particles to include the rare particles with the same frequency as they are present in the whole batch. The size of a representative sample is expressed as the number of particles ‘n’. It is demonstrated that a representative sample of a batch must contain 100 particles of interest (the critical particles of the last centiles) to have a coefficient of variation of

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[33] Vencovsky D, Garrett S, Vencovska J, Shapland I, La Vedrine M, Ciatti F, White S, Webb S, Postle M, Hennebert P, Bisson M, Biaudet H, Lestremeau F, Cavalieri L, Mudgal S. (2021) Study to support the assessment of impacts associated with the review of limit values in waste for POPs listed in annexes IV and V of Regulation (EU) 2019/1021. Report for the Directorate General Environment of the EU. March 2021. Final Report. 427 p.

[34] Hennebert P. (2021). The substitution of regulated brominated flame retardants in plastic products and waste and the declared properties of the substitutes in REACh.

repeated measurements of 10%, and a 95% confidence interval of repeated measurements of 20% [33, 35, 36]. As 'p' is the frequency of rare particles, it follows that the number of these particles in a representative sample is $n*p = 100$, and that $n = (100/p)$ parts or shreds. This formula is very useful in practice: once p is known or estimated, the number of particles that a representative sample must contain can be determined. Two types of rare particles can be defined: a) 'rare particles with regard to concentration' can be defined as particles with a concentration greater than any given concentration of interest and 'rare particles with regard to size' can be defined as particles with a size range being the one that is less present in the particle size distribution. The resulting size of a representative sample is large if the batch contains only a few concentrated particles and can be smaller if the fraction of particles with a concentration greater than a concentration limit is higher and is known.

When p is known (typically in more homogeneous waste), n is calculated as 100/p. For instance, if $p > 0.1$ (case of highly brominated plastic fraction of separately collected fluorescent lamps), $n = 100/0.1 = 1{,}000$. If a single post-shredder particle weighs two grams, a representative sample would weigh 2 kgs.

When p is not known (in mixed waste), it can be taken as $p = 0.001$ (CEN TR 15310-1)[37] or it can be for POPs estimated by the ratio of their concentration limits (CLs) that must not be exceeded for regulatory or quality compliance and their functional concentrations (FCs) in products: $p = CL/FC$[34,35]. It is simply the fraction of POP-containing particles that must not be exceeded to have the whole batch not exceeding the CL. For PBDE with a hypothetical CL of 200 mg/kg, $p = 200$ mg/kg / 180 000 mg/kg ≈ 0.001. This value is probably reached for decaBDE in low-density sorted fraction of shredded end-of-life vehicles and large household electrical appliances. If $p \approx 0.001$, $n \approx 100/0.001 \approx 100\,000$, and if one particle weighs 10 grams, a representative sample would weigh ≈ 1 tonne. For a CL of 100 mg/kg for HBCDD in expanded polystyrene EPS and extruded polystyrene XPS: $p = 100$ mg/kg / 40 000 mg/kg = 0.0025, and a representative sample of mixed packaging waste with unknown frequency of parts/shreds with HBCDD should $n = 100/0.0025 = 40\,000$ parts/shreds. This number can be reduced to some increments if the batch of non-mixed waste is homogeneous, like uniform external, floor or roof insulation of individual parts of a building. For a SCCPs CL of 420 mg/kg: in unknown mixed waste, $p = 420$ mg/kg / 30 000 mg/kg = 0.014, and $n = 100/0.014 \approx 7{,}000$. For homogeneous waste from one known product (e.g. old underground conveyor belts), the sample size can be significantly reduced.

One or two steps of size reduction, mixing and subsampling are necessary to produce a laboratory sample of one/several dozen of kg containing for instance 100 000 particles. In the laboratory, other similar operations of size reduction (< 0.5 mm), mixing and subsampling are necessary to produce the test portion of ≈ 2 grams (containing about 100 000 spherical particles if size < 0.3 mm) that will be extracted and quantified.

2.5.2.3 Transport and storage of samples

Samples 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).

The pre-screening of samples can include specific approaches:

a) Considerations on the different use areas (see Annex 1)

b) CAS numbers, chemical names or product names (see Annexes 1 and also the respective inventory guidance documents[2,3,4,5,6]).

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[35] Hennebert P, Beggio G. 2021. Sampling and sub-sampling of granular waste: Part 1 - Size of a representative sample in terms of number of particles and application to waste containing rare particles in concentration. Submitted to Detritus.

[36] Beggio G, Hennebert P. 2021. Sampling and sub-sampling of granular waste: Part 2 - Size of a representative sample in terms of number of particles with different distributions of particle concentration and particle size. Submitted to Detritus.

[37] CEN/TR 15310-1: 2007. Characterization of waste - Sampling of waste materials Part 1: Guidance on selection and application of criteria for sampling under various conditions. CEN, Brussels, Belgium.

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 field sampling. Non-destructive methods can even be used for selections of individual 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., the simple “droplet test” can be used as indication for PFASs (Section 3.4.2); or mobile screening techniques for bromine can detect bromine below 100 mg/kg or even below 10 mg/kg (e.g., for some XRFs). If legislation requires that a POP 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^2) then some screening methods cannot be used for pre-selection of samples for assessment of compliance with the limit value.

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

Sampled products 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 the determination of the presence of target chemicals in a sample (see e.g., the DART method described for PFOS and other PFASs or the pyrolysis GC/MS method for 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.

2.5.4 Step 4: Quantification

Usually, quantification requires that the POP is extracted from the sample and the extract subjected to a clean-up procedure. Extraction methods and clean-up procedures should be 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 data acquisition and quantification. Quantification is either done with internal standards (e.g., isotope labelled standards, such as carbon ^{13}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 3 in combination with its chromatogram.

Specific care should be given to cross contamination from POPs in products in the laboratory which are often present in percent range in products, in particular if the laboratory also analyses 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, PFOA and related compounds listed in the Convention and other PFASs (not listed in the Convention but as an emerging issue under SAICM)[38] 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 PFASs can adsorb fast and strongly to glass.

2.5.5 Step 5: Documentation and reporting

The result of the monitoring should be documented in an appropriate form. The reporting might include the compilation of 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

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[38] In the Stockholm Convention only PFOS and related ca. 160 precursor chemicals are considered while all PFASs/PFCs are addressed under the Strategic Approach for International Chemical Management (SAICM) as an emerging policy issue.

validation of the methodology used and the results. The results should be communicated to the stakeholders concerned as appropriate.

2.6 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 some of the POPs the use of liquid chromatography (LC) has advantages and is recommended (PFOS, PFOA, HBCD and Chlordecone) (see Figure 2-1).

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

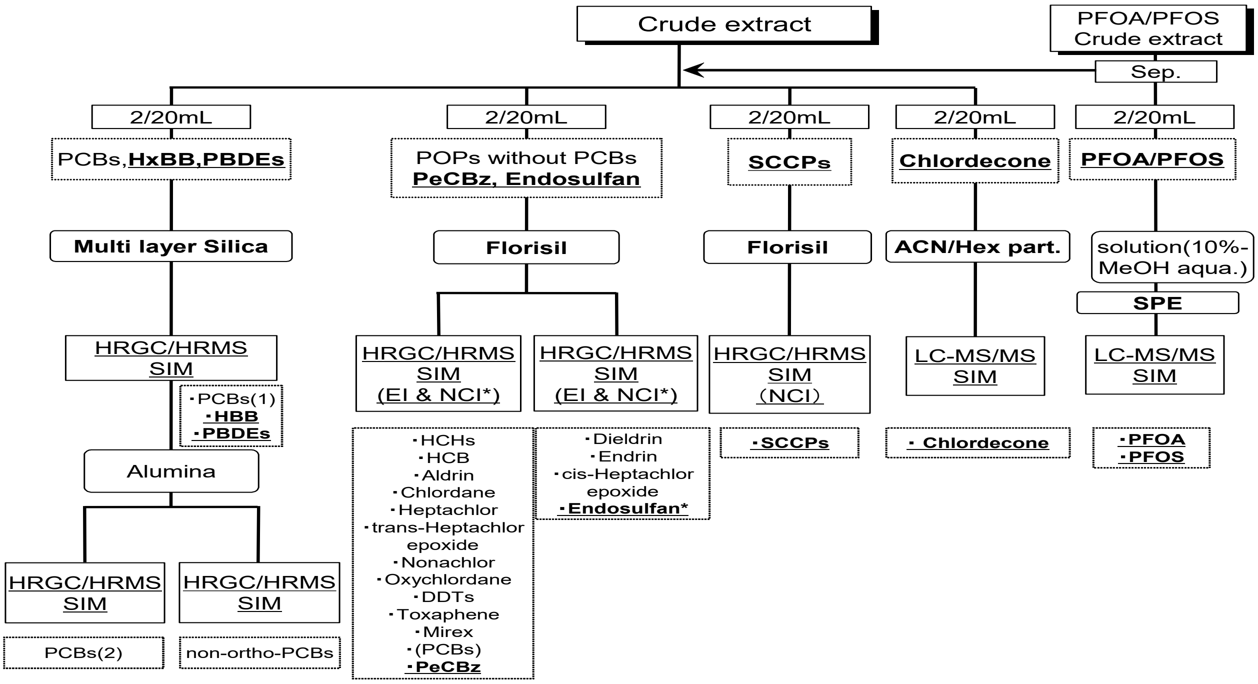

Figure 2-1: Clean-up of an air sample and instrumentation for analysis of all listed POPs in air (courtesy Prof. Takumi Takasuga; Shimadzu Techno Research, Japan).

Please note: For analysis of POPs in products, low resolution GC or ECD is normally sufficient (see respective sections in this document and Annex 3). PFHxS is recommended for listing in the Stockholm Convention at COP 10.

3 Sampling, screening and analysis of PFOS, PFOA and related compounds in products and recycling

3.1 PFOS, PFOA and related compounds in the Stockholm Convention

Perfluorooctane sulfonate (PFOS) is a fully fluorinated anion which is used as such or as salt in a range of applications (see Section 3.2 and Annex 1-A). Perfluorooctane sulfonyl fluoride (PFOSF) was/is used to produce a wide range of PFOS related compounds including side-chain fluoropolymers which have fat- and water-repellent properties. These PFOS-related compounds are precursors of PFOS and can be degraded to PFOS. PFOS, its salts and PFOSF have been listed in 2009 under Annex B with acceptable purposes[39] and specific exemptions (Decision SC-4/17).[40] Detailed information for listing has been compiled in their Risk Profile[41] and Risk Management Evaluation (RME).[42] In 2019, most of these exemptions were removed by decision SC-9/4[43] since alternatives are available for these uses.

Similarly, perfluorooctanoic acid (PFOA) has a wide range of application (see Section 3.2 and Annex 1-A). PFOA, its salts and PFOA-related compounds[44] were listed in 2019 in Annex A of the Convention with a wide range of exemptions (Decision SC-9/12).[45] Detailed information for listing of PFOA related compounds has been compiled in the Risk Profile[46] and RME of POPRC.[47]

Recently, perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds have been suggested for listing as POPs by the POPRC (POPRC-15/1).[48]

PFOS, PFOA and PFHxS are extremely persistent and have substantial bioaccumulating and biomagnifying properties. These PFASs do not follow the classic pattern of other POPs by partitioning into fatty tissues but instead binds to proteins in the blood and the liver and other protein rich organs.[50]

Due to the chemical stability and the strength of the carbon-fluorine bond these substances are extremely persistent and make them suitable for high-temperature applications and for applications in contact with strong acids or bases. The estimated half-life of PFOS in a hydrolysis test in water is reported as >41 years.[49]". Biodegradation of PFOS has also been evaluated under aerobic and anaerobic conditions but no apparent degradation occurred.[50] PFOA is also highly stable and persistent in the environment[51] and does not undergo

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[39] http://chm.pops.int/Implementation/Exemptions/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx

[40] UNEP (2009) SC-4/17: Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.4-SC-4-17.English.pdf

[41] UNEP (2006) Risk profile on perfluorooctane sulfonate. UNEP/POPS/POPRC.2/17/Add.5 http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.2-17-Add.5.English.pdf

[42] UNEP (2007) Risk management evaluation on perfluorooctane sulfonate. UNEP/POPS/POPRC.3/20/Add.5 http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.3-20-Add.5.English.PDF

[43] http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.9-SC-9-4.English.pdf

[44] UNEP (2020) Compilation of the information submitted by Parties and others pursuant to section III of decision SC-9/13 and an indicative list of substances covered by the listing of PFOA and PFOA-related compounds. UNEP/POPS/POPRC.16/INF/12.

[45] UNEP (2019) SC-9/12: Listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.9-SC-9-12.English.pdf

[46] http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.12-11-Add.2.English.pdf

[47] http://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.14-6-Add.2.English.pdf

[48] UNEP (2019) POPRC-15/1: Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds.

[49] Hekster FM, de Voogt P, Pijnenburg AM Laane RW (2002) Perfluoroalkylated substances. Aquatic environmental assessment Report RIKZ/2002.043. 1 July 2002.

[50] OECD (2002) Co-operation on Existing Chemicals - Hazard Assessment of Perfluorooctane Sulfonate and its Salts, Environment Directorate Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, Organisation for Economic Co-operation and Development, Paris, November 2002.

[51] Lau et al. (2007) Perfluoroalkyl acids: A review of monitoring and toxicological findings. Toxicol Sci 99(2), 366-394.

degradation under relevant environmental conditions.[52] Since no measurable degradation of perfluorinated PFAS is detected under environmental conditions they are called "forever chemicals"[53].

3.2 Products possibly containing PFOS, PFOA and related compounds

The use of PFOS and related chemicals in China (the largest producer and user) was estimated to be less than 100 tonnes/year, mainly used for plating industry (30 – 40 t/y), specific firefighting foams (25 to 35 t/y) and sulfluramid insecticides (4-8 t/y).[54] This use is decreasing due to a GEF project of China for reduction and elimination of PFOS.[55]The use of PFOS precursors as pesticide has meanwhile stopped in China but is ongoing in Brazil with approx. 50 t/y import from China for the use against leaf-cutting ants still listed as acceptable purpose.[56]

PFOA, its salts and PFOA-related compounds are widely used in the production of fluoroelastomers and fluoropolymers, for the production of non–stick kitchen ware and food processing equipment. PFOA-related compounds, including side-chain fluorinated polymers, are used as surfactants and surface treatment agents in textiles, paper, paints and firefighting foams. A range of PFOS, PFOA and related compound are used in products[57] (e.g., specific firefighting foams, chromium plating mist suppressants and pesticides) or used for coating of products (e.g., carpets, textiles, furniture and paper). Several of these applications were granted specific exemptions or acceptable purposes and therefore such newly manufactured products containing these POPs can still be produced and traded nowadays. Furthermore, a range of products with long service life formerly produced containing PFOS or related chemicals, might be in use (e.g., carpets, textiles, furniture and firefighting foams).

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

3.3 Step by step approach for analysis of PFOS, PFOA and related compounds in products and recycling

The step-by-step approach for monitoring POPs in products and recycling is described in Chapter 2.5. To determine the occurrence and quantities of PFOS, PFOA and its related compounds in different products, 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, PFOA and related compounds in products, other materials and recycling.

Please note: The analysis of Perfluorooctane sulfonyl fluoride (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 is not used in products. Instead PFOSF is only used as intermediate for the production of PFOS related compounds. Therefore, no description of analysis for PFOSF is needed in this

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[52] OECD: SIDS Initial Assessment Report after SIAM 22—Ammonium Perfluorooctanoate & Perfluorooctanic Acid. 2006.

[53] Kwiatkowski CF, Andrews DQ, Birnbaum LS et al Scientific Basis for Managing PFAS as a Chemical Class Environ. Sci. Technol. Lett. 2020, 7, 8, 532–543.

[54] Zhang L, Liua J (2012) The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China. Environmental Pollution 165, 193-198.

[55] GEF, FECO, World Bank (2015) Reduction and Phase-out of PFOS in Priority Sectors.

[56] UNEP (2018) Draft report on the evaluation of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. UNEP/POPS/POPRC.14/INF/9

[57] 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.)

guidance and it should not be requested in tenders for monitoring of PFOS and related compounds or be included in request from a laboratory. A method for derivatisation of PFOSF for analysis has been established.[58]

Step 1: Survey of products and recycling possibly containing PFOS, PFOA and related compounds

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 monitoring PFOS, PFOA and other per- and polyfluoroalkyl substances (PFASs) described below developed a survey approach. Relevant stakeholders for different use groups might be contacted for support, input and 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.[59] Sampling campaigns can also be conducted by research institutions.

The following criteria and information may be used by stakeholders:

a) The product contains PFOS, PFOA and its related compounds identifiable by the chemical names, CAS numbers or if their structural formulas contain more than three fluorine atoms; or

b) The product contains fluorinated chemicals identifiable by their trade names; or

c) Products potentially containing PFOS, PFOA or related compounds compiled in Annex 1-A; or

d) The product was identified as having certain properties that are common for products treated with PFOS, PFOA and its related compounds (e.g., stain resistant, water repellent and anti-grease), as can be identified with e.g., the droplet test (Section 3.4.2).

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

Sampled products or recyclates 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. The fluorine content can be determined by using wavelength dispersive (WD), X-ray fluorescence (XRF) or laboratory spectrometry. Instrument and operating parameters for these methods 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 ^{19}F NMR can be applied (see below 3.4).

Typically, 0.05 to 0.5% (500 to 5000 mg/kg) of the PFAS by weight[60] of the article is used to ensure durable repellence. Thus, samples containing 0.01% (100 mg/kg) cut-off might be included for further analysis, provided an adequate safe margin to ensure that all sample products treated with fluorinated chemicals are included. Sample products containing less than 0.01% fluorine by weight can therefore be discarded if no specific legislation requires that PFOS, PFOA or related compounds are below such level. However, e.g., the European legislation set a limit value for unintentional PFOA trace contaminant in products, substances and mixtures at 0.025 mg/kg for PFOA including its salts, and at 1 mg/kg for individual PFOA-related compounds or a combination of those compounds.[61] In this case, screening methods cannot be used for a pre-selection of samples but only confirmation measurements can be used.

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[58] Sun C, Sun H, Lai Y, Zhang J, Cai Z (2011) Liquid chromatography/mass spectrometry method for determination of PFOSF upon derivatization with benzylamine. Anal Chem. 83(15):5822-6.

[59] Stockholm Convention (2012) Guidance for the control of the import and export of POPs (Draft).

[60] 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%.

[61] European Commission (2020) Commission Delegated Regulation (EU) 2020/784 of 8 April 2020 amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council as regards the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. Official Journal of the European Union 15.6.2020 L 188 I/1.

Step 4: Quantification

Different analytical methods can be applied as e.g., described in Section 3.5 below and in Annex 3-D. Some methods have been described in national surveys with quantifications of PFOS, PFOA and other PFASs in consumer products (see case studies in Annex 2).

3.4 Screening methods for fluorine/organofluorine chemicals

3.4.1 Introduction

For a pre-selection of samples, screening methods for PFOS/PFOA and related compounds are valuable. Most of such screening methods cannot identify specifically PFOS/PFOA and related compounds but need then a confirmation analysis for PFOS/PFOA and to distinguish from other PFASs by MS methods (see below 3.5 and Annex 3H).

Some of the screening methods can (semi-)quantify the organofluorine content. Such a measurement might be valuable in cases where PFOS or PFOA is partly chemically bound or where a larger share of PFOS/PFOA is present as PFOS/PFOA precursor for which no analytical standard method exists.

Most screening tools provide only (semi-)quantitative information on total fluorine but not on the PFAS structure. In case of spectroscopic approaches (WDXRF – laboratory method, SSS – sliding spark spectrometry –hand-held method or portable method if combined with an IR spectrometer, see below) only total fluorine present at the sample surface is detected and semi-quantified. The fluorinated polymers (polytetrafluoroethylene PTFE, polyvinyldifluoride PVDF) must be identified by short-wave infra-red spectrometry on the same sample, to attribute the fluorine to these polymers or to the PFOS/PFOA and related compounds. The LOQ of total fluorine by SSS is 0.1% (1000 mg/kg).

Regarding laboratory methods, in case of GC-EPED (Echelle-Plasma-Emission-Detector) coupled to a headspace or a purge & trap sampler, mostly volatile precursors of PFOS or PFOA are detected and levels of precursors do not necessarily give robust hints on PFOS levels. Fluorine ^{19}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.[62] Another option is to make extracts of the sample and screen for PFOS, PFOA and other PFASs 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 PFASs containing hydrogen). This methodology has been used to screen industrial blends and paper extracts with typical CnFm fragments (e.g., m/z 119, 131, 169, 195, 231, 331).[62]

However, in view of the numbers of PFOS, PFOA and PFHxS precursors and other PFASs, sum parameter methods for organically bound fluorine are a valuable complementary tool for the screening of PFOS/PFOA and related compounds. A large bias in view of mass balance is reported for extractable PFOS/PFOA and other PFASs when compared to total Fluorine.[63] Different analytical methods are available such as combustion ion

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[62] Trier X, Granby K, Christensen JH. (2011) Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. Environ Sci Pollut Res Int. 18(7),1108-1120. doi: 10.1007/s11356-010-0439-3

[63] Willach S, Brauch H-J, Lange FT. Contribution of selected perfluoroalkyl and polyfluoroalkyl substances to the adsorbable organically bound fluorine in German rivers and in a highly contaminated groundwater. Chemosphere. 2016;145:342–50. https://doi.org/10.1016/j.chemosphere.2015.11.113.

chromatography (CIC),[64] HR-CS-GFMAS[65,66], or the Total Oxidisable Precursor Assay (TOP assay) among others.[67] These technologies are shortly introduced in the following sections.

3.4.2 Screening with the "droplet test"

When PFOS/PFOA and related compounds (or other PFASs) 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[68] surface. Similarly, also for other surface like paper.[69] 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, the surface energy for oil.[68] 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, θ, 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 value of contact angle (θ) indicates that the liquid spreads, or wets well, while a high contact angle indicates poor wetting. If the angle θ 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.[68]

The wetting angle can be used for screening materials treated with PFOS/PFOA and related compounds as well as other PFASs including PFHxS. The droplet test has recently been used to assess the efficiency of PFOA and other PFASs on paper repellency from paper.[69] If compliance need to be demonstrated, the contact angle can be measured using DROPImage Advanced software in accordance with ASTM D7334-08(2013) (ASTM 2013).[70]

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[64] Wagner A, Raue B, Brauch HJ, Worch E, Lange FT. (2013) Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography. J Chromatogr A. 1295, 82–89. https://doi.org/10.1016/j.chroma.2013.04.051.

[65] Metzger M, Ley P, Sturm M, Meermann B. (2019) Screening method for extractable organically bound fluorine (EOF) in river water samples by means of high-resolution-continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS). Anal Bioanal Chem. 411(19), 4647–4660. https://doi.org/10.1007/s00216-019-01698-1.

[66] Gehrenkemper L, Simon F, Roesch P, et al. (2020) Determination of organically bound fluorine sum parameters in river water samples – Comparison of combustion ion chromatography (CIC) and high resolution-continuum source-graphite furnace molecular absorption spectroscopy (HR-CS-GFMAS), Anal. Bioanal. Chem., DOI: 10.1007/s00216-020-03010-y.

[67] Janda J, Nodler K, Scheurer M, Happel O, Nurenberg G, Zwiener C, Lange FT, (2019) Closing the gap - inclusion of ultrashort-chain perfluoroalkyl carboxylic acids in the total oxidizable precursor (TOP) assay protocol, ENVIRONMENTAL SCIENCE-PROCESSES & IMPACTS, 21 (11), 1926-1935, DOI: 10.1039/c9em00169g

[68] Posner S. 2011. Occurrence and uses of PFC in products. In Handbook of Environmental Chemistry, Volume 17, Polyfluorinated Chemicals and Transformation Products, Knepper, T. P.; Lange, F. T., Eds. Springer.

[69] Curtzwiler GW, Silva P, Hall A, Ivey A, Vorst K. (2021) Significance of Perfluoroalkyl Substances (PFAS) in Food Packaging. Integr Environ Assess Manag. 17(1), 7-12.

[70] ASTM. 2013. Standard practice for surface wettability of coatings, substrates and pigments by advancing contact angle measurement. West Conshohocken, PA: ASTM International.

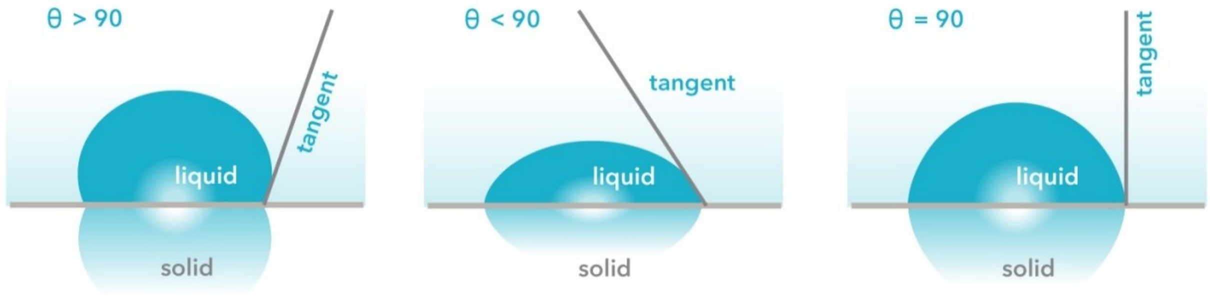

Figure 3-1: Contact angle θ categories of a droplet on a surface

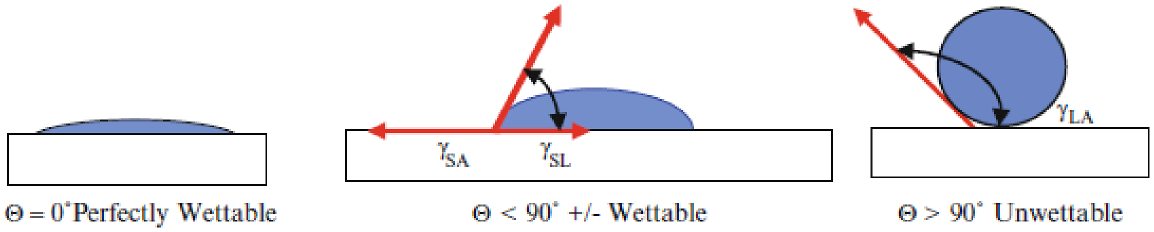

Figure 3-2: Contact angle versus wettability of a substrate surface. When angle Θ is > 90˚, liquid will not wet the surface; when angle Θ is <90˚, liquid will wet surface partially; when angle Θ = 0˚, complete spreading & wetting of the surface by the liquid.[71]

3.4.3 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.[72,73] 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 portable/mobile and can detect organofluorine (such as PFOS and PFOA related compounds and other PFASs) at a concentration of approximately 0.1% (1000 mg/kg).

3.4.4 Screening of Fluorine with WD-XRF-Analysis

Wavelength dispersive XRF (WD-XRF) systems (e.g. Table 3-1) are able to detect fluorine in vacuum mode. Respective systems (e.g., S8-TIGER; Bruker AXS, Karlsruhe) are used to analyse products on their fluorine content. It is important to understand that for fluorine the depth of signal saturation is limited to the first micrometer, 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% (500 mg/kg) 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% (1000 mg/kg) might be too high for very thin coatings or those containing only low levels of fluorine.

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[71] Spreading coefficient: $S = \gamma_{SV}-(\gamma_{LV} + \gamma_{SL})$ (S =solid, L = liquid, A = air. where γSA = surface energy of the substrate (e.g., polymer surfaces), γLA = surface tension of the liquid and γSL = interfacial tension). Spreading occurs only if S >0.

[72] Seidel T, Golloch A, Beerwald H, Böhm G, (1993) Fresenius' Journal of Analytical Chemistry 347, 92-102.

[73] GUT Environmental Technologies and Iosys. mIRoSpark 2.0 Sliding Spark Spectrometer part. http://www.gut-stuttgart.de/en/products.html

Table 3-1: 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.

*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 aluminium foil cover.

3.4.5 Fluorine screening with ^{19}F NMR spectroscopy

Fluorine has an uneven number of protons, and hence has an unpaired proton with spin ½, 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, PFOA and other PFASs, makes ^{19}F NMR a sensitive screening technique, capable of screening down to approximately 300 ng/g (ppb) in samples of e.g., paper and board.[74]

Extracts of samples, containing no particulates, are made with organic solvents and evaporated down to approximately 100 μL, and redissolved in deuterated solvent (e.g., MeOD), so that max. 10% of the solvent is hydrogenated (e.g., H_2O or 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. Cr(III) acetate is added as relaxation agent, and an internal standard with chemical shifts of the PFOS, PFOA or other PFAS analytes is added too.[74,63,75] The screening can be made semi-quantitative and is capable of detection unknown organofluorines. The instrumentation is highly specialised, costly and immobile.

3.4.6 Screening of Fluorine: P&T-GC-EPED[76]

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[76].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[77] (peak width of 10 sec) and a linearity about 3-4 orders of magnitude. The equipment is stationary in laboratory and not mobile.

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[74] Trier X (2011) Polyfluorinated surfactants in food packaging of paper and board. PhD Danish Technical University, Copenhagen/Denmark.

[75] Ellis DA, Martin JW, Muir DCG, Mabury SA (2000) Development of an 19F NMR Method for the Analysis of Fluorinated Acids in Environmental Water Samples Anal. Chem. 72, 726-731.

[76] Wolz G, Gruber L, Ewende J, Fiedler D, Schlummer M (2010) Development of screening methods for fluorinated coatings of food contact materials and other everyday commodities. Organohalogen Compounds. 72, 1173-1176. http://dioxin20xx.org/wp-content/uploads/pdfs/2010/10-1444.pdf

[77] 100 pg may be purged from 10 ml of extract from 0.5 g of coated paper corresponding to 200 pg/g paper.

3.4.7 Particle-Induced Gamma Ray Emission (PIGE) spectroscopy[78]

Particle-Induced Gamma Ray Emission (PIGE) spectroscopy was developed as a rapid screening method for total fluorine and applied to quantify PFASs on consumer papers and textiles.[78] PIGE provides a non-destructive and quantitative measurement of total fluorine on papers and textiles. In short, each sample was irradiated with approximately 10 nA of 3.4 MeV protons for 180 s. The characteristic γ-rays emitted from the de-excitation of 19F at 110 and 197 keV had background-subtracted integrations summed for each sample irradiation. Integrated γ-ray counts in the 110 and 197 keV peaks per microcoulomb of beam on target (counts per microcoulomb) were converted to concentrations of total fluorine (in nanomoles of F per square centimeter) using PFAS standards dissolved in methanol and dried onto filter paper. This technique is both rapid and sensitive, with a limit of detection (LOD) of 13 nmol F/cm^2 for papers and 24–45 nmol F/cm^2 for textiles, with reproducibility of ±12% RSD for both. The limit of quantification (LOQ) was 50 nmol of F/cm^2.[79] PIGE is a high throughput (>20 samples/hr typically) method that was applied to 50 papers and 50 textiles in commerce to demonstrate the method.[78]

3.4.8 Screening of PFASs via high resolution-continuum source-graphite furnace molecular absorption spectrometry (HR-CS-GFMAS)[80]

Extracted PFASs (EOF, AOF) can be screened via HR-CS-GFMAS. Based on the formation of a diatomic molecule in the gas phase and molecular absorption detection on a specific wavelength allows for a highly selective as well as sensitive detection of fluorine. The LOD (upon concentration) is in the low ng/L range[80]. HR-CS-GFMAS allows for a fast hot-spot screening of PFASs (as sum parameter) in environmental samples (e.g., surface water, soil, air). Complementary HR-CS-GFMAS sum parameter method allows for closing mass-balance gaps since routinely applied target analysis covers just a small number of PFASs.

3.4.9 Determination of total fluorine/PFASs via combustion ion chromatography (CIC)[64,66,81,82,83]

Extracted PFASs (EOF, AOF) can be screened via combustion ion chromatography (CIC). Based on the combustion of PFAS, trapping of generated hydrogen fluorine (HF) as well as analysis of fluoride via ion chromatography.[64] CIC is widely used for ionisable chemicals in commercial product, waste material and environmental sample. CIC is a commonly used technique for PFAS sum parameter analysis. The first application of CIC for investigation of PFASs in water and human blood were reported in 2007.[81] Inorganic fluorine was measured by direct injection to ion chromatography (IC) after clean-up by an on-guard cartridge (Supelco Inc.). It has also been applied to firefighting foam[82] or rice.[83]

A Combination of bulk measurement of organic fluorine and individual PFASs using LCMS/MS enable “Mass balance analysis of PFASs in organic fluorine” according to following equation.

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[78] Ritter EE, Dickinson ME, Harron JP, et al. (2017) PIGE as a screening tool for Per- and polyfluorinated substances in papers and textiles. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 407, 47-54.

[79] Schaider LA, Balan,SA, Blum A et al. (2017) Fluorinated Compounds in U.S. Fast Food Packaging. Environ Sci Technol Lett. 4(3), 105-111

[80] Gehrenkemper L, Simon F, Roesch P, Fischer E, von der Au M, Pfeifer J, Cossmer A, Wittwer P, Vogel C, Simon F-G Meermann B, Determination of organically bound fluorine sum parameters in river water samples – Comparison of combustion ion chromatography (CIC) and high resolution-continuum source-graphite furnace molecular absorption spectroscopy (HR-CS-GFMAS), Anal. Bioanal. Chem., 2020, DOI: 10.1007/s00216-020-03010-y.

[81] Miyake Y, Yamashita N, Rostkowski P, So MK, Taniyasu S, Lam PK, Kannan K. (2007) Determination of trace levels of total fluorine in water using combustion ion chromatography for fluorine: a mass balance approach to determine individual perfluorinated chemicals in water. J Chromatogr A. 1143(1-2), 98-104.

[82] Taniyasu S, Yamashita N, Yamazaki E, et al., (2015) Contamination Profiles of Perfluorinated Chemicals in the Inland and Coastal Waters of Japan Following the Use of Fire-Fighting Foams in Water Challenges and Solutions on a Global Scale, ACS books, Vol 1206, 221-244. DOI: 10.1021/bk-2015-1206.ch011.

[83] Yamazaki E, Taniyasu S, Noborio K, et al. (2019) Accumulation of perfluoroalkyl substances in lysimeter-grown rice in Japan using tap water and simulated contaminated water. Chemosphere 231:502-509.

Cf = nMf / Mpfas x Cpfas.

"Cf" is concentration of PFAS converted to fluoride ion (ng-F/L).

"Cpfas" is the concentration of PFAS (ng/L).

"Mpfas" is molecular weight of individual PFAS (g/mol).

"n" is the number of fluorines in individual compound.

"Mf" is the molecular weight of fluorine (g-F/mol).

LOD and LOQ can lack behind some other techniques due to a high background concentration if activated carbon is used in CIC.[66] Furthermore, conductivity detection in ion chromatography is less specific and sensitive. Normally the limit of detection of F in commercially available CIC is about 50 ng in single combustion. However, after careful customizing of instrument to decrease interferences highly sensitive CIC can determine 0.5 ng of F.[83]

3.4.10 Screening of PFOS, PFOA and related compounds: 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 dm² 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 (e.g., m/z 119, 131, 169, 195, 231, 331) are then monitored in order to identify the presence of organofluorine compounds. If run with chemical ionisation even molecular ions can be detected enabling an identification of the detected PFASs.

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

3.4.11 Screening PFOS, PFOA and related compounds in products 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 the screening of PFASs on paper, such as polyfluoroalkyl phosphoric acid diesters (DiPAPS up to 1500 Dalton),[84] there is currently no monitoring of PFOS and precursors reported.

3.4.12 Screening of PFOS, PFOA and related compounds in products 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 (CnFm fragments (e.g., *m/z* 119, 169, 219, 269, etc. – these ions are prevalent for perfluorinated compounds, such as PFOS, PFOA or PFHxS) 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 PFASs containing hydrogen). This methodology has been used to screen industrial blends and paper extracts.[74] The method is fast, simple and specific, but the instrumentation is costly and not mobile.

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[84] Ackerman LK, Noonan G, Begley T (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, 1611-18.

3.5 Qualitative and quantitative analysis of PFOS, PFOA and related compounds

3.5.1 Background and general challenges for the analysis of PFOS, PFOA and related compounds

Analytical standard methods for quantification of PFOS, PFOA and other PFASs are under development, and some technical standards have been defined (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 PFASs are multiple, and include diverse aspects such as unique physical-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, PFOA, PFHxS and its related compounds, caution should be given to follow the measures needed to assure that they provide reliable results. The challenges associated with quantification methods for PFASs are described in the literature.[85]

The analytical detection method of choice for PFOS/PFOA and most PFASs is LC-MS or LC-MS/MS[86] for the anionic compounds (including PFOS, PFOA and PFHxS), 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 and PFOA. 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 PFASs. 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 PFASs, usually the dissociated acid (pseudo molecular) ion $[M\text{-}H]^-$ 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 PFASs 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/PFOA and its related compounds occur in a large range of materials and liquids, it is advisable to use 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 on UNEP website (http://informea.pops.int/HgPOPsLabs/index.html).

It has to be underlined, that LC-MS systems have to be especially prepared for PFOS, PFOA and other PFAS analysis, due to blank issues related to fluorinated compounds in LC systems or laboratory equipment (e.g., from PTFE/Teflon parts). In addition, there are further important issues required for a reliable PFAS analysis:

a) use of specific standards for target analytes (not available for most PFOS/PFOA precursors, mixed chain length PFASs 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.

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[85] 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 perfluoralkyl research. Env. Sci. & Tech. 38, 248A–255A.

[86] http://www.youtube.com/watch?feature=player_embedded&v=Rcjgq8HTMxs

Both volatile and non-volatile PFOS/PFOA/PFHxS precursors and other PFASs are analysed using well established analytical methods applying GC/MS and LC/MS techniques. Quality assurance measures are required to ensure the best possible quality of data. Liquid samples are diluted and extracted for both volatile and ionic PFASs, 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 [µg/L] for liquids, [µg/kg] for solid materials or in [µg/m^2] for textiles, paper and leather. Since PFOS/PFOA/PFHxS and related compounds 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.

Analysis of chemically bound PFOS, PFOA and PFHxS related compounds

The current available standards to analyse PFOS or PFOA in articles focusses on the extractable PFOS and PFOA and some other extractable related compounds. In some applications, however, some PFOS, PFOA and PFHxS related compounds are chemically bound to the surface. Therefore, the largest part of chemically bound PFOS, PFOA or PFHxS related compounds could remain on/in the article, leading to a considerable underestimation of POP-PFAS related compounds in these products.

3.5.2 Analysis of PFOS, PFOA and PFHxS related compounds (precursors) and the use of PFAS Total Oxidisable Precursor Assay (TOP-Assay)

Analysis of PFOS and PFOA related compounds (precursors)

The OECD compiled a list of 165 PFOS related compounds (OECD 2007).[87] Only for a few of those PFOS related compounds and chemicals a standard analysis is available (Table 3-2). Therefore, most PFOS related compounds are currently not covered by standard analysis. While for environmental samples this might be of minor relevance due to the degradation of those precursors into PFOS (e.g., as frequently observed in sewage treatment plants, where the mass balance of PFOS concentrations shows higher PFOS levels in sludge and outflow compared to the inflow).[88] However, PFOS precursors might be used in products but they are not detected by routine PFOS analysis or even state-of-the-art analysis, including several PFOS precursors (Table 3-2). The same is true for the large number PFOA or PFHxS related compounds.

Therefore, the Total Oxidisable Precursor Assay (TOP-Assay) was firstly developed in 2012, which can convert precursors into quantifiable perfluoroalkyl acids (PFAAs).[89] The mechanism of conventional TOP-Assay is to activate persulfate at 85 °C and generate sulfate radical anions ($SO_4\bullet^-$), which then rapidly reacts with hydroxyl and generates hydroxyl radicals (•OH) under alkaline condition. During the TOP-Assay, pH is a key parameter, because the $SO_4\bullet^-$ generated under neutral and acidic condition could degrade perfluoroalkyl carboxylic acids (PFCAs). In addition, the activation temperature of persulfate has been optimized to be 85°C. It was reported that perfluorooctane sulfonate (PFOS) could not be oxidized under heat-activated persulfate condition.[90] Such heat-based TOP-Assay has been widely adopted in various environmental samples, including drinking water,[91] groundwater and soil,[92] as well as wastewater.[93] In addition, this method has also been applied to some

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[87] 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

[88] 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.

[89] Houtz E F, Sedlak D L (2012). Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environmental Science & Technology, 46(17): 9342-9349

[90] Park S, Lee L S, Medina V F, Zull A, Waisner, S (2016). Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation. Chemosphere, 145: 376-383

[91] Qu Y, Jiang X, Cagnetta G et al., (2019). Poly- and perfluoroalkyl substances in a drinking water treatment plant in the Yangtze River Delta of China: Temporal trend, removal and human health risk. Science of the Total Environment, 696, 133949

[92] Houtz E F, Higgins C P, Field J A, Sedlak D L, (2013). Persistence of perfluoroalkyl acid precursors in AFFF-Impacted groundwater and soil. Environmental Science & Technology, 47, 8187-8195

[93] Houtz E F, Wang M, Park J S (2018). Identification and fate of aqueous film forming foam derived per- and polyfluoroalkyl substances in a wastewater treatment plant. Environmental Science & Technology, 52(22), 13212-13221

industrial products, such as firefighting foam surfactants[94] and textile finishing agents.[95] It has been included as a monitoring technique in the national environmental management plan by the Australian government.[96]

The sample pretreatment for the conventional heat-based TOP-Assay is quite time-consuming and normally take approx. 6 hours. Recently, an alternative TOP-Assay was developed to convert the precursors, in which the persulfate was activated by UV under alkaline condition. The UV-based TOP-Assay was evaluated for three precursors, 6:2 fluorotelomer sulfonate (FTS), 8:2 FTS and perfluorooctanesulfonamide (FOSA). Then the method was applied on 23 fluorocarbon surfactants (FSs) for firefighting foam used in the Chinese market, the PFAAs concentration before and after UV-based TOP-Assay were analyzed. This approach provided a more comprehensive PFAS profile of major commercial products, and a a more appropriate risk assessment when emitting firefighting wastewater containing these products into the environment. In addition, the applicability of the UV-based TOP-Assay was used for water, which was impacted by firefighting foam due to extinguishing activity. The heat-based TOP-Assay was also conducted as control to further assess advantages of the UV-based TOP-Assay method.[97]

3.5.3 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 compounds 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 mm², whereas for paper a max size of 1 cm² is given.

3.5.4 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 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)

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[94] Mumtaz M, Bao Y, Li W, Liu L, Huang J, Cagnetta C, Yu G (2019). Per- and polyfluoroalkyl substances in representative fluorocarbon surfactants used in Chinese film-forming foams: Levels, profile shift, and environmental implications, Environmental Science & Technology Letters, 6, 259−264

[95] Mumtaz M, Bao Y, Li W, Kong L, Huang J, Yu G (2019). Screening of textile finishing agents available on the Chinese market: an important source of per-and polyfluoroalkyl substances to the environment polyfluoroalkyl substances to the environment. Frontiers of Environmental Science & Engineering 13(5), 29-38

[96] NEMP, PFAS National Environmental Management Plan, Australia. 2018. https://www.environment.gov.au/system/files/resources/2fadf1bc-b0b6-44cb-a192-78c522d5ec3f/files/pfas-nemp-2.pdf

[97] Fan X, Bao Y, Mumtaz M, Huang J, Yu G (2021) Determination of total oxidizable precursors in foam surfactants and its contaminated water based on UV-activated persulfate oxidation. Science of the Total Environment. 763: 142943

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_2O (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_2O (1/1; vol/vol).

3.5.5 Clean-up

Three clean-up procedures can be recommended for PFOS and other perfluorinated carboxylates, phosphates and sulfonate acids. For challenging matrices, combinations of those may be applied as well. Descriptions of extractions of neutral PFOS-precursors or volatile PFASs such as FTOHs can be found elsewhere, e.g., Benskin et al. 2012.[98]

A fast and easy clean-up makes use of powder activated carbon (e.g., Envicarb), which is directly applied to samples to adsorb interfering matrix components and finally be 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 form 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_{18} 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_3).

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_2O (1/1; vol/vol).

3.5.6 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 PFASs are prone to matrix enhancement when analysed by LC-Electrospray ionisation (ESI)-MS, thus, it is advised that either matrix matched or standard addition calibration curves are used. External calibration

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[98] Benskin JP, Ikonomou MG, Gobas FA, et. al. (2012) Observation of a novel PFOS-precursor, the perfluorooctane sulfonamido ethanol-based phosphate (SAmPAP) diester, in marine sediments. Environ Sci Technol. 46, 6505-6514.

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 analysed. 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.

3.5.7 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 reanalyse the extract.

3.5.8 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 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 PFAS precursors, e.g., esters.

If PFOS levels in method blank samples increase, it is recommended to compare these with levels in pure solvent blanks, e.g., 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.

3.5.9 PFOS, PFOA and selected related compounds monitored

In Table 3-2 PFOS and related compounds are included, which can be considered to be part of state-of-the-art analysis of PFASs. However as mentioned above, most of the 165 PFOS related compounds are not covered by the current used state-of-the-art analysis.

A list of more than 100 PFOA related substances is compiled in a POPs Review Committee document and as many substances as feasible should can be integrated in the measurements.[99] PFHxS related substances have been compiled from the European Chemical Agency for the Annex XV restriction dossier.[100]

Due to the complexity of PFOS, PFOA and PFHxS related compounds, a combination with TOP Assay measurements (see Section 3.5.2) for determining the total concentration PFOS, PFOA and PFHxS related

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[99] UNEP (2020) Compilation of the information submitted by Parties and others pursuant to section III of decision SC-9/13 and an indicative list of substances covered by the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds. UNEP/POPS/POPRC.16/INF/12.

[100] ECHA (2019) ANNEX XV RESTRICTION REPORT PROPOSAL FOR A RESTRICTION: Perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related substances See Appendix 1 overview-Table PFHxS, salts and related substances.

compounds is recommended. This concentration might have relevance of restriction of products and recyclates.

In Table A3-I-2 in Annex 3-I PFASs are listed which are covered by state-of-the-art analysis.

Table 3-2: PFOS and related compounds included in state-of-the-art monitoring. (from approx. 165 PFOS related compounds; *Analytes listed in CEN/TS 15968:2010)

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

3.6 Example for a LC/MS setting and parameters

3.6.1 LC/MS parameters and mass settings for PFOS

The selected LC/MS conditions differ slightly between laboratories and instruments. In Annex 3-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 3-G.

3.7 Selected international/national standards for analysis of PFOS and PFOA

Some standards for measuring PFOS and PFOA in products have been developed and are shortly introduced.

ISO 23702-1:2018 Leather — Organic fluorine — Part 1

ISO 23702-1:2018 is a standard for the determination of the non-volatile PFAS compound content by an extraction method using liquid chromatography/tandem mass spectrometry detector (LC-MS/MS). The standard specifies a test method for detection and quantification of extractable neutral, ionic, long, medium and short chain PFASs in leather and coated leather.

Classes of regulated compounds listed in include acids, telomers, sulfonates and sulphonamide alcohols which includes PFOS, PFOA, PFHxS and some of related compounds.

NPR-CEN/TS 15968:2010[101]

The NPR-CEN/TS 15968:2010 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 POPs. An international standard has been developed here for the “Determination of extractable perfluorooctane sulphonate (PFOS) in coated and impregnated solid products, liquids and firefighting foams - Method for sampling, extraction and analysis by LCqMS or LC-tandem/MS”.

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[101] Preview of NPR-CEN/TS 15968 content: http://www.evs.ee/preview/cen-ts-15968-2010-en.pdf

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 3-2 and Table A2-14 in Annex 3). The standard does not address the chemically bound-PFOS related compounds and also does not describe a holistic analysis of PFOS related compounds.

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 and ISO21675:2019)

Two ISO standard methods are available for the measurement of PFASs in water samples. ISO 25101:2009 is firstly developed specially for analysis of PFOS and PFOA in unfiltered samples of drinking water, 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.

ISO 21675:2019 specifies a method for the determination of selected PFASs including PFOS and PFOA in non-filtrated waters, for example drinking water, natural water (fresh water and sea water) and waste water containing less than 2 g/l solid particulate material (SPM) using liquid chromatography-tandem mass spectrometry (LC-MS/MS). The group of compounds determined by this ISO method are representative of a wide variety of PFASs. Thirty PFASs are specified in this ISO method. The applicability of the method to further substances, not listed in this ISO method, or to further types of water is not excluded, but is intended to be validated separately for each individual case. The compounds monitored by this method are typically the linear isomers. The branched isomers can be present in environmental samples, especially for PFOS. Therefore, Annex provides an example of an analytical approach to the chromatographic and spectroscopic separation of individual 9 isomers of PFOS and PFOA. The lower application range of this ISO method can vary depending on the sensitivity of the equipment used and the matrix of the sample. For most compounds to which this document applies ≥0,2 ng/l as limit of quantification can be achieved. Actual levels can depend on the blank levels realized by individual laboratory.

Validated national standards used for compliance measurement of PFOS or PFOA in products

National standards for measuring PFOS and PFOA in products have been developed in China for specific assessment purposes, e.g., the export into the EU having regulatory limits for PFOS in products (Table 3-3). 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 and some include PFOA (Table 3-4).

A Japanese national standard (JIS K 9450-70-10 (2011)) was established as modified method of ISO25101 in 2011. This standard method is applicable to not only water but also solid materials and some industrial product with necessary extraction procedure.

Table 3-3: National standards for testing PFOS and PFOA in products 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 μg/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: Determination 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
GB 5009.253-2016	Determination of perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) in animal derived foods, National Food Safety Standard	This method specifies the HPLC-MS/MS method for the determination of PFOS and PFOA in animal derived foods. The MDL for PFOS and PFOA is 0.01μg/kg and 0.1μg/kg, respectively.	2017-03-01
GB31604.35-2016	Determination of perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) in food contact materials, National Food Safety Standard	This method specifies the HPLC-MS/MS method for the determination of PFOS and PFOA in food contacting materials. The MDL for PFOS and PFOA is 2.0 ng/g and 1.0 ng/g, respectively.	2017-04-19
GB/T 33893-2017	Determination of perfluorooctane sulfonates (PFOS) and perfluorooctanoic acid (PFOA) for separation membranes - Liquid chromatography-tandem mass spectrometry method	This method specifies the HPLC-MS/MS method for the determination of PFOS and PFOA in separation membranes. The MDL for PFOS and PFOA is 2 μg/kg and 1 μg/kg, respectively.	2018-02-01
GB/T 36929-2018	Leather and fur -Chemical tests - Determination of perfluorooctane sulfonates (PFOS)and perfluorooctanoic acid (PFOA) content	The method specifies the HPLC-MS/MS method for the determination of extractable PFOS and PFOA in leather and fur. The MDL is 0.5 mg/kg for both PFOS and PFOA.	2019-07-01

Table 3-4: Industrial testing standards for PFOS, PFOA in products in China (all based on HPLC-MS/MS)

No.	Name	Date of 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/T3544-2013	Determination of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in food for export: LC-MS/MS method	2013-09-06

4 Sampling, screening and analysis of POP-BFRs (PBDEs, HBB, and HBCD) in products and recycling

4.1 Brominated flame retardants listed in the Stockholm Convention

4.1.1 PBDEs listed in the Stockholm Convention

Polybrominated diphenyl ethers (PBDEs; Figure 4-1) are a group of aromatic brominated flame retardants (BFRs) that have been produced in large volumes (Table 4-1) and used since the 1970s as additive flame retardants in a wide range of products such as plastic and other polymers in electronics, vehicles and construction as well as certain textiles (see Annex 1B).

PBDEs were produced as commercial mixtures with three different degrees of bromination, and marketed as commercial PentaBDE (c-PentaBDE), commercial OctaBDE (c-OctaBDE) and commercial DecaBDE (c-DecaBDE). Typical homologue distributions of c-PentaBDE and c-OctaBDE are shown in Table 4-2 and Table 4-3. c-DecaBDE typically contain 90 to 99% DecaBDE (BDE-209), and up to 10% mainly nonaBDE and lower levels of octaBDE[102,103]. DecaBDE was by far the major PBDE produced in history (Table 4-1).

Tetrabromodiphenyl ether (tetraBDE) and pentabromodiphenyl ether (pentaBDE)[104] from the c-PentaBDE as well as hexabromodiphenyl ether and heptabromodiphenyl ether[105] from c-OctaBDE, have been listed in the Stockholm Convention in 2009 in Annex A. The production and use of the PBDEs listed in 2009 are to be eliminated by Parties. However the PBDEs listed in 2009 were listed with a recycling exemptions and therefore recycling is allowed by the Convention if a Party has registered for this exemption. Since the production of c-PentaBDE and c-OctaBDE stopped in 2004, no production of these POPs have taken place the past 17 years. However these POPs are still in products and in recycling (see below).

DecaBDE has been listed in the convention in 2017 with a range of exemptions (Table 4-4). For decaBDE no exemption for recycling has been included. Since decaBDE is the major PBDE produced/used, the recycling of PBDE containing plastic/polymer fraction above low POPs limits is restricted triggered by decaBDE and need to be separated.

The Basel Convention has provisional definitions of low POP content which includes three provisional low POP content for PBDEs 50 mg/kg, 500 mg/kg and 1000 mg/kg.[106] Monitoring of products and recyclates need to consider these limits

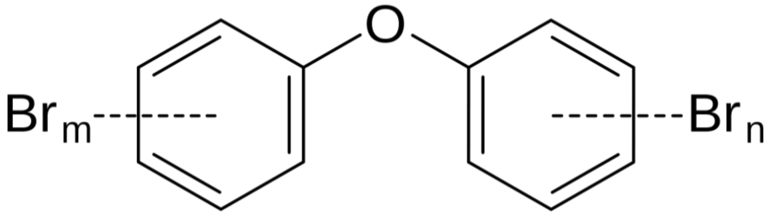

Figure 4-1: Structure of polybrominated diphenyl ethers (PBDEs)

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[102] 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. Environmental Science and Technology, 40, 6247-6254.

[103] Risk and Policy Analysts (RPA) (2014) Support to an Annex XV Dossier on Bis-(pentabromophenyl) ether (DecaBDE). Final Report prepared for ECHA.

[104] 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 (see Annex 1).

[105] 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 (see Annex 1).

[106] UNEP (2019) General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants. UNEP/CHW.14/7/Add.1/Rev.1

Table 4-1. Estimated total production of PBDE commercial mixtures (1970-2005)[107]

Commercial mixture	Tonnes
c-pentaBDE	91,000 to 105,000
c-octaBDE	102,700 to 118,500
c-decaBDE	1,100,000 to 1,250,000

Table 4-2. Composition of c-PentaBDE* (derived from La Guardia et al. 2006; SFT 2009; Schlummer et al. 2011)

Categories of PBDE	Tribromodi-phenyl ethers		Tetrabromodi-phenyl ethers	Pentabromodi-phenyl ethers		Hexabromodi-phenyl ethers		Heptabromodi-phenyl 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%**		**33%*****	**58%*****		**8%*****		**0.5%*****

*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 listed PBDEs.

Table 4-3. Composition of c-OctaBDE* (from La Guardia, 2006; SFT, 2009; Schlummer 2011)

Categories of PBDE	Hexabromo-diphenyl ethers		Heptabromodiphenyl ethers			Octabromo-diphenyl ethers			Nonabromodi-phenyl 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*	**11%*****		**43%*****			35%**			10%**		**1%*****

*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 PBDEs.

Table 4-4. Specific exemptions for Decabromodiphenyl ether (BDE-209) present in commercial decabromodiphenyl ether (CAS No: 1163-19-5) for production and use

Specific exemptions as allowed for the Parties listed in the Register in accordance with Part IX of this Annex:
• Parts for use in vehicles specified in paragraph 2 of Part IX of this Annex (see Annex 1-B) • Aircraft for which type approval has been applied for before December 2018 and has been received before December 2022 and spare parts for those aircraft* • Textile products that require anti-flammable characteristics, excluding clothing and toys • Additives in plastic housings and parts used for heating home appliances, irons, fans, immersion heaters that contain or are in direct contact with electrical parts or are required to comply with fire standards, at concentrations lower than 10% by weight of the part • Polyurethane foam for building insulation

*The specific exemptions for spare parts for aircraft for which type approval has been applied for before December 2018 and has been received before December 2022 shall expire at the end of the service life of those aircraft.

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[107] UNEP (2019) Preliminary draft guidance on preparing inventories of decabromodiphenyl ether. April 2019. UNEP/POPS/COP.9/INF/18

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%).[108] Also, decabromobiphenyl (DecaBB) has been produced and used as flame retardant but is not listed in the Stockholm Convention. However, DecaBB is listed in the Restriction of Hazardous Substance (RoHS) directive. The overall production of PBBs were however low and stopped for HBB in 1976 and are not detected in relevant concentrations even in end-of-life products.[109]

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; EPS/XPS) 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).[110] 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% γ-HBCD and 3–30% of α- and β-HBCD (European Commission 2008).[111] Two other stereoisomers (δ-HBCD and ε-HBCD) have also been found by Heeb et al. (2005)[110] in commercial HBCD in concentrations of 0.5% and 0.3%, respectively. Major production stopped after 2013 and the last productions in China plan to stop production by 12/2021.

4.2 Products possibly containing PBDEs, PBB and HBCD

A list of potentially PBDE containing products and materials are listed in Annex 1-B. If a study on the presence of PBDE containing materials is planned, this list can be consulted for possible relevant samples for the country. Case studies on monitoring of PBDEs in products and recycling are compiled in Annex 2-B.

Hexabromobiphenyl (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 products and recyclates sampled/assessed for PBDEs might be analysed for HBB if required.

A list of potentially HBCD containing products 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 products and recycling are compiled in Annex 2-C.

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

To determine the occurrence and quantities of POP-BFRs in different 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 recycling streams possibly containing 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.

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[108] Pijnenburg AMC, Everts JW, de Boer J, Boon JP. (1995) Polybrominated biphenyl and diphenlylether flame retardants: Analysis, toxicity, and environmental occurrence. Reviews of Environmental Contamination and Toxicology 141, 1-26.

[109] Wäger P, Schluep M, Müller E (2010) RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. Final Report Swiss Federal Laboratories for Materials Science and Technology Empa.

[110] 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.

[111] European Commission. (2008). Risk Assessment: Hexabromocyclododecane CAS-No.: 25637-99-4 EINECS No.: 247-148-4, Final Report May 2008. Luxembourg

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

Also, some materials known to possibly contain PBDEs or HBCD and further used in recycling (e.g., plastic from WEEE recycling or PUR or polystyrene foams from different end-of-life products) would be targeted. Stakeholders for the different 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 product is listed in Annex 1-B (for 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 labelled as containing HBCD).

b) The product is listed in Annex 1-B (for PBDEs) or Annex 1-C (for HBCD) and bromine is being detected by a bromine screening method (see Chapter 4.4.).

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 de-pollution – General. Also a sampling methodology and a sampling protocol has been developed for WEEE plastic shredder by Wäger et al. (2010)[112] and is described in the study.[112] 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.

For all sampling the POP-BFR distribution in the waste need to be considered and the samling size and particle size need to be appropriate for a representative sample (see Section 2.5.2.2 Representative sampling from recyclates and mixed waste containing POPs).

An approach of sampling individual EEE for screening of PBDEs in e.g., Cathode Ray Tube casings of TV and PC is shortly described in Annex 2-B.

Currently there is no standardized method for sampling of HBCD in products such as foams in buildings or packaging materials, furniture or textiles and recycling but monitoring studies show that HBCD containing EPS is partly recycled into new EPS products[113].

Step 3: Optional (further) screening in the laboratory

Sample products 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 PBDEs, which would lead to false positive results. Also, HBCD is sensitive to degradation and individual methods need to be validated.

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[112] Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. Final Report. https://resource-recovery.net/sites/default/files/empa_2010_rohs_substances_in_mixed_plastic.pdf

[113] Abdallah MA, Sharkey M, Berresheim H, Harrad S (2018) Hexabromocyclododecane in polystyrene packaging: A downside of recycling? Chemosphere 199, 612-616.

Recently a simple wipe test has 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.[114] Rinsing this filter paper resulted in determination of BFRs present even in a semi-quantitative manner.[114]

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 PBDEs and HBCD have been described or reviewed.[115,116] One accredited method used for commercial analysis for PBDEs is described in Annex 3-A and for HBCD in Annex 3-G. Further methods are described in the listed case studies below.

Extraction and clean-up of selected samples are described below.

4.4 Screening methods for bromine and other screenings 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 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).[117] 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)[118] and can be used for the screening of bromine in consumer goods in the field or in recycling plants (see also PBDEs BAT/BEP Guidelines[7]:

- 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.

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[114] 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.

[115] 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

[116] 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.

[117] 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.

[118] 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.

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 mg/kg. 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%.

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 products 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}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: e.g. Thermo Scientific Niton; Olympus; Bruker; Analyticon; and 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 compliance to RoHS Directive. Such equipment can be used for screening bromine and might be sufficient for this purpose.

Rapid onsite distinction between EPS/XPS containing HBCD and brominated polymeric alternatives with XRF

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)[119] developed a screening method for identifying expanded and extruded polystyrene foams containing HBCD 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.[119] 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.[119] Since in recent years also other additive BFRs are used in EPS/XPS this test is only specific for EPS/XPS in constructions this test becomes less specific for EPS/XPS produced since 2019.

4.4.2 Sliding spark spectroscopy (Table 4-3)[120]

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 handy, compact non-conductive material without

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[119] 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.

[120] Seidel T, Golloch A, Beerwald H, Böhm G (1993) Sliding spark spectroscopy. Fresenius' Journal of Analytical Chemistry 347, 92-102.

prior sample preparation. Using handheld instruments, the time requirement for a measurement lies within seconds.

Care has to be taken with screening methods if plastic is coated. Then the coatings need to be removed by scratching. Dirt should also be removed for a 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 products 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 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).[121]. The instrument costs approximately USD 6,000.

Table 4-4: Comparison of handheld 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 florescence 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 known 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
Accuracy	Very good – mg/kg levels of elements	Sufficient – to nearest 1% on Br/Cl concentration.
Repeatability	Excellent	Good – some noise around 0-1% level

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[121] 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.

Type:	X-Ray Fluorescence	Sliding Spark spectral analysis
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

4.4.3 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.[122] 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.

4.4.5 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 is a reliable method for the quantitative determination of bromine in polymers in laboratory. Since the method takes some time (ca. 30 minutes) it cannot be considered a screening method but rather a precise confirmation method for the total bromine content.

4.4.6 Fourier-transform infrared (FTIR) spectroscopy

Fourier-transform infrared (FTIR) spectroscopy is a non-destructive analytical technique used to identify organic, polymeric, and inorganic materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties based on well-known infrared absorption bands. There are several types of FTIR instruments: benchtop instruments for use in the laboratory, and smaller or handheld devices that can be used outdoors. The attenuated total reflectance (ATR) FTIR spectroscopy can be used for rapid identification of decaBDE in polymers with a detection limit of several % by weight. The main advantage of ATR-FTIR is that, unlike other BFR screening technologies, which detects the presence of Br, ATR-FTIR can identify a compound by its molecular structure, thus distinguishing decaBDE from other BFRs (Figure 4-2).

Recently, to extract peaks characteristic of decaBDE a screening survey on ATR-FTIR spectra of flame-retarded plastic of household appliances were performed using a portable ATR-FTIR spectrometer.[123] Agilent 5500 Compact FTIR was used to collect spectra from 4000 cm^{-1} to 650 cm^{-1}. Spectral resolution was set at 8 cm^{-1}. Each sample was compressed against the ATR diamond crystal to ensure good contact between sample and crystal. Measuring time was approximately 6 sec. Spectra of flame-retarded plastic housings tested are shown in Figure 4-2. From the comparison of the IR spectra, a characteristic peak at a wavenumber of 1340 cm^{-1} was

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[122] 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.

[123] Kajiwara N, Matsukami H (2019) Rapid identification method of plastic components flame-retarded by decabromodiphenyl ether. Abstact Book 39th International Symposium on Halogenated Persistent Organic Pollutants, DIOXIN2019.

confirmed in the decaBDE-treated CRT television chassis. When the absorbance at wavenumber 1340 cm^{-1} is subtracted from the absorbance at wavenumber 1364 cm^{-1}, only the plastic containing decaBDE showed a positive value, and the plastics containing other major BFRs (TBBPA or DBDPE) showed negative values (Figure 4-2). Therefore, by setting the subtraction value of these absorbances as the threshold value, plastic intentionally containing high concentration decaBDE (percent range) can be identified easily.

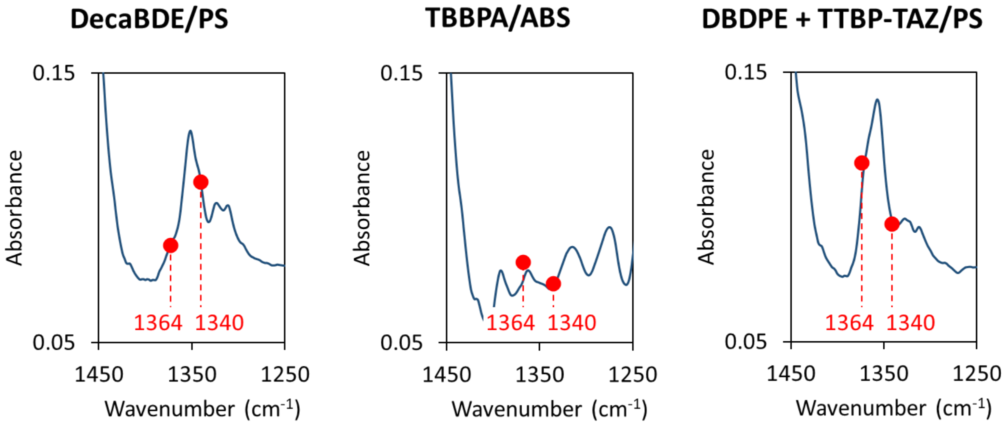

Figure 4-2: IR spectra of flame-retarded plastic housings. PS: polystyrene; TBBPA: tetrabromobisphenol A; ABS: acrylonitrile butadiene styrene; DBDPE: decabromo-diphenyl ethane; TTBP-TAZ: 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine.

4.4.7 Rapid determination techniques for HBCD, PBDEs and PBB

For more rapid analysis (compared to the standard GC methods with clean-up) some qualitative techniques have been developed which determines the respective POP-BFR. Fast analytical techniques might be important for high throughput of samples and for a quick monitoring. In most cases this is achieved by faster (but less effective) extraction techniques or to omit the clean-up steps.

Combination of XRF screening and wipe testing and analysis

Gallen et al. (2014)[124] 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)[125] 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)[126] used online pyrolysis of pulverised plastic and analysed samples with gas chromatography coupled to mass spectroscopic detection (py-GC/MS).

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[124] 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.

[125] 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.

[126] Danzer B, Riess M, Thoma H, Vierle O, van Eldik R (1997) Pyrolysis of Plastics Containing Brominated Flame Retardants. Organohalogen Compounds 31, 108-113

A thermo-desorption method for polymers was developed for rapid screening of polymers of 100 TV sets and 80 computers (Riess et al. 2000).[127] The pyrolysis GC/MS method has since been developed to a commercially available application by Shimadzu with a 48 sample auto-sampler (Shimadzu 2010).[128]

Further considerations regarding 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 PBDEs including debromination reactions [129] which have been reported for GC/MS analysis.

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 can shorten 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-BFR screenings. This is in particular relevant for developing countries where maintenance/repair of instruments and cost of repair and columns are often a challenge.

4.5 Sample preparation, extraction and clean-up

Key matrices of PBDEs in products are (see PBDEs BAT/BEP Guidance):

- Flame retarded plastic of electronics (e.g., ABS, HIPS, PP);
- Flexible PUR foam (furniture, vehicle seating, mattresses), and rigid PUR 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 products 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 (90%) has been used in PUR foam. The use of c-DecaBDE was more diverse and used in plastic of electronics, automobile, and polymers/plastic in construction with minor uses in textiles.

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.

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[127] 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.

[128] Shimadzu (2010). Pyrolysis GC/MS of Brominated Flame retardants
http://www2.shimadzu.com/applications/gcms/Appl_GCMS_PBDE_07C_070_en.pdf

[129] UNEP (2010) Debromination of brominated flame retardants. 6th POPs Reviewing Committee meeting Geneva 11-15. October 2010 (UNEP/POPS/POPRC.6/INF/20).

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).[130]

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, Soxhlet extraction, 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 PUR 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, the 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

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

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[130] Dietrich Braun, Simple methods for identification of plastics, 4th ed., 1999, Carl Hanser Verlag, Münich, Germany.

degradation. This approach yields good recovery efficiency for the respective BFR. For some polymer types (e.g., PUR foam), 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 PBDEs, HBB or HBCD and other BFRs from the most relevant polymers for POP-BFRs (ABS, PS, ABS/PC blend, PPE/PS blends, PVC,) is performed by dissolution with tetrahydrofuran (THF) or toluene and precipitation is done with either ethanol [131], 1-propanol [132] or *n*-hexane[133] .[134] 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 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 a shaker for 15 min. 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.

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[131] 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.

[132] 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.

[133] n-hexane can be substituted by the less toxic n-hepane

[134] 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

Also, the standard analytical procedures with GC-FID developed by PlasticsEurope and Cefic use a dissolution and precipitation method.[135] The polystyrene sample including additives is dissolved in dichloromethane (CH2Cl2) 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 analysed in the GC-FID system.[135] 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 place 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).[136]

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 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_2SO_4 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 the target 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.

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

[136] Braun D (1999) Simple methods for identification of plastics, 4th ed. 1999, Carl Hanser Verlag, Munich, Germany

Gel permeation chromatography for extraction and clean-up

Gel permeation chromatography (GPC) provides an alternative separation approach, isolating flame retardants with molecular masses below 1000 µ from polymers with molecular masses larger than 10,000 µ.[137] 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.[137]

4.5.3 Extraction of PBDEs in flexible and rigid polyurethane foam[138]

For extraction of PBDE from polyurethane, solid-liquid extraction is sufficient to achieve an excellent recovery of PBDEs (Bergmann 2006).[138] Soxhlet extraction with toluene was found to be the most effective. After 2 hours extraction time, exhaustive extraction is achieved without detection of PBDEs in extracted PUR foam.

4.5.4 Extraction of HBCD from textiles

Kajiwara et al. (2009)[139] compared different extraction methods for HBCD containing textiles: Soxhlet extraction (16 h) with dichloromethane (DCM) and toluene, ultrasonic extraction (1 h) and soaking extraction with DCM resulted in complete extraction. However, it needs to be highlighted that ultrasonic extraction with toluene resulted in low efficiency of less than 5%. Also, Soxhlet extraction using toluene resulted in a slight increase of α-HBCD and a slight reduction of γ-HBCD. It seems that γ-HBCD starts isomerization at the temperature at the boiling point of toluene (110.6 °C) to some extent. Care needs to be taken with Soxhlet and elevated temperature when the HBCD isomer ratio is targeted for specific interpretations and then other extraction methods/solvents than Soxhlet and toluene would be used. Therefore, soaking extraction with DCM was found to be the most facile procedure to analyse HBCD diastereomers in textiles.

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 of POP-BFRs

4.6.1 Measurement standards for PBDEs, other PBDEs and interfering BFRs

A measurement method for PBDEs for Stockholm Convention purposes needs to cover tetraBDEs, pentaBDEs, hexaBDEs, heptaBDEs, and decaBDE.

PBDE standards and interfering BFRs

For the quantification of PBDE in products normally external standardization is used. In the standard approach of Fraunhofer Institute, which has been working on recycling of WEEE polymers for two decades (Schlummer

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[137] 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.

[138] Bergmann M (2006) Bestimmung polybromierter Diphenylether in Kunststoffen und Untersuchungen zum Emissionsverhalten. PhD, Technical University Berlin.

[139] Kajiwara N, Sueoka M, Ohiwa T, Takigami H. (2009) Determination of flame-retardant hexabromocyclododecane diastereomers in textiles. Chemosphere. 74, 1485-1489.

et al. 2006)[140], the following PBDE and BFR standards are used for monitoring of PBDEs and other relevant BFRs[141]: 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 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, preferably used 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 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 PBDEs. On the column used the TBBPA co-elutes with BDE-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 µg/mL. Working solutions are prepared directly before use by diluting the standard to 5 concentrations between 1 and 100 µg/mL. 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 POP' limit would be established from the 1000 mg/kg limit used for RoHS.[142] Currently the Basel Convention includes 1000 mg/kg, 500 mg/kg, and 50 mg/kg as low POP limit.

Also, ^{13}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 ^{13}C-PBDEs, they are closely similar to the parent PBDEs in terms of physical-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 ^{13}C isotopes. They can be used with GC-ECD detection while coeluting ^{13}C-labelled standards cannot.

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

4.6.2 Instrumental analysis of PBDEs and HBB

Separation techniques

The state-of-the-art analytical technique for the analysis of PBDEs listed in the Stockholm Convention (tetraBDE to heptaBDE, and decaBDE) and for HBB are chromatographic techniques.[143]

As chromatographic technique gas chromatography (GC) is normally used for PBDEs and HBB (see e.g., IEC 62321-6).[144] 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 coupled to Ultra Violet detection (HPLC/UV). GC separation is normally performed on a non-polar 10-30 meter GC column.[145] 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 3-A for PBDEs and in Annex 3-B for HBB.

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[140] 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.

[141] Major flame retardants should be included in the standard to ensure that BFRs are separated from 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.

[142] 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.

[143] 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.

[144] 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 chromatograhy -mass spectometry (GC-MS)

[145] If also DecaBDE is to be monitored, shorter columns (preferably 15 meter) are normally used.

Detectors: Mass spectrometer, Electron Capture Detector (ECD)

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 PBDEs and for the monitoring of PBDE in products it has the advantage of a higher robustness and simpler cleaning of the detector (Table 4-5). The advantages and drawbacks of the main utilized detection techniques are described in the Table 4-5.

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 its 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.

Table 4-5: Advantages and drawbacks of different detection techniques for PBDE/BFRs are highlighted in the table (Covaci et al., 2003 and 2007)[146]

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
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"

PBDE detection with mass spectrometry

Sensitive EI-MS analysis is performed in selected ion reaction mode (e.g. selected 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 3-1).

For analysis of PBDE/BFR polymers low resolution mass spectrometry (LRMS)[147] 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 ^{13}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 ^{13}C-labelled internal standards cannot be used for each individual analyte.

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.

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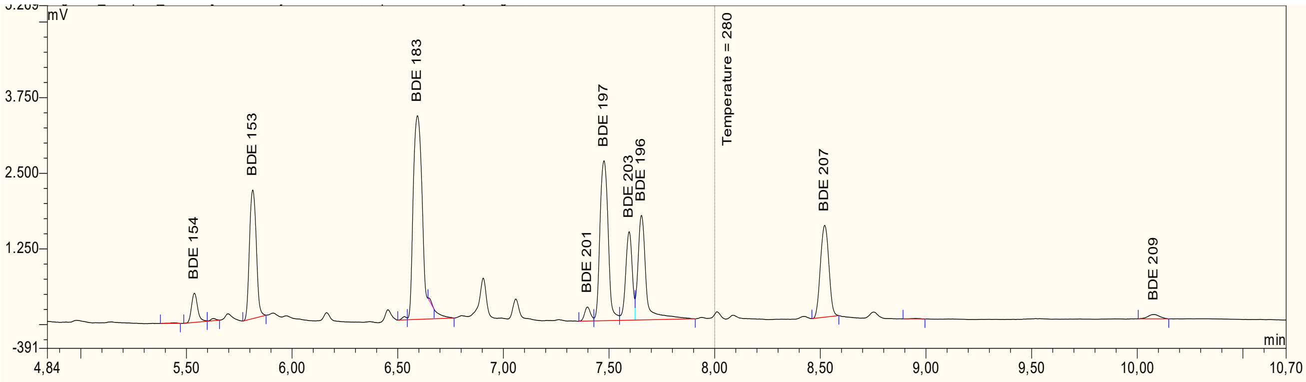
[146] Covaci A, Voorspoels S, Ramos L, Neels H, Blust R (2007) Recent developments in the analysis of brominated flame retardants and brominated natural compounds. Journal of Chromatography A 1153, 145-171.

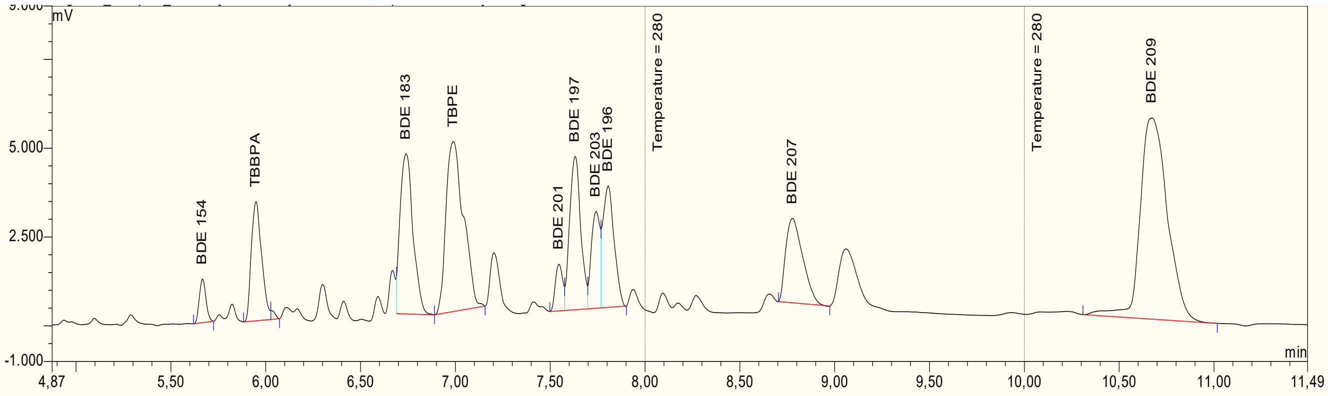
[147] The more sensitive and expensive HRMS requires highly trained and experienced lab personnel and is not necessary for this matrix.

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.[148]

The recognition and interpretation of chromatograms from ECD detector need some experience to determine PBDEs in particular if BFR mixtures are present in recycled plastics (see examples in Figure 4-3 below). This might be more critical in future since the number of BFRs 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 (5 µg/mL)



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

Figure 4-3: 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))

Recently, Eguchi et al. (2021)[149] developed a rapid analytical method that can be used with conventional GC–qMS and GC-ECD equipped with a short 5 m GC column. The run times of the developed method were less than 10 min to simultaneously detect PBDEs and HBCD in plastic waste (Figure 4-4) and their method detection

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[148] 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.

[149] Eguchi A, Matsukami H, Takahashi A, Kajiwara N (2021) Simultaneous determination of polybrominated diphenyl ethers and hexabromocyclododecane in plastic waste by short-column gas-chromatography-quadrupole mass spectrometry and electron capture detector. Chemosphere 277, 130301.

limits were below the upper threshold of the low POP content limits as defined by the Basel Convention (<1,000 mg/kg for both PBDEs and HBCD).

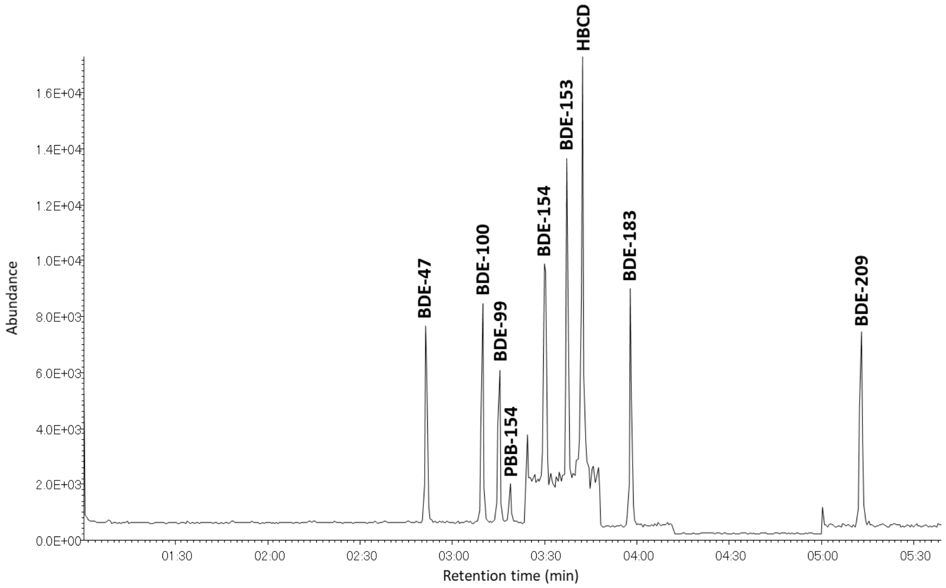

Figure 4-4. Chromatograms of the standard mixture of PBDEs and HBCD using a DB5-ht GC column

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

The selected GC/MS conditions differ slightly between laboratories. Also different GC columns can be used. In Annex 3-A an example of GC/MS condition for the analysis of PBDEs and in Annex 3-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 analysis of PBDEs and PBB

International Standard for determination of regulated substances in electronics

An International Standard IEC 62321 ed.1[150] 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.

EN ISO 17881-1:2016 for determining some brominated flame retardants in textiles

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[150] 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.

ISO 17881-1:2016 specifies a test method for determining some brominated flame retardants in textiles by gas chromatography - mass spectrometry (GC-MS). The standard cover PBDEs, PBBs and HBCD in textile.

The method is applicable to all kinds of textile products. The committee responsible for this document is ISO/TC 38, Textiles.

ISO 17881 consists of the following parts, under the general title Textiles — Determination of certain flame retardants:

- — Part 1: Brominated flame retardants
- — Part 2: Phosphorus flame retardants

German national standard for determination of c-PentaBDE and c-OctaBDE in plastic materials in respect to the RoHS directive[151]

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).[151] 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 ΣPentaBDE and ΣOctaBDE with a limit of 0.1% each.

US EPA method 1614*[152]* for PBDE in water, soil, sediments and tissue

The US Environmental Protection Agency (USEPA) developed a standard for the analysis of PBDEs in water soil, sediment and tissue by HRGC/HRMS (US EPA method 1614).[152]

The GC/MS analysis described in this standard available on the internet can also be used for the analysis of PBDEs from products, waste or recyclates 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.[153] The interlaboratory comparison included the determination of total bromine, the total sum of PBB, total sum of PBDEs and several individual brominated diphenyl ethers (BDE-47, BDE-99, BDE-183 and BDE-209) and decabrominated biphenyl (BB-209) in plastic. The study is available on the internet.[153]

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[151] 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.

[152] USEPA (2007) EPA method 1614 Brominated Diphenyl Ethers in Water Soil, Sediment and Tissue by HRGC/HRMS http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_09_11_methods_method_1614.pdf

[153] 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

4.6.6 Instrumental analysis for HBCD

4.6.6.1 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.[154]

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 (e.g., 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.[155]

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.[156] Recently, Eguchi et al.[149] developed a rapid GC analytical method with a short 5 m DB-5HT GC column to simultaneously detect HBCD and PBDEs in plastic waste (Figure 4-4). The injector was held at 300 °C and operated in the splitless mode. The effect of HBCD thermal decomposition was negligible as a result of the significant reduction in GC analysis time.

When analysing HBCD by GC-MS, care need to be taken that the liner is changed at appropriate time to keep it as clean. Co-elution of HBCD with certain PBDEs can also be a problem.[156]

Mainly non-polar columns are used, for example, HT-8, DB-5, DB-5HT and STX-500. Splitless, pulsed-splitless, programmed temperature vaporizer (PTV), and on-column injectors have been used for the determination of HBCD.[156] Automatic sample injection should be used if possible, to improve the reproducibility of injection and the precision of the overall method.[156]

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.[156] 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.[156]

A validated/accredited method for analysis of HBCD with HPLC-MS is described in Annex 3-H.

4.6.6.2 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 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

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[154] 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.

[155] 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

[156] 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

PBDEs such as MS and ECD, (Table 4-5) can be used for HBCD. In addition, also FID and NMR have been used to detect HBCD for specific purposes.

A) 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.[156] When GC-ECNI-MS is used, only the bromine ion is monitored; therefore, isotopically labelled standards (^{13}C) cannot be used as internal standards for quantification purposes. Larger fragment ions, required for structural confirmation, are not formed in ECNI mode.[156]

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 and 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 GC-MS, with the sensitivity being approximately ten times less than that of the GC-NCI/MS method. LC-MS-MS can usually overcome the problem of higher detection limits.[156]

B) 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.[157] If the total amount of HBCD needs to be determined, GC-FID represents a sensitive, reliable and less cost intensive solution. The FID can reach detection limits of low mg/kg for the developed standard for HBCD in EPS/XPS. While the developed standard state to aim for a reliable detection of 1000 mg/kg[157], it needs to be assured that also 100 mg/kg are robustly detected since the Basel Convention low POP limit list 1000 mg/kg or 100 mg/kg[158] 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.[157]

C) HBCD monitoring/detection in 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.[159] 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 products are normally above 5000 mg/kg, NMR can be used for the detection of such originally HBCD treated products. However, NMR cannot be used for the assessment of low POP 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 LC columns can be used.

In Annex 3-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.

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[157] 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

[158] It is noted that further work to agree on one value will be undertaken according to decision BC-12/3

[159] 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.

4.6.8 International standards for HBCD analysis

International Standard for determination of regulated substances in electronics

For the analysis of HBCD in plastics used for electrical products, standard ‘*IEC 62321-9 ED1: Determination of certain substances in electrotechnical products - Part 9: Hexabromocyclododecane in polymers by chromatography-mass spectrometry (GC-MS)* has been developed.

EN ISO 17881-1:2016 for determining some brominated flame retardants in textiles

ISO 17881-1:2016 specifies a test method for determining some brominated flame retardants in textiles by gas chromatography - mass spectrometry (GC-MS). The standard cover PBDEs, PBBs and HBCD in textile.

Analytical standard procedures are developed for environmental matrices like biota and sediments.[160]

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[160] 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

5 Sampling, screening and analysis of PCNs and PCBs in products and recycling

A "*Draft guidance on preparing inventories of polychlorinated naphthalenes (PCNs)*"[161] has been developed, which for specific Tier III inventory tasks suggests screening and analysis of PCNs for selected products in use and stock. Sind PCBs have been used in the same application in particular open applications like sealants or paints, the inventory suggest to combine PCBs and PCNs in POP inventories. For the sampling and monitoring of PCNs in wastes, the Basel Convention technical guideline considering PCNs can be consulted which also addresses PCNs and PCBs in one guideline.[162]

5.1 PCNs listed in the Stockholm Convention

Polychlorinated naphthalenes (PCNs) comprise 75 possible congeners in eight homologue groups with one to eight chlorine atoms substituting the planar aromatic naphthalene molecule. The basic structure of the PCNs is shown in Figure 5-1 and has the molecular formula $C_{10}H_8$-nCl_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.

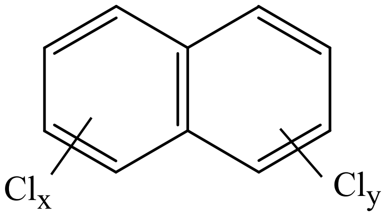

Figure 5-1: General structure of polychlorinated naphthalenes (PCNs)

5.2 Products and recycling possibly containing PCNs

PCNs as commercial mixtures were mainly produced and used between 1920 and 1970.[161] Some companies have used PCNs in products until around 2000.[163,164] The total former production volume of commercial PCNs is estimated to around 150,000 t and therefore around 10% of former PCB production.[161] PCNs have been less used in closed applications (to some extent in capacitors) and more in a wide range of open applications including cable insulation, as additive in paints and dye carriers, feedstock for dye, wood preservation, and in lubricants.[161]

A list of potentially PCN containing products 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 PCNs were mainly produced from 1930s to 1970s and has largely been phased out in the 1980s and 1990s, most products containing PCNs have reached their end-of-life or have already been disposed. Some

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[161] Secretariat of the Stockholm Convention (2017) Draft guidance on preparing inventories of polychlorinated naphthalenes. UNEP/POPS/COP.8/INF/19

[162] 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.

[163] 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.

[164] 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.

PCNs are unintentionally formed in the production of organochlorine chemicals and in thermal processes (see Annex 1-E).[161]

Since SCCPs (see Chapter 6) and PCBs 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 SCCPs, where appropriate.

5.3 Step by step approach for PCN/PCB monitoring in products and recycling

To determine the occurrence and quantities of PCNs in different products and construction, the former use of PCNs in the country should be assessed (see draft PCN inventory guidance[161]). Since PCBs were also used in the same open and close applications[161], 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 been substituted by SCCPs, which are listed in the Convention since 2017, SCCPs should be included in such a monitoring.

Step 1: Survey of products and recycling possibly containing PCNs and PCBs

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

A list of major uses and related products and wastes containing PCNs is described in Annex 1-E and includes capacitors, certain paints, cables, Neoprene rubber and wood (see Annex 1-E).

Furthermore, PCNs are formed unintentionally in certain organochlorine production and in thermal processes. Therefore, those product wastes and recycling streams can also be considered and assessed (see Annex 1-E and Stockholm Convention PCN draft inventory guidance[161]).

The screening of PCNs in the end-of-life and recycling can be combined with Basel Convention activities and also the related Basel Convention technical guideline[162] should be consulted.

Step 2: Sample collection

Samples can be collected e.g., by relevant authorities such as the ministry of construction or consumer protection authorities and related institutions. Since PCNs and PCBs have been used in open applications like paints and sealants in construction, this sector is of particular relevant for assessment and collection.

Sampling campaigns might also be conducted by research institutions possibly in collaboration with a concerned 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 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 PCB 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 for these samples.

For PCNs in open applications 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 product categories are described in Annex 1-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 1-E and Stockholm Convention PCN inventory guidance[161]). For the sampling of unintentional PCNs see Annex 1-E.

Recycling streams possibly impacted by PCNs and PCBs are certain construction and demolition waste, waste wood, waste oils and cables.

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

Sample products can be screened for the presence of chlorine in the field or in the laboratory. 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. Since PCBs need to be assessed in such screenings the test for chlorine has to be applied in any case, but differentiations need to be carried out later.

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 and 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 be screened with XRF for chlorine. In this case, a chlorine positive sample is also not specific for PCNs or PCBs. However, it indicates that the material might contain PCNs, PCBs or SCCPs. Other chlorine containing materials like chloroprene rubber or PVC give also a positive signal.

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

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.[165] Rinsing this filter paper resulted in determination of BFRs present even in a semi-quantitative manner.[114] 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.[166]

Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of PCNs (see Section 5.6) and PCBs. One accredited method used for commercial analysis is described for PCNs in Annex 3-D. Further methods are described in the listed case studies in Annex 2-E.

Extraction and clean-up of selected samples are described below in Section 5.5.

5.4 Screening methods for chlorine as indication for PCNs and PCBs

5.4.1 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.[167] Samples tested positive for chlorine can be further analysed in laboratory for POP content (PCNs or PCBs).

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[165] 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.

[166] 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

[167] UNEP (1999) Guidelines for the Identification of PCBs and Materials Containing PCBs.

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 PCB or PCN 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 most XRF equipment does not reach a detection limit of 50 mg/kg chlorine for oil.

5.4.2 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 are higher compared to bromine. Handheld XRFs have detection limits for chlorine around 100 mg/kg. Laboratory XRF equipment can reach detection limits of 10 mg/kg.

For sealants and chalks, screening with XRF can detect PCN and PCB containing sealants. Additive levels in sealants are normally between 5 and 25%.[168] Since SCCPs 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 .[169] All PVC and chloroprene coatings give a chlorine positive signal with XRF or other screening technologies not specific for PCNs. 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 confirmation analysis in laboratory can reveal the respective additive.

5.5 Sample preparation, extraction and clean-up

Extraction

Samples are normally extracted with standard methods like Soxhlet extraction. Soxhlet extraction with toluene was used by Yamamoto et al.[170] 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 2-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.[171] Here e.g., silica gel-impregnated activated carbon columns can be applied.

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[168] 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.

[169] BUWAL 2000

[170] 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

[171] 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.

Details on some clean-up procedures used can be found in the references of the case studies compiled in Annex 2-E.

5.6 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 an 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 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)-methylpoysiloxane) by Falandys et al.[172] and for a DB 1701 column (low/mid-polarity, bonded, cross-linked and solvent-rinsable) by Yamashita et al.[173]

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

5.7 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 method for analysing PCNs has been developed for water by the International Organization for Standardization (ISO): ISO/TS 16780.[174]

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[172] 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.

[173] 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.

[174] 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

6 Sampling, screening and analysis of short-chain chlorinated paraffins (SCCPs) in products and recycling

A "*Detailed guidance on preparing inventories of short-chain chlorinated paraffins (SCCPs)*"[175] has been developed, for which specific Tier III inventory tasks suggests screening and analysis of SCCPs in products in use and stock and in material and substance streams. For the sampling and monitoring of SCCPs in wastes, additionally the Basel Convention technical guidelines for waste containing SCCPs[176] can be consulted.

6.1 SCCPs in the Stockholm Convention

Chlorinated paraffins (CPs) are produced by the chlorination of n-alkane feedstocks to different degrees, typically with a chlorine content ranging from 40 to 70% by weight. CPs are generally subdivided in three chain-length categories: short (SCCPs – C_{10}-C_{13}), medium (MCCPs – C_{14}-C_{17}), and long chain CPs (LCCPs – C_{18}-C_{30}). However, these three subdivisions do not cover all possible chain lengths, which are known to range from C_6 to C_{38}.[177] In May 2017, SCCPs (Figure 6-1) with a chlorine content >48% by weight were listed under the Annex A of Stockholm Convention on POPs.[178] MCCPs and LCCPs are not listed in the Convention and, thus, not restricted in most countries. However, CP mixtures with a SCCP content >1% are also considered POPs. SCCPs were listed with various specific exemptions, covering most of their main applications:[178]

- Additives in the production of rubber transmission belts;
- Spare parts of rubber conveyor belts in the mining and forestry industries,
- Leather industry, in particular fat-liquoring in leather;
- Lubricant additives, in particular for engines of automobiles, electric generators and wind power facilities, and for drilling in oil and gas exploration, petroleum refinery to produce diesel oil; and metal processing;
- Secondary plasticizers in flexible PVC, except in toys and children's products.
- Tubes for outdoor decoration bulbs;
- Waterproofing and fire-retardant paints;
- Adhesives;

Furthermore, it has been cautioned by science that also MCCPs present POP-like characteristics, such as persistence, toxicity, long-range transport and bioaccumulative potential.[179; 180]

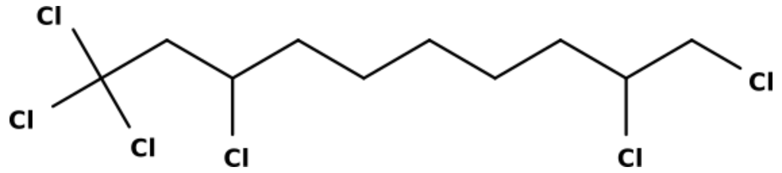

Figure 6-1: Structure of a short-chain chlorinated paraffin (SCCPs – e.g., $C_{10}Cl_6$)

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[175] UNEP (United Nations Environment Programme) (2019). Detailed Guidance on Preparing Inventories of Short-Chain Chlorinated Paraffins (SCCPs), Draft of 2019.

[176] UNEP (2018) Draft technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with short-chain chlorinated paraffins (UNEP/CHW/COP.14/7/Add.2)

[177] Guida Y, Capella R, Weber R. (2020) Chlorinated paraffins in the technosphere: A review of available information and data gaps demonstrating the need to support the Stockholm Convention implementation. Emerg. Contam. 6, 143–154.

[178] UNEP (United Nations Environment Programme) (2017). Eighth Conference of the Parties – COP 8. Decision SC 8-11. Listing of short-chain chlorinated paraffins.

[179] Glüge J, Schinkel L, Hungerbuehler K, Cariou R, Bogdal C. (2018) Environmental Risks of Medium-Chain Chlorinated Paraffins (MCCPs) - A Review, Environ. Sci. Technol. 52, 6743-6760.

[180] Yuan B, Vorkamp K, Roos AM, Faxneld S, Sonne C, Garbus SE, Lind Y, Eulaers I, Hellstro P, Dietz R, Persson S, Bossi R, De Wit CA. (2019). Accumulation of short-, medium-, and long-chain chlorinated paraffins in marine and terrestrial animals from Scandinavia, Environ. Sci. Technol. 53, 3526-3537.

6.2 Products and recycling streams possibly containing SCCPs

CPs are chemicals with high versatility due to their flexibility in chlorination degrees and chain length. Moreover, the CP content can account for up to 70% of the total product mass (UNEP, 2019) and the global production of CPs has been estimated to exceed one million tonnes per year.[181] CPs have been produced since the 1930s for a wide range of applications such as metalworking fluids, lubricants and additives (flame retardants, softeners, waterproofing, fat-liquoring, anti-incrusting, etc.) in rubber, plastic, polyvinyl chloride (PVC), paints, coatings, sealants, adhesives,).[182] Due to the use as additive in PVC and rubber, SCCPs are detected in a wide range of consumer goods (e.g. toys, sports equipment, mats) and construction.

Major recycling streams possibly impacted by SCCPs are recycling of (soft) PVC, cable sheathing, rubber, leather, waste oils and construction and demolition waste.

A list of possibly impacted applications of SCCPs are given in Annex 1-E. The list contains major SCCP applications in products, 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 sources are also mentioned. This list can be used when selecting samples for screening. If a study on the presence of SCCP containing materials is planned, this list can be assessed for possible relevant samples for the country. Case studies on monitoring of SCCPs in products are compiled in Annex 2-E.

6.3 Step-by-step approach for SCCP monitoring in products and recycling

SCCPs and CPs containing more than 1% SCCPs are still produced in large scale and therefore present as additives in current products and in use in industrial processes.[175,177] SCCPs and other CPs containing SCCPs have been produced and used since the 1930s with higher historical production compared to most other POPs and are therefore present in waste and in recycling streams. [181,183,184] Due to the large increase in production volumes over the last 20 years, the volume of CPs in affected waste and recycling streams will continue to increase accordingly. The Basel Convention defines what concentrations of specific POPs in a waste classify it as a POP waste. For SCCPs there are currently two provisional low POP contents of 100 mg kg^{-1} (0.01%) and 10,000 mg kg^{-1} (1%) SCCPs[185] since the COP of the Basel Convention had a split opinion on the low POP content. The final selection of a limit will have implications on recycling. There is no exemption in the Stockholm Convention for the recycling of SCCP containing waste. However, waste categories containing SCCPs might be recycled without recyclers being aware of their POP content and the recycling will increase with the global strive to more circular economy. Only initial studies on CPs in waste or recycling fractions have been conducted including method development.[186,187,188] The monitoring of SCCPs can be combined with monitoring of PCBs and PCNs due to the former use in the same application and the uninintentional PCB/PCN content.

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[181] Glüge J, Wang Z, Bogdal C, Scheringer M, Hungerbühler K. (2016) Global production, use, and emission volumes of short-chain chlorinated paraffins e a minimum scenario, Sci. Total Environ. 573, 1132-1146.

[182] Van Mourik LM, Gaus C, Leonards PEG, De Boer J. (2016) Chlorinated paraffins in the environment: a review on their production, fate, levels and trends between 2010 and 2015. Chemosphere 155, 415-428

[183] UNEP (2018). Draft Technical Guidelines on the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Short-Chain Chlorinated Paraffins.

[184] ESWI (2011). Study on Waste Related Issues of Newly Listed POPs and Candidate POPs. Consortium ESWI (Bipro, Umweltbundesamt and Enviroplan) for the European Commission.

[185] UNEP (2019) Technical guidelines, Addendum - General Technical Guidelines on the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Persistent Organic Pollutants.

[186] Xu C, Gao L, Zheng M, Qiao L, Cui L, Wang K, Huang D. (2019) Short- and medium-chain chlorinated paraffins in commercial rubber track products and raw materials, J. Hazard Mater. 380, 120854.

[187] Brandsma SH, Brits M, Groenewoud QR, Van Velsen MJM, Leonards PEG, De Boer J. (2019) Chlorinated paraffins in car tires recycled to rubber granulates and playground tiles, Environ. Sci. Technol. 53, 7595-7603.

[188] Matsukami H, Takemori H, Takasuga T, Kuramochi H, Kajiwara N. (2020) Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes, Chemosphere. 244, 125531

Step 1: Survey of products and recycling streams possibly containing SCCPs

Before collecting samples, a survey should be conducted to preliminarily determine relevant products currently in production or use or at the end of their lifespan that might contain SCCPs. A list of major uses and related products and wastes containing SCCPs are described in Annex 1-E. Relevant stakeholders for the different use groups might be contacted for support and input and for samples and are listed in Annex 1-E. It is recommended to consult the Stockholm Convention inventory guidance for selection. SCCPs have substituted PCBs and PCNs in open application in 1970s to 2000. Therefore, the survey of end-of-life products and recycling streams can be combined with monitoring of PCBs and PCNs in open applications (see Chapter 5).

The screening of SCCPs in end-of-life products and waste can be combined with Basel Convention activities (Synergy) and also the Basel Convention's guideline can be consulted.[176]

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.

The following criteria and information can be used for the collection:

a) Technical CP mixtures should be assessed for the SCCP content for confirmation if the mixtures contain more than 1% SCCPs defining them as POPs. SCCPs and other CP mixtures are identifiable by their chemical names, CAS numbers or commercial names (see Annex 1F);

b) CP based products, such as lubricants, metalworking fluids or fatliquoring liquids, should be assessed when CPs are identifiable in their trade names or in their composition by chemical names or CAS numbers or the information that they contain chlorine or are identified by screening to contain chlorine (see Step 3 below);

c) Products listed in Annex 1-F, where high shares of CPs can be found, with identifiable CP additive characteristics, such as flame-retardancy, waterproofing, fat-liquoring and anti-incrusting such as flame retarded rubber products, soft PVC products known to frequently contain could be sampled for SCCP assessment.

d) Products made out of recycled rubber, PVC or other polymer with identifiable CP additive characteristics should also be considered for SCCP monitoring.

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

Sample products can be screened for the presence of chlorine in the field or in the laboratory see Section 6.4. SCCPs in 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 provisional low POP content is [100] or [10,000] mg/kg.[200]

Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of SCCPs and is described in Annex 3-G. One accredited method used for commercial analysis is described for SCCPs in Annex 3-G. Methods used in are described in the listed case studies in Annex 2-F.

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

6.4 Screening methods as indication for SCCPs

On the other hand, products can be easily and quickly screened for the presence of chlorine in the field or in the laboratory. X-ray fluorescence (XRF) and sliding spark spectroscopy are examples of techniques that can detect chlorine. The detection limit depends on the instrument. For XRF the detection limit of chlorine is higher than the detection limit of bromine. Handheld XRF devices have detection limits for chlorine around 100 mg/kg and laboratory XRF equipment can reach better detection limits as of 10 mg/kg.

Considering that SCCP additives are used in percent range in products (see Annex 1-E), a handheld XRF screening should be enough to select samples for chemical confirmation in laboratory. As SCCPs were listed with a chlorine content >48% by weight, a detection limit of 100 mg/kg of chlorine content should also be able to meet the European Union regulatory limit of 1500 mg/kg for SCCPs in products.

It is important to mention that some chlorine-containing polymers such as PVC and chlorinated rubber could not be screened for chlorine as an indicative of SCCP application. Moreover, not only SCCPs would give a positive signal even in non-chlorinated polymers. A chlorine content in the percent rate of a product weight could also be an indicative of CPs with different chain-lengths, such as MCCPs and LCCPs, or of PCBs and PCNs used in past in rubber, PVC, sealants, paints, coatings, adhesives, and others and substituted by SCCPs after their restrictions or phase-out. Still, any CP mixture or CP containing product should be assessed for the low SCCP content of 1% established by the Stockholm Convention as well as other POPs like PCBs and PCNs also need to be screened and monitored.

6.5 Sample preparation, extraction and clean-up

Extraction

In broad terms, CPs are efficiently extracted with low-polarity solvents or with non-polar and polar solvent mixtures, like many hydrophobic organic compounds, such as other organochlorine POPs. Although tetrahydrofuran (THF) has been highlighted as a more efficient solvent for extracting CPs from certain polymer matrices than acetone and hexane/dichloromethane mixture[190,] a recent study has shown that toluene was more efficient than THF for extracting CPs from rubber and PVC products.[189] Ultrasonic bath has been the most used method for extracting CPs from products, but liquid-liquid/shacking extraction has also been used for lubricants and cutting fluids. For extraction methods and solvents see case studies in Annex 2-F.

Clean-up

A clean-up step is generally necessary to isolate CPs and prevent interferences in instrumental analysis caused by co-extracted compounds. Clean-up methods used for the determination of other organochlorine POPs are also usually adaptable for CP isolation. The most common co-extracted interferences are lipids, pigments and elemental sulphur. Lipids and pigments can be easily removed by sulfuric acid attack. Extracts can be treated by adding concentrated sulfuric acid or sulfuric acidified silica gel and/or by eluting the extract into a chromatographic column packed with sulfuric acid silica gel. Elemental sulphur can be eliminated with activated copper (washed with hydrochloric or nitric acids). Moreover, gel permeation chromatography can be used to remove lipids and elemental sulphur.[190]

Since CP extraction and clean-up methods are generally the same as those used for other organochlorine POPs, it can be expected that they would go through those steps and interfere in the instrumental analysis of CPs. However, many of these interferences – such as, chlorinated benzenes and aromatics, cyclodienes (e.g. aldrin, dieldrin, endosulfan…) PCBs, DDT and its metabolites – have been shown to be removed in chromatographic column clean-ups with different sorbents.[190] On the other hand, toxaphene, chlorinated oleofins/di-oleofins (COs/di-COs), MCCPs and LCCPs are major interferences in SCCP instrumental analysis that have not been

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[189] McGrath TJ, Poma G, Matsukami H, Malarvannan G, Kajiwara N, Covaci A. (2021). Short- and Medium-Chain Chlorinated Paraffins in Polyvinylchloride and Rubber Consumer Products and Toys Purchased on the Belgian Market. Int. J. Environ. Res. Public Health. 18, 1069.

shown to be completely separated from SCCPs by chromatographic clean-up steps. But, COs/di-COs are expected to be removed by concentrated sulfuric acid attack due to the nature of their double bond(s).[190]

6.6 Quantitative (and semi-quantitative) analysis

Several different analytical methods have been applied for the instrumental quantification of SCCPs.[190] Thus far, gas chromatography coupled with electron capture negative ionization and low-resolution mass spectrometry (GC/ECNI-LRMS; see Annex 3-G1) is the most widely used instrument for CP determination despite its limitations. The two major drawbacks when working with GC/ECNI-LRMS are that i) higher chlorinated CP homologues are more efficiently ionized than the lower chlorinated homologues – which can result in an overestimated overall chlorine content or in the non-ionization and consequently non-measurement of congener groups with less than five chlorines – and ii) LRMS suffers serious interference of different chain-length CPs with each other and even of other POPs, such as PCBs, chlordane and toxaphene in environmental samples. In products like PVC or rubber such interferences are not relevant. Since CPs contain PCBs and PCNs as unintentional POPs up to several 100 mg/kg these UPOPs need to be separately analysed and do not interfere with the SCCP analysis. Nominal masses can be produced from congener groups which are two and five carbon atoms apart. A methodology for GC/ECNI-LRMS is provided in Annex 3G-1.

A high-resolution HRMS (>50,000) is necessary to resolve individual carbon-chlorine congener groups and provide an optimal quantification of CPs (Annex 3G-2).[188,190,191] Thus, some of the drawbacks of the method described in Annex 3-H1 can be compensated by using high resolution MS instruments, e.g., Orbitrap-MS (Annex 3-H2), Time-of-fight (TOF)-MS or Fourier-transform ion cyclotron resonance (FT-ICR)-MS. For negative chemical ionization (NCI) or ECNI, target ions are $[M\text{-}Cl]^-$ and, for isomer groups/homologues with low overall chlorination degree, $[M\text{-}HCl]^-$.

Further information might also be found in the EURL POPs Guidance Document on CP analysis in food and feed (LINK available 05-2021##), where several LRMS, HRMS methods for GC and LC are described along with chromatograms and possible quality criteria. Moreover, The Orbitrap Method of the European Reference Laboratory for POPs is described in Annex 3G-2.

For the simultaneous analysis of SCCPs, MCCPs and LCCPs liquid chromatography is recommended. LCCPs are not effectively determined when one- or two-dimensional GC (or GCxGC) are used, due to their low vapour pressure. Therefore, a liquid chromatography (LC)-based method is recommended to higher chain-length CPs.[192] A LC/MS method developed by the Japanese National Institute of Environmental Science (NIES)[192] is described in Annex 3G-3.

Different case studies of SCCPs in products are compiled in Annex 2-F where also the respective methodologies are mentioned.

6.7 International standards for measuring SCCPs in products

6.7.1 Determination of chlorinated hydrocarbons in leather (ISO 18219:2015)[193]

Describes a GC-MS method to determine the amount of SCCPs in processed and unprocessed leathers. This method is currently being revised in ISO/FDIS 18219-1[194] (Leather — Determination of chlorinated

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[190] Yuan B, Muir D, Macleod M. (2019) Methods for trace analysis of short-, medium-, and long-chain chlorinated paraffins: Critical review and recommendations. Anal. Chim. Acta. 1074, 16-32.

[191] Mézière M, Krätschmer K, Rkons IP, Zacs D, Marchand P, Dervilly G, le Bizec B, Schächtele A, Cariou R, Vetter W. (2020) Addressing Main Challenges Regarding Short- and Medium-Chain Chlorinated Paraffin Analysis Using GC/ECNI-MS and LC/ESI-MS Methods. J. Am. Soc. Mass Spectrom. 2020, 31, 1885–1895.

[192] Matsukami H, Takemori H, Takasuga T, Kuramochi H, Kajiwara N. (2020) Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes, Chemosphere. 244, 125531

[193] https://www.iso.org/standard/61790.html

[194] https://www.iso.org/standard/77798.html

hydrocarbons in leather – Part 1: Chromatographic method for short-chain chlorinated paraffins (SCCPs)) which is under development.

6.7.2 Determination of certain flame retardants in textiles (ISO/TR 17881-3:2018)[195]

Part 3: Chlorinated paraffin flame retardants – Describes a method to determine SCCPs in textiles using carbon skeleton reaction gas chromatography with a flame ionization detector (GC-FID). This method is applicable to all kinds of textile products.

6.7.3 Determination of SCCPs and MCCPs in in textiles (ISO 22818 – under development)[196]

Will describe a gas chromatography negative ion chemical ionization mass spectrometry (GC-NCI-MS) method to determine SCCPs and MCCPs in textile products out of different matrices.

6.7.4 Determination of SCCPs in sewage sludge/bio-solids, soil, sediment and suspended (particulate) matter (ISO 18635:2016)[197]

Describes a GC-ECNI-MS method for the quantitative determination of the sum of SCCPs with a chlorine content between 50% and 67%, including approximately 6000 of approximately 8000 congeners. This method could be applied to samples containing from 0,03 µg/g to 3 µg/g of SCCPs, depending on the matrix and the detection capabilities of the GC-ECNI-MS.

6.7.5 Determination of SCCPs in water (ISO 12010:2019)[198]

Describes a GC-ECNI-MS method for the quantitative determination of the sum of SCCPs with a chlorine content between 50% and 67%, including approximately 6000 of approximately 8000 congeners in unfiltered surface water, ground water, drinking water and wastewater. This method could be applied to samples containing from 0,1 µg/L or lower to 10 µg/L. This method reviewed the method ISO 12010:2012 (Determination of short-chain polychlorinated alkanes (SCCPs) in water).

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[195] https://www.iso.org/standard/70258.html

[196] https://www.iso.org/standard/73989.html

[197] https://www.iso.org/standard/63093.html

[198] https://www.iso.org/standard/72127.html

7 Sampling, screening and analysis of PCP and its salts and esters in products and recycling

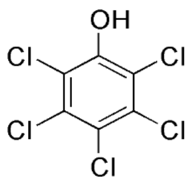
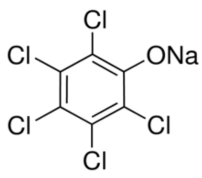
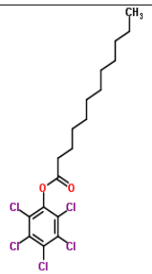
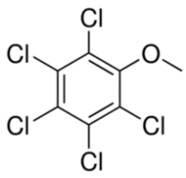
A "*Draft guidance on preparing inventories of pentachlorophenol and its salts and esters and on identifying alternatives for the phase-out of those chemicals*"[199] has been developed, which for specific Tier III inventory tasks suggests screening and analysis of PCP for selected products in use and 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.[200] The particular challenge with PCP is the high PCDD/PCDF content and the high formation potential for PCDD/PCDFs.

7.1 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 POPs (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[199]

	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_6HCl_5O	C_6Cl_5ONa	$C_{18}H_{23}Cl_5O_2$	$C_7H_3Cl_5O$
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				

7.2 Products and recycling streams possibly containing PCP

PCP has been produced commercially since the 1930s. At the height of its production, global output of PCP was around 90,000 tonnes per year. Total historic production is likely in the million-tonne scale. However, by the

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[199] UNEP (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.

[200] 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.

1990s, the widespread use of PCP was discontinued in most countries.[201] PCP and its salt and esters are currently produced in Mexico and in India, with formulation taking place in the US.[202]

PCP is a general biocide and has been used extensively as a fungicide, bactericide, herbicide, molluscicide, algaecide, insecticide, disinfectant, defoliant, anti-sap stain agent and anti-microbial agent in various industries including wood treatment, leather, textiles, paints, oil drilling, agriculture, and forestry.[199]

Major recycling streams possibly impacted are waste wood and leather.

A list of potentially PCP containing products 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 relevant samples for a Tier III assessment (see Annex 1-D and the SC PCP inventory guidance [161]).

7.3 Step-by-step approach for PCP monitoring in products and recycling

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[199]).

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 have been used in some countries/regions and could be integrated in such screening.

Step 1: Survey of products and recycling streams 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 unintentionally formed 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/wastes 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*"[200] would be consulted. Within this assessment related recycling streams would be flagged and sampled.

Step 2: Sample collection

For imported treaded wood such as utility poles but also other treated wood samples can be taken by customs at the import point of entry or by relevant authorities such as factory control. Samples can be collected, for example, in respective recycling facilities of waste wood and leather. One recycling stream with direct exposure to humans are animal bedding made out of recycled wood.

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 chemicals, 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 product or recycling stream is listed in Annex 1-D and has been produced or applied during the time when PCP has been produced and used;

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[201] (UNEP, 2013) Risk profile on pentachlorophenol and its salts and esters. UNEP/POPS/POPRC.9/13/Add.3

[202] (UNEP, 2014). Risk management evaluation on pentachlorophenol and its salts and esters. UNEP/POPS/POPRC.10/10/Add.1

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 products, 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. Product categories and recycling streams 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 products can be screened for the presence of chlorine in the field or in the laboratory see Section 7.4. PCP in 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 100 mg/kg.[185]

Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of PCP and some are described in Section 0. One accredited method used for commercial analysis of PCP is described in Annex 3-C. Further methods are described in the listed case studies in Annex 2-D.

Extraction and clean-up of selected samples are described below in Section 7.5.

7.4 Screening methods as indication for PCP

7.4.1 XRF screening of treated wood

XRF screening of chlorine might be used for a pre-screening of samples for further analysis. µ-XRF can reach detection limits for screening of PCP and other POP pesticides in wood, including wooden art objects[203]. In some countries the screening of chlorine in wood with XRF is relative specific for POP pesticides (e.g. PCP or DDT/HCHs) when mainly these pesticides have been used for wood applications in the past. Also if it is known that only PCP or other POP pesticides have been used for certain wood applications (e.g., electricity poles or railway sleepers) countries might only screen for chlorine to identify or to separate in recycling.[204]

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.[205]

7.4.2 Screening of treated textiles

XRF spectroscopy has also been used for screening of POPs in textiles in a museum.[206]

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[203] 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.

[204] 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.

[205] Bensch H, Engelhardt J, Katzung W, Jürgen Prof. Leonhardt Method and device for patterning of waste wood translated from German. Patent DE 19941124 B4.

[206] 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.

7.5 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.[207] Method 2 is a more complex procedure in which 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 is used. This method has been shown to be equivalent to the methanol extraction.[208]

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 7-1). Also, derivatization with methyl or ethyl ether or acetic anhydride has been described.[209]

These methods can also be applied for textiles or leather.

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[207] 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.

[208] 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).

[209] 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.

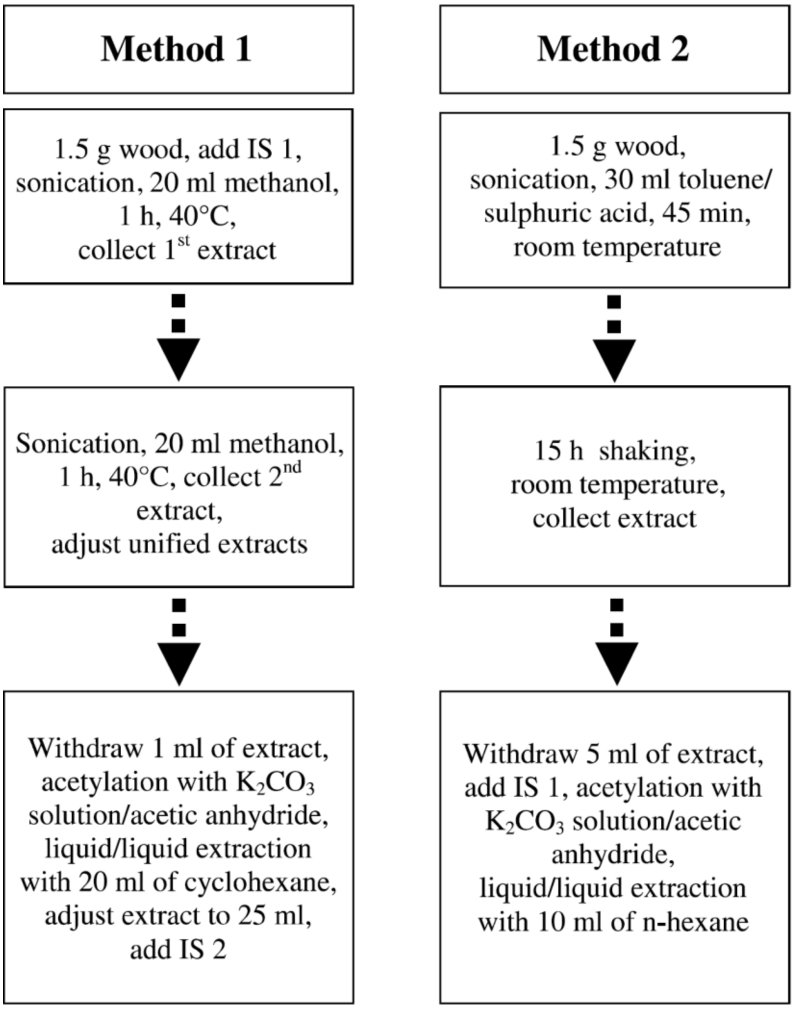

Figure 7-1: Extraction procedure of PCP and PCPNa from wood[207] (IS: Internal Standard)

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).[210] As extraction procedure the method use a steam distillation.[210] 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.[211] 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.

7.6 Quantitative (and semi-quantitative) analysis

Analytical detection of PCP, its salts or esters is typically performed by capillary gas chromatography.[207,210,212] One study compared GC with micellar electrokinetic capillary chromatography (MEKC) methodology and found comparable results.[213]

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[210] DIN EN ISO 17070:2015-05 (E) (2015) Leather - Chemical tests - Determination of tetrachlorophenol-, trichlorophenol-, dichlorophen ol-, monochlorophenol-isomers and pentachlorophenol content (ISO17070:2015). https://www.iso.org/obp/ui/#iso:std:iso:17070:ed-2:v1:en

[211] 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

[212] 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.

[213] 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.

As detectors, standard methods use normally either GC-ECD[207,210] or GC/MS.[210,212]

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

A quantitative method for measuring PCP concentrations in textile samples by isotope dilution liquid chromatography-mass spectrometry were calibration range of 1 to 50 ng/g[214] not validated for PCP levels above Basel Convention low POP content.

DIN EN ISO 17070:2015-05[210] 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 3-C.

7.7 International standards for PCP in products and materials

7.7.1 CEN/TR 14823:2003 Standard for PCP and TeCP in wood

Standard CEN/TR 14823:2003 specifies a laboratory method for the determination of PCP and all isomers of TeCP in wood with a gas chromatographic method. The method is applicable to all types of PCP- treated wood and wood-based materials as well as for the analysis of waste timber with respect to its PCP content. The method has a quantification limit corresponding to 100 µg PCP per kilogram of wood material expressed as dry matter. The method described has a measurement range up to PCP contents of 25 mg/kg of dry matter. If lower quantification limits are required, a higher volume of extract aliquot can be used for derivatisation.

7.7.2 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[215]. 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.[215]

7.7.3 ISO 17070:2015-05 Standard for the determination of PCP in leather

An ISO standard (DIN EN ISO 17070:2015-05)[210] has been developed for the determination of PCP (and other chlorophenols) in leather products. The standard includes extraction and clean-up procedure and instrumental analysis with GC-ECD.[210]

7.7.4 German Reference method for determination of PCP in leather and textile

A reference method (LFGB B 82.02-8 2001-06)[216] has been developed for determination of PCP content leather and textile for the (reference method).

7.7.5 ISO 15320:2011 Standard for the determination of PCP in pulp and paper

ISO 15320:2011 specifies a test method for the determination of pentachlorophenol (PCP) in an aqueous extract of pulp, paper and board. Although it was developed for paper and board intended to come into contact with foodstuffs, it is applicable to all kinds of pulp, paper and board.

The working range for acetylation is 0.05 mg/kg to 0.5 mg/kg. This method is based on GC-MS

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[214] 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.

[215] 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

[216] LFGB B 82.02-8 2001-06Nachweis und Bestimmung von Pentachlophenol in Bedarfsgegenständen, insbesondere aus Leder und Texilien.

7.7.6 USEPA Method 8270[212] for determination of semi-volatile organic compounds by GC/MS

USEPA Method 8270[212] 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.[212]

8 Sampling, screening and analysis of unintentional POPs in products and recycling

8.1 Background and need for monitoring of UPOPs in products

For thermal processes and chlorine production most unintentional POPs (UPOPs) are formed and released in parallel to the formation and release of PCDD/PCDFs and therefore are present in the same thermal processes and related wastes as the PCDD/PCDFs. [217,218] Therefore the UNEP Toolkit recommends that PCDD/PCDFs are used as surrogate for all UPOPs listed in Annex C, which can be minimized or eliminated by the same measures that are used to address PCDD/PCDF releases. The Toolkit recommends, for practical reasons, that inventory activities mainly be focused on PCDD/PCDFs, as these substances are indicative of the presence of other unintentional POPs (see UNEP Toolkit[217]) which is true for thermal sources like incineration, metal industries but also chlorine production.[217,218] However, on the other hand the formation of certain unintentional POPs can be very specific for chemical processes and products.[219] For example PCBs and HCB are present in certain pigments without emission (factor) for PCDD/PCDFs[217]. Also certain productions of chlorinated solvents have high formation of new listed HCBD, PeCB[220] and PCNs[221] but do not have an emission factor for PCDD/PCDFs. For such products and processes unintentional POPs other than PCDD/PCDF need to be monitored/analysed and inventoried. In addition for some chemicals high levels of PCDD/PCDFs are formed while other UPOPs might not be formed in relevant concentration. This is the case for certain pesticides in particular chlorophenol based pesticides[222] which were responsible for the largest historic PCDD/PCDF contamination with contemporary relevance[223] far exceeding today's total PCDD/PCDF releases[224]. The importance to better monitor UPOPs in chemicals was recently highlighted by a study on PCDD/PCDF releases to water from industrial processes where it was highlighted that the variability of releases for several processes might have resulted from the chemicals used in the processes.[225]

The UPOPs content in the same product from different producers can differ several orders of magnitude due to different processes and due to cleaning steps of a pesticide or pigment in the production. This is reflected in the UNEP toolkit by the range of emission factors with several orders of magnitude for the same

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[217] 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. http://toolkit.pops.int/Publish/Main/I_01_Intro.html

[218] Takasuga T, Takemoria H, Yamamoto T, Higashino K, Sasaki Y, Weber R (2020) Comprehensive monitoring of chlorinated aromatic and heteroaromatic pollutants at sites contaminated by chlorine production processes to inform policy making. Emerging Contaminants 6, 133-142. https://doi.org/10.1016/j.emcon.2020.03.001.

[219] UNEP (2015) Formation and release of UPOPs 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

[220] 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. www.dioxin20xx.org/wp-content/uploads/pdfs/2011/5002.pdf

[221] Zhang L, Yang W, Zhang L, Lib 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.

[222] 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.

[223] Weber R, Gaus C, Tysklind M, et al. (2008) Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. Env Sci Pollut Res Int. 15, 363-393.

Weber R, Herold C, Hollert H, et al. (2018) Reviewing the relevance of dioxin and PCB sources for food from animal origin and the need for their inventory, control and management. Environ Sci Eur. 30:42. https://rdcu.be/bax79

[224] Wang B, Fiedler H, Huang J, et al. (2016) A primary estimate of global PCDD/F release based on the quantity and quality of national economic and social activities. Chemosphere 151, 303-309.

[225] Kawamoto K, Weber R (2021) Dioxin sources to the aquatic environment: Re-assessing dioxins in industrial processes and possible emissions to the aquatic. Emerging Contaminants 7, 52-62. https://doi.org/10.1016/j.emcon.2021.01.002

product/chemical (see UNEP Toolkit Source Group 7 for e.g. 2,4-D, chloranil or triclosan)[226,227]. Therefore for products/chemicals and processes individual monitoring is needed to clarify the emission factor category of a certain chemical if e. Furthermore for a wide range of organochlorine chemicals it is known that they contain PCDD/PCDF but the data were too weak to derive an emission factor for these products yet and therefore they were compiled in Tables in Annex 2 of the UNEP toolkit.[228] Furthermore for most organochlorine products measurements of UPOPs other than PCDD/PCDF are weak. Therefore more monitoring of unintentional POPs in organochlorine chemicals and related products is needed.

Also the manufacturing of products from recycling can lead to increased UPOP contamination in sensitive uses. Two examples are $CuSO_4$[229] and ZnO[230] as feed additives. Also the recycling of PBDE containing plastic is associated with PBDD/PBDFs having similar toxicity as PCDD/PCDFs and were recently documented in high levels in children toys[231].

8.2 (New) listed unintentional POPs in the Stockholm Convention and potentially contaminated products and recycling streams

8.2.1 Unintentional pentachlorobenzene (PeCB) and hexachlorobenzene (HCB)

PeCB (CAS number 608-93-5) has been listed in 2009 under Annex C and Annex A without specific exemptions (decision SC-4/16). HCB (CAS number 118-74-1) was already listed in the initial 12 POP in 2001 under Annex C and Annex A without exemptions. PeCB was used in PCB products, in dyestuff carriers, as a fungicide, a flame retardant and as a chemical intermediate e.g. previously for the production of quintozene. The degradation of quintozene was the largest source of unintentional PeCB in the past.[232]

HCB and PeCB are unintentionally formed in productions of certain chemical in particular high concentrations including certain pigments, tetrachlorophtalate, other chlorobenzenes or chloranil.[233,234,227] HCB and PeCB are also UPOPs in the production of major organochlorine solvents[220,235] (Figure 8-1). Systematic studies on ratio of HCB, PeCB and other UPOPs in products/chemicals and related processes are missing. Depending on the purification process of these chemicals, PeCB and HCB (and other unintentionally POPs) remain in the products or are transferred into production residues or released to the environment.

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[226] UNEP (2013) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs. http://toolkit.pops.int/Publish/Main/II_07_Chemicals.html

[227] 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.

[228] UNEP (2013) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs. http://toolkit.pops.int/Publish/Annexes/A_02_Annex02.html

[229] Wang P, Zhang Q, Lan Y, Xu S, Gao R, Li G, Zhang H, Shang H, Ren D, Zhu C, Li Y, Li X, Jiang G (2014) Dioxins contamination in the feed additive (feed grade cupric sulfate) tied to chlorine industry. Sci Rep. 2014 Aug 7; 4:5975.

[230] Kim MK, Choi S-W, Park J-Y, Kim D-G, Bong Y-H, Jang J-H, Song S-O, Chung G-S, Guerrero P (2009) Dioxin contamination of Chilean pork from zinc oxide in feed. Organohalogen Compounds 71, 173-176.

Kim M, Kim DG, Choi SW, (2011) Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/PCDFs) from a refinery process for zinc oxide used in feed additives: a source of dioxin contamination in Chilean pork. Chemosphere. 82, 1225-1229.

[231] Budin C, Petrlik J, Strakova J, et al. (2020). Detection of high PBDD/Fs levels and dioxin-like activity in toys using a combination of GC-HRMS, rat-based and human-based DR CALUX® reporter gene assays. Chemosphere. 251:126579.

[232] UNEP (2010) Additional consideration of new POPs: pentachlorobenzene. UNEP/POPS/POPRC.6/INF/21.

[233] 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. www.env.go.jp/en/chemi/bat/BAT_first_report1.pdf

[234] 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. www.meti.go.jp/english/report/downloadfiles/BATReport_2nd.pdf

[235] 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.

8.2.2 Unintentional PCNs

PCNs are listed since 2017 in Annex A (see Chapter) and C. PCNs are unintentionally formed in *de novo* synthesis together with PCDD/PCDF and other UPOPs.[236] Therefore PCNs are formed and released in thermal processes together with PCDD/PCDFs.[237,]

High PCN contamination can be formed when naphthalene is present in certain processes with elemental chlorine/chlorination and can contaminate products and wastes. For example PCNs were unintentionally formed in the production of PCBs at concentration of 100 to 900 mg/kg. Also unintentional PCNs are formed in the production of chlorinated paraffins sometimes at several 100 mg/kg[238] and therefore significantly above the low POP content of 10 mg/kg (see case study in Annex 2-G). PCNs are also formed in condensation reactions in the production of chlorinated solvents as by-product at high concentration[221] (Figure 8-1) and are released in by-products/waste, products and the environment from these processes.

For monitoring products containing technical PCN mixtures please see Chapter 5.

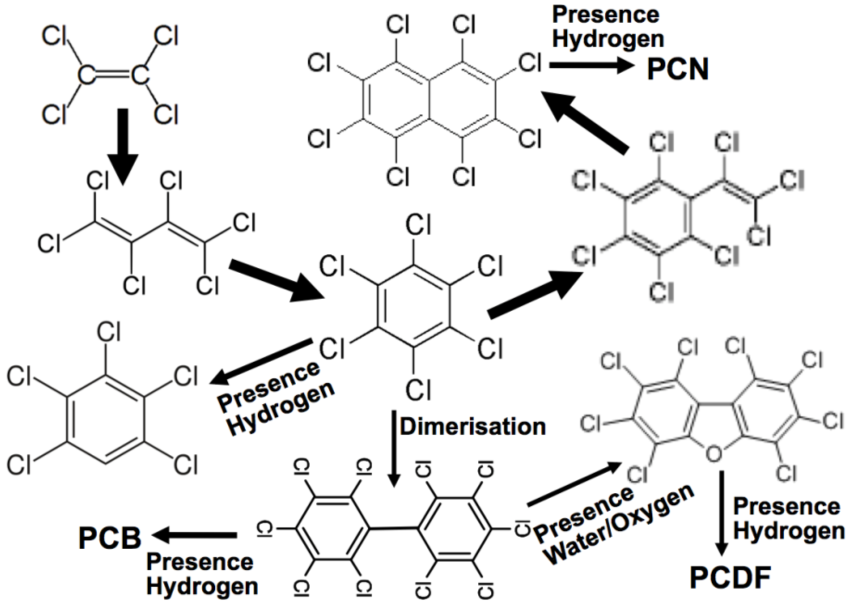

Figure 8-1: Simplified mechanism of formation of unintentionally produced POPs in the production of tetrachloroethylene (similar tetrachloromethane) (note: the presence of hydrogen is inherent e.g. in the production of trichloroethene) (Weber et al. 2011)[220]

8.2.3 Unintentional PCBs

PCBs were listed in the in Annex A and C in the initial POPs. PCBs are unintentionally formed in *de novo* synthesis together with PCDD/PCDF and other UPOPs.[236] Therefore PCBs are formed and released in thermal processes together with PCDD/PCDFs. [239]

For some specific processes high levels PCBs can be specifically formed in certain processes if biphenyl are present in processes where chlorination and can contaminate products or wastes. For example unintentional PCBs can be formed in the production of chlorinated paraffins sometimes above the low POP content[238] (see also case study in Annex 2-G).

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[236] 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: Mechanisms and Correlation to Fluidized Bed Incinerators. Chemosphere 44, 1429-1438

[237] Liu G, Cai Z, Zheng M (2014) Sources of unintentionally produced polychlorinated naphthalenes. Chemosphere. 94:1-12.

[238] Takasuga T, Nakano T, Shibata Y (2012) Unintentional POPs (PCBs, PCBz, PCNs) contamination in articles containing chlorinated paraffins and related impacted chlorinated paraffin products. Dioxin 2012, 26-31. August, Cairns/Australien.

[239] Sakurai T, Weber R, Ueno S, Nishino J, Tanaka M. Relevance of Coplanar-PCBs for TEQ Emission of Fluidized Bed Incineration and Impact of Emission Control Devices. Chemosphere 53, 619-625 (2003).

Also pesticides can contain unintentional PCBs and in Quintozene the TEQ for dioxin-like PCBs were higher than for PCDD/PCDF highlighting that more monitoring for dl-PCBs are needed.[240]

PCBs are also formed in the production of certain pigments when particular PCB precursors are present.[219,241,242] PCBs are also formed during curing of silicone with 2, 4-dichlorobenzoyl peroxide[243] with related indoor exposure to PCB-47, PCB-51 and PCB-68 from sealants[244].

PCBs are also formed in condensation reactions in the production of chlorinated solvents as by-product at high concentration[221] (Figure 8-1) and are released in by-products/waste, products and possibly released into the environment from these processes.

Also PCB (and chlorobromo biphenyls) can be contaminants in inorganic chlorides e.g. $FeCl_3$.[245]

For monitoring products containing technical PCB mixtures please see Chapter 5.

8.2.4 PCDD/PCDFs

PCDDs and PCDFs (also collectively referred to as PCDD/PCDFs) were listed in the initial dirty dozen POPs. They have never been intentionally manufactured for any reason other than laboratory purposes. They are by far the best assessed UPOPs and most information and emission factors in the UNEP Toolkit are compiled for PCDD/PCDFs. For UPOPs in chemicals and products most data have been published for PCDD/PCDFs and where sufficient data for individual chemicals/products were available, emission factors were developed and are compiled in the UNEP Toolkit in Source Group 7[226] e.g. for certain pesticides (e.g. 2,4-D and derivatives, PCP) or pigments (e.g. Phthalocyanine copper; Phthalocyanine green; Blue 106 (CAS 6527-70-4); Violet 23 (CAS 6358-30-1)).[226] Since production routes and processes and the refining of chemicals can be very different in individual companies, the PCDD/PCDF levels can vary several orders of magnitude for the same chemical (see emission factors e.g. for 2,4-D or triclosan) [226]. For the production of chloranil these differences has been described in a study.[227] Also HCl can have orders of magnitude different PCDD/PCDF content depending on the production process.[219,229] Today most HCl is produced as a secondary product of about 40 manufacturing processes often from the organochlorine industry and this result in different PCDD/PCDF (and other UPOP) level and pattern.[219,229] Since some uses of HCl are sensitive for human exposure such as the production of gelatine[246] or vegetable food fat, monitoring of HCl on the market for Dioxin/UPOP contamination and minimizing contamination and exposure is important. Also for the emission from industrial processes the contamination of HCl (or other used chemicals) can play an important role and that such chemicals are monitored to not contribute to emissions from processes to e.g. water.[225]

In certain thermal recycling processes PCDD/PCDF can contaminate inorganic products with relevant human exposure like ZnO[230], $CuCl_2$, or $CuSO_4$[229] used as feed additive. Also for these chemicals the PCDD/PCDF (and other UPOPs content) vary orders of magnitude depending on the thermal process[247], if the chemicals has been refined after the recycling process to reach a “food grade” PCDD/PCDF content or if the chemical were

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[240] Huang J, Gao J, Yu G, Yamazaki N, Deng S, Wang B, Weber R (2015) Unintentional formed PCDDs, PCDFs, and DL-PCBs as impurities in Chinese pentachloronitrobenzene products Env Sci Pollut Res 22, 14462–14470

[241] Anezaki K, Nakano T (2014) Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments. Environ Sci Pollut Res Int. 21, 998-1009.

[242] Anezaki K, Kannan N, Nakano T. (2014) Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments. Environ Sci Pollut Res Int. 22(19), 14478-14488.

[243] Inman W (2016) Post-Curing of Silicone Elastomers: When is it Necessary? Dow Chemical Company. FormNo. 52-1265-01

[244] Herkert NJ, Jahnke JC, Hornbuckle KC. (2018) Emissions of Tetrachlorobiphenyls (PCBs 47, 51, and 68) from Polymer Resin on Kitchen Cabinets as a Non-Aroclor Source to Residential Air. Environ Sci Technol. 52(9), 5154-5160.

[245] Nakano T, Matsumura C, Tsurukawa M., Moriguchi Y (2007) Detection of poly halogenated biphenyls in the FeCl3 manufacturing process. Organohalogen Compounds 69, 2777-2780.

[246] Hoogenboom RLAP, van Eijkeren J, Zeilmaker MJ, et al. (2006) A novel source for dioxins present in recycled fat from gelatin production. Chemosphere 68(5):814-23

[247] Mager K., Meurer U., Wirling J. (2003) Minimizing Dioxin and Furan Emissions during Zinc Dust Recycle by the Waelz Process. JOM 55, 20–25.

produced from primary ores. Therefore such basic chemicals which can be produced from recycling or virgin materials[219] need some UPOP monitoring/supervision in particular when they are used in sensitive applications. Also recycling of plastic containing PBDD/PBDF into toys and other products need monitoring.[231]

8.2.5 Hexachlorobutadiene (HCBD)

HCBD (CAS number 87-68-3; Figure 8-2) has been listed in 2015 under Annex A without specific exemptions (Decision SC-7/12) and 2017 under Annex C as unintentional POP (Decision SC-8/12). HCBD is a halogenated aliphatic substance, mainly generated as a by-product in the manufacture of chlorinated solvents (tri- and tetrachloroethylene and tetrachloromethane) (Figure 8-1) or hexachlorocyclopentadiene..[248,249,250] HCBD was separated from these productions and marketed in high volumes mainly in the 1970s/1980s. HCBD is also generated in the production of hexachlorocyclopentadiene (intermediate of cyclodiene pesticide) and other organochlorine chemicals. Worldwide production was estimated to be about 10,000 tonnes in 1982. Former uses of HCBD are compiled in the SC HCBD inventory guidance. [250] Monitoring data from East Asia suggest that intentional production and/or unintentional generation and release have continued at least until recently and are offered in tonnes scale in the internet.[251]

Basic information on HCBD including chemical and physical properties of HCBD or the former uses of HCBD has been compiled in the SC inventory guidance and POPRC documents.

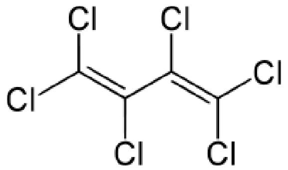

Figure 8-2: Structure of hexachlorobutadiene (HCBD)

8.3 Step by step approach for monitoring UPOPs in products and recycling

To determine the occurrence and quantities of UPOP in different products, processes and materials, the known sources and products and potentially impacted products and recycling processes should be assessed. Depending on the products screened, all UPOPs might be monitored or only specific UPOPs can be analysed. Also for the screening of UPOPs in products a stepwise approach can be applied.

8.3.1 Step 1: Survey of products and recycling streams possibly containing UPOPs

Before collecting samples, a survey should be conducted to preliminarily determine relevant products in current imports, use or recycling/end-of-life that might contain UPOPs.

The UNEP Toolkit has an Annex 2 “Guidance on Identifying Sources of PCDD/PCDF” (http://toolkit.pops.int/Publish/Annexes/A_02_Annex02.html)[228] which can be used as a start for identifying products containing or contaminated with PCDD/PCDFs and other UPOPs.

Basically most organochlorine chemicals might contain some UPOPs at different levels. In particular aromatic products containing chlorine. Products with known PCDD/PCDF contamination are listed in Source Group 7 of the Toolkit[226]. For some of these POPs also PCB or HCB emission factors are established which are compiled in

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[248] BUA (1991) Hexachlorobutadiene. BUA Report 62. German Chemical Society, S. Hirzel Wissenschaftliche Verlagsgesellschaft Stuttgart.

[249] Lecloux A (2004) Hexachlorobutadiene – Sources, environmental fate and risk characterisation Science Dossier for Euro Chlor. October 2004.

[250] Secretariat of the Stockholm Convention (2017) Draft guidance on preparing inventories of hexachlorobutadiene (HCBD). UNEP/POPS/COP.8/INF/18

[251] 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

Annex 48 of the UNEP Toolkit.[252] As can be seen in Annex 48[252], emission factors for only a few products for PCBs, dioxin-like PCB and HCB are established and need more monitoring data. Therefore a priority in selecting samples could be the production or import of listed chemicals and monitoring could be conducted for all UPOPs to conclude on impact factors and risks for UPOPs in these products.

Furthermore, the Toolkit contains in Annex 2 in Tables III.2.1, and Table III.2.2 lists of industrial chemicals and pesticides that are potential new sources of UPOPs for which impact factors have not derived yet (http://toolkit.pops.int/Publish/Annexes/A_02_Annex02.html).[228] If such chemicals are produced or imported into a country they might be sampled and analysed for UPOP content.

Also for the production of chlorinated solvents only one dataset for the whole range of UPOPs is available and more monitoring is necessary for the overall releases and in particular also the products sold on the market.

Also inorganic chemicals known to possibly contain UPOPs are important to monitor in particular if they are used as feed additive or other sensitive uses. Compounds are also compiled in the UNEP Toolkit and in a report of UNEP BAT/BEP group.

8.3.2 Step 2: Sample collection

Samples can be collected by responsible authorities such as factory control at production sites. The major factories are those producing organochlorine compounds such as pesticides, biocides, pigments or selling secondary HCl. The highest priority have aromatic or consumer protection authorities or customs. Sampling campaigns might also be conducted by research institutions possibly in collaboration with the Ministry of Environment or Ministry of Industry or other relevant competent 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 for sampling:####

a) Listed in the UNEP Toolkit in Source Group 7[226], the lists in UNEP Toolkit Annex 2[228] or described in the UNEP Dioxin Toolkit group report[219].
b) CAS numbers of the respective chemicals. CAS numbers are listed in the UNEP Toolkit for chemicals listed in Source Group 7[226] and in the lists in UNEP Toolkit Annex 2[228].
c) Chemical names of the respective chemicals. Chemicals/names are compiled in the UNEP Toolkit in Source Group 7[226] and in the lists in UNEP Toolkit Annex 2[228].
d) Chemical structure – all aromatic chemicals containing a one or more chlorine might be contaminated to some extent with PCDD/PCDF or other UPOPs.

Products, materials and samples compiled in Annex 1-F might be used as a start.

8.3.3 Step 3: Pre-screening of products

A pre-screening of samples for chlorine is often not possible since the products are mostly organochlorine compounds or contain organochlorine compounds. Also the unintentional POP content is often small (low mg/kg or lower) and might be below the detection limit of screening tools like XRF with detection limits for chlorine above 50 mg/kg. This is a too low sensitivity to detect the low POPs content for PeCB, HCB and PCBs (50 mg/kg) or PCNs (10 mg/kg) and certainly not for PCDD/PCDF where detection is needed at µg/kg level or lower.

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[252] UNEP (2013) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs. http://toolkit.pops.int/publish/Main/III_00_Annexes.html

For PCDD/PCDF, PCBs and PCNs (and other dioxin-like compounds), bio-assays that can reliably detect dioxin-like toxicity in products (e.g. CALUX, DRCALUX or EROD)[253].[254] Such screening has been applied to pesticides[255], other organochlorines, feed additives,[254] plastic products such as toys[231] and are used on routine base for food monitoring. A governmental institute in The Netherlands screened industrial processes of the chlorine industries for dioxin-like toxicity[256] which can be recommended for other countries. See case studies Annex 2-G.

A sophisticated screening can be conducted by TOF-MS and has been applied to soils contaminated by the chlorine industry.[218] This might allow a semi-quantitative screening.[218]

For some specific samples like the screening of oils of transformers, heat exchangers and hydraulic equipment for PCBs, PCNs or HCBD, screening test kits for oil such as Clor-N-Oil or Dexsil test or the L2000 PCB/Chloride Analyzer can be used.[257] Samples tested positive for chlorine can be further analysed in laboratory for POPs content.

8.3.4 Step 4: Quantification

Different analytical methods can be applied for the instrumental quantification of unintentional POPs mostly using GC/MS methods (see below). Accredited methods used for commercial analysis is described for PCNs, HCBD and PeCB/HCB in Annex 3-E, 3-F and 3-G. Further methods are referenced in Section 8.5 on international standards and in the listed case studies in Annex 2-F.

8.4 Quantitative (and semi-quantitative) analysis

8.4.1 Analysis of HCBD

Analytical detection of HCBD is typically performed by capillary gas chromatography,[258,259]
As detectors, standard methods use normally either GC-ECD[258] or GC/MS.[258,259]

A standard analysis of HCBD with gas chromatography with electron-capture (GC-ECD) as well as gas chromatography with/mass spectrometer (GC-MS) have been developed for e.g. fish, vegetable, eggs, milk extracts, wastewater and soils (Section 8.5.1).

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

Also GC-FID analysis is used in standard analysis for HCBD in air (Section 8.5.1).

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[253] Behnisch PA, Hosoe K, Sakai S. (2001) Bioanalytical screening methods for dioxins and dioxin-like compounds a review of bioassay/biomarker technology. Environ Int. 27(5):413-439.

[254] Behnisch PA, Gras N, Guerrero P, et al (2010) First surveillance monitoring results of feed/food items from Chile by DR CALUX®. Organohalogen Compounds 72, 1715-1718 http://dioxin20xx.org/wp-content/uploads/pdfs/2010/10-1649.pdf

[255] Huwe JK, Clark GC, Chu AC, Garry V (2003) CALUX and high resolution GC/MS analysis of dioxin-like compounds of chlorphenoxy pesticides. Organohalogen Compd, 60, 227-230. http://dioxin20xx.org/wp-content/uploads/pdfs/2003/03-58.pdf

[256] van Hattum B, Senhorst H, Tukker A, Lamoree M, Sanderson T, de Koning A (2004) Evaluation of current emissions of chlorinated microcontaminants from the Dutch chlorine chain: Final Technical Report. IVM Report E-04/08, Vrije Universiteit, Amsterdam. http://www.ivm.vu.nl/en/Images/OVOC_final_technical_report_tcm234-189202.pdf

[257] UNEP (1999) Guidelines for the Identification of PCBs and Materials Containing PCBs.

[258] USEPA (1984) Method 612: Chlorinated Hydrocarbons
https://www.epa.gov/sites/production/files/2015-10/documents/method_612_1984.pdf

[259] ISO (1997) Water quality - Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods (ISO 10301:1997). https://www.iso.org/standard/18345.html

Organochlorine chemicals or waste from organochlorine production

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 in the assessment of the heavy fraction from chloromethane production. [260]

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

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.[258,259] Also headspace GC/MS can be used.[259] The methods should be able to detect HCBD for regulatory and health guiding values. WHO has establishing a limit for HCBD of 0.6 µg/L considering current TDI.[261] Due to the genotoxic potential of HCBD[262], Switzerland set a drinking water limit of 0.075 µg/l.[263] These limit values could be used for considering a groundwater contaminated in particular if the groundwater is in the vicinity or used as drinking water.

8.4.2 Quantitative instrumental analysis for PeCB and HCB

For PeCB/HCB, the measurement can be performed with low resolution MS or ECD. Conditions for GC/MS are described in Annex 3-G. HCB and PeCB can be measured within the analytical method for POPs pesticides or in a separate analysis of all chlorobenzenes (MonoCBz to HCB.).

8.4.3 Analysis of PCNs

Analysis of PCNs can be performed with low resolution MS or ECD. The instrumental analysis of PCNs is described in Chapter 5.6 and a GC/MS method for PCNs is described in Annex 3-E.

8.5 International standards for UPOPs analysis in products & other matrices

8.5.1 Standards for analysis of HCBD

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

HCBD in water (ISO 10301:1997)[259]

An ISO method has been established to detect HCBD in water.[259]

HCBD in water (USEPA Method 612)[264]

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

HCBD in air (ISO 16000-6:2011)[265]

The ISO method for detect HCBD in indoor air samples HCBD on a Tenax TA sorbent and then analyse it by thermal desorption by either gas chromatography using MS or MS-FID.[265]

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[260] 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.

[261] WHO, HCBD in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.

[262] Brüschweiler BJ, Märki W, Wülser R (2010) In vitro genotoxicity of polychlorinated butadienes (Cl4-Cl6). Mutation Research - Genetic Toxicology and Environmental Mutagenesis 699, 47-54.

[263] Swiss Federal Office of Public Health (2010) Toxikologische Beurteilung von polychlorierten Butadienen im Trinkwasser. Faktenblatt, Bern, 27.4.2010.

[264] USEPA Method 612 https://www.epa.gov/sites/production/files/2015-10/documents/method_612_1984.pdf.

[265] ISO (2011) ISO 16000-6:2011 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

8.5.2 Standards for analysis of PCNs

International standards for analysis of PCNs are listed in Section 5.7 in Chapter 5 on monitoring industrial PCN mixtures in products and waste. A GC-MS method for analysis of PCNs is described in Annex 3-E.

8.5.3 Selected standard for analysis of PCBs in products

PCBs in pigments (ISO 787-28:2019)

General methods of tests for pigments and extenders — Part 28: Determination of total content of polychlorinated biphenyls (PCB) by dissolution, cleanup and GC-MS. This standard specifies a method for determining the total content of PCBs, checking for all 209 possible congeners in pigment materials. This standard is applicable to a working range from1 mg/kg to 150 mg/kg. The lower quantitation limit of this method is 1 mg/kg per congener. Results below 1 mg/kg are considered to be qualitative only.

8.5.4 Selected standards for PCDD/PCDFs

For the PCDD/PCDF analysis different international standards have been developed (e.g. ISO 18073:2004; USEPA Methods 8280B[266] and 8290A[267]; EN 1948-3; HJ-77.3-2008; and JIS K 0311:2005). More details can be found in the Basel Convention guideline.[268]

The USEPA has also published a Method TO-9 for the analysis of PBDD/PBDFs.[269]

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[266] US EPA Method 8280B; https://www.epa.gov/sites/production/files/2015-12/documents/8280b.pdf

[267] US EPA Method 8290A; https://www.epa.gov/sites/production/files/2016-01/documents/sw846method8290a.pdf

[268] UNEP (2015) Technical guidelines on the environmentally sound management of wastes containing or contaminated with unintentionally produced PCDDs, PCDFs, HCB, PCB or PeCB. UNEP/CHW.12/5/Add.4/Rev.1

[269] US EPA method TO-9 https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-9arr.pdf

ANNEX 1 Selected products and recycling streams which might contain industrial POPs or unintentional POPs

Annex 1-A PFOS, PFOA, PFHxS and related compounds in products

PFOS, PFOA, PFHxS and related compounds in production and as products

Recently a review on the use of PFAS in different products and industries which are using PFAS containing products.[270]

PFOS and related compounds are currently still produced in China but with an ongoing phase-out project. Also PFOA and PFHxS and related compounds are still produced and .

Firefighting foams (PFOS, PFOA, PFHxS and related compounds)

Specific firefighting foams (aqueous film forming foams (AFFF)) with PFOS, PFOA or other PFASs are used for extinguishing liquid fuel fires. They are especially used at installations and plants where large quantities of flammable liquids are stored. PFOS, PFOA, PFHxS containing firefighting foams are still on the market. Table A1-1 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.

Firefighting foam is listed as a specific exemption for PFOS and PFOA. Therefore, countries can register for this use, which has to be considered then for monitoring. [271] Firefighting foams can be sampled at import from customs. Additionally, stocks on the firefighting services level would be sampled and analysed.

Table A1-A1: Firefighting services and locations where AFFF foams are mainly used

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

Metal plating industries (PFOS and related compounds)

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 of plastic, and plating with precious metals.

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[270] Glüge J, Scheringer M, Cousins IT, et al. (2020) An overview of the uses of per- and polyfluoroalkyl substances (PFAS). Environ Sci Process Impacts. 22(12), 2345-2373.

[271] 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 use in metal plating in closed loop systems is listed as specific exemption. Therefore, countries can register for this use. This use has to be considered then for monitoring.

The main stakeholders to monitor the import and presence of 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 were listed as specific exemptions but exemption were stopped.

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.

Insect baits and insecticides (PFOS related compound)

A PFOS related compound (sulfluramid/Mirex-S[272]) is used as insecticide against ants, termites, cockroaches, 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 was 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. The authorities could check for sulfluramid containing insecticides at pesticide producers, formulators, and in stores selling pesticides. Samples might be obtained from these stakeholders or purchased on the market.

PFOA and other PFASs in pesticide containers

The USEPA has informed on PFOA (and other PFAS) contamination in fluorinated HDPE containers for pesticides indicates that they are treated inside and outside through fluorination.[273] This process that creates a chemical barrier for a pre-produced container to prevent changes in chemical composition. Using fluorous sealed technology improves container stability, and is intended to make containers less permeable, reactive and dissolvable. Testing was performed by rinsing both the interior and exterior of the container with methanol and analyzing the rinsates using a method modified from the EPA Method 537.1.

Industries where specific exemptions have stopped for PFOS in 2015 but might still be allowed for PFOA or PFHxS (surface treatment of carpet, leather, paper, textile)

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[272] 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

[273] USEPA (2021) Per- and Polyfluoroalkyl Substances (PFAS) in Pesticide Packaging. https://www.epa.gov/pesticides/pfas-packaging

The specific exemption for surface treatment of carpets, leather, paper and textiles expired for PFOS in 2015 and countries cannot register for this exemption. For these uses often alternative PFASs are used including PFOA and PFHxS, listed 2019 and 2021 respectively. 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 should be directly contacted. 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, PFOA, PFHxS and related compounds

A part of PFOS, PFOA, PFHxS and related compounds and other PFASs might enter a country by impregnated products (see *PFOS and related chemicals Inventory Guidance*[2] 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 PFASs (for details on labelling approach see "POPs labelling Guidance" (Stockholm Convention 2017[274])). 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 PFASs, an indication for furniture, carpets, textile, leather, stone or other fabrics that possibly contain PFOS or other PFASs is a "stain resistant" label or advertisement for this property. For paper and paperboards, an indication for possible use of PFOS, PFOA, PFHxS and other PFASs 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, PFOA and related compounds and other PFASs for stain resistance. For details see Section 2.1.3 of "Guidance on BAT and BEP for the use of PFOS and related chemicals". Synthetic carpets contain a wide range of pollutants in the past making the recycling of synthetic carpets a problem.[275]

Textiles and leather

PFOS, PFOA and related compounds including polymers have been used to treat textiles and leather to provide oil and water repellency and soil and stain release properties. For details see Section 2.1.2 of "Guidance on BAT and BEP for the and use of PFOS and related chemicals"

Furniture

PFOS, PFOA and related compounds have been used in particular in textiles and leather on 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"[5]

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[274] Guidance on labelling of products or articles that contain new POPs or use new POPs during manufacture – initial considerations.

[275] Onyshko J, Hewlett R (2018) Toxics in Carpets in the European Union. Report of Anthesis Consulting Group PLC

Impregnated paper/food contact paper

PFOS and other PFASs containing chemicals have been used in food contact paper to provide oil, grease and water repellence (see Table A1A2, 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 seem to have been phased out in European countries, these and other PFOS based chemicals (e.g., SN-diPAPs also called SamPAPs[98,276]) were sold in China, as industrial blends for paper coating purposes). The industrial blends contained considerable amounts of PFOS impurities. Mc Donald's phased out PFOS and PFOA 2008 and will phase out other PFASs (including PFHxS) by 2025.[277]

Table A1-A2: Some categories of food contact paper/packaging possibly using PFOA and related compound or other PFASs 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, PFOA and related chemicals in products and articles with unknown relevance

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 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"[2]. 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[278] is estimated to be approximately 96,000 tonnes and 26,500 tonnes of related production wastes.[279] A large share of the produced PFOS and related chemicals was applied for surface treatment of carpets, textiles, paper, leather, and furniture. PFOA and PFHxS have also been used in these uses and are still used. Therefore, the stock of PFOS, PFOA and PFHxS and related chemicals

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[276] Trier X, Granby K, Christensen JH (2011) Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging, Environ. Sci. Pollut. Res. 18, 1108-1120.

[277] https://corporate.mcdonalds.com/corpmcd/our-purpose-and-impact/our-planet/packaging-and-waste.html/asdf

[278] In 2002, 3M ended PFOS production with more than 95% of the worlds PFOS production capacity.

[279] Paul AG, Jones KC, Sweetman AJ (2009) A First Global Production, Emission, And Environmental Inventory for Perfluorooctane Sulfonate. Environ Sci Technol. 43, 386-392.

in use is large. Therefore, monitoring efforts need also to consider the stocks of articles currently in use. The same articles mentioned in above section “PFOS, PFOA and related chemicals in production and as products” might be considered for the assessment of stocks. An overview on sectors should have been gained in the development of the PFOS/PFOA inventory. Samples might be taken from private households and businesses (e.g., hotel carpets). Also, samples might be purchased on the second-hand market.

Since PFOS and PFOA have been used for more than 50 years the amount of PFOS and PFOA deposited in landfills in these products might have major relevance (in particular when considering the lower use volume today).

Monitoring of PFOS, PFOA and related chemicals in reuse and recycling

Products potentially in recycling or reuse (possibly) treated with PFOS or PFOA and related chemicals are carpets, textiles, paper, leather, or furniture. Carpets with high use share and long service life has likely relevant PFOS, PFOA and PFHxS in the recycling streams. Also textile recycling is likely affected by PFOS and particularly PFOA still use in textiles. Paper is recycled to a high degree in some countries, but due to the rather short use phase, the paper formerly impregnated with PFOS largely before 2002 (when 3M stopped such PFOS use) has largely entered the recycling chain years ago. PFOA and PFHxS might still be used in a range of production and are therefore present longer in recycling.

The main stakeholders to monitor the recycling of PFOS, PFOA or PFHxS 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, PFOA and related chemicals 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, PFOA and other PFAS productions and industrial use) [280,281,282] on agricultural areas have resulted in large scale contaminated sites, e.g. in Germany[282] and the USA (Decatur Alabama)[281] 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.[282]

Therefore, the use and import of biosolids can be a relevant source of PFOS and PFOA. Limit values of 100 µg PFOS+PFOA/kg (0.1 mg/kg) have been set e.g., in Germany by the fertilizer ordinance.[283]

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

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[280] 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.

[281] USEPA (2011) Q&A’s - Perfluorochemical (PFC) Contamination of Biosolids near Decatur, AL Prepared by U.S. Environmental Protection Agency.

[282] Kröfges P, Skutlarek D, Färber H, Baitinger C, Gödeke I, Weber R (2007) PFOS/PFOA Contaminated Mega sites in Germany Polluting the Drinking water Supply of Millions of People. Organohalogen Compounds 69, 877-880.

[283] 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).

sampled directly from sewage treatment plants. PFOS, PFOA, and other PFAS levels in sewage sludge can reveal and direct to point sources.

PFOS and related chemicals in feed, food and drinking water

The monitoring of food, feed and drinking water goes above the scope of this guidance and matrices are not covered by described methodologies but are addressed in the GMP. However, 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.

Annex 1-B: PBDEs and HBB in products and recycling

c-DecaBDE is still produced and used in new products (see exempted uses Table A-1B) and has been the most frequently used PBDE with a total historic production of approx. 1,200,000 t. [284]

The production of c-PentaBDE (containing tetraBDE to heptaBDE) and c-OctaBDE (containing hexaBDE and heptaBDE) has stopped in 2004 with a total production volume of 100,000 t for each technical mixture. Therefore, the monitoring of c-PentaBDE and c-OctaBDE can largely concentrate on products in use, recycling, and end-of-life. Recycling of PBDEs contained in c-PentaBDE and c-OctaBDE is exempted if a country has registered for exemption.[284] However there is no exemption for the recycling of products containing c-DecaBDE.

For c-DecaBDE and 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).[284] Large amounts of EEE and WEEE have been exported from industrial countries with former major use of c-DecaBDE and c-OctaBDE (e.g., Europe, Japan or USA) to developing countries. Furthermore, polymers from recycling of WEEE are partly sent for recycling to developing/transition economies (e.g., China or India). Recent studies have shown that recycled polymers containing PBDEs have been used to produce products for which no flame retardancy is required including, for example, children's toys, kitchen tools, household goods, and video tapes. 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 with a minor use in insulation in construction and textiles. Also, c-DecaBDE has been used in these applications and is still used with exemptions for textiles & insulation foam (Table A-1B).

Therefore, the current use, reuse and recycling of these major material streams need to be monitored and managed. More information on the PBDEs material streams is given below and in the POPRC documents[285], the "PBDEs inventory Guidance documents" [284,286] and "PBDEs BAT/BEP Guidelines" [287] or national studies.[288]

Considering the major uses of c-DecaBDE, c-PentaBDE and c-OctaBDE, the following products and recycling would be assessed (in country and in imports):

PBDEs as chemicals and in chemical products

C-DecaBDE is still produced as flame retardant. The production of c-DecaBDE by bromination of diphenlylether has other PBDEs as intermediates. Therefore c-DecaBDE could possibly contain heptaBDE or hexaBDE as contaminants which are, however, restricted from production. Therefore, c-DecaBDE could be monitored for the restricted PBDEs. Furthermore c-DecaBDE debrominates under various conditions resulting in the formation of other PBDEs.[289]

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[284] UNEP (2015) Guidance for the Inventory of commercial Pentabromodiphenyl ether (c-PentaBDE), commercial Octabromodiphenyl ether (c-OctaBDE) and Hexabromobiphenyls (HBB) under the Stockholm Convention on Persistent Organic Pollutants; Draft. UNEP/POPS/COP.7/INF/27.

[285] UNEP (2010) Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. (UNEP/POPS/POPRC.6/2) and Supporting Document (UNEP/POPS/POPRC.6/INF/6).

[286] UNEP (2019) Preliminary draft guidance on preparing inventories of decabromodiphenyl ether. April 2019. UNEP/POPS/COP.9/INF/18;

[287] UNEP (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.

[288] Swiss Agency for the Environment and Forests (2006) Substance flow analysis - Selected polybrominated flame retardants PBDEs and TBBPA. ENVIRONMENTAL SERIES No. 338.

[289] UNEP (2010) Debromination of brominated flame retardants. 6th POP Reviewing Committee meeting Geneva 11-15. October 2010 (UNEP/POPS/POPRC.6/INF/20).

Although production has officially stopped and is banned under the Convention, some companies still offer c-PentaBDE (CAS 32534-81-9) and c-OctaBDE (32536-52-0) for sale in the public domain. Therefore, illegal trade of these chemicals might still take place.

DecaBDE in manufacturing and in products

c-DecaBDE is still used in a range of manufacturing and in current products and have several exempted uses (Table A1-B). Products with highest priority for assessment are those which are exempted for these uses of c-DecaBDE. These products can be screened on the market in particular if a country has not listed for the exemptions. During manufacturing of products, decaBDE might debrominate to lower PBDEs including heptaBDE and hexaBDE which are not allowed to be used in new products. Furthermore, decaBDE can form polybrominated dibenzofurans and are restricted in some countries.

Table A1-B. Specific exemptions for decabromodiphenyl ether (BDE-209) present in commercial decabromodiphenyl ether (CAS No: 1163-19-5) for production and use

Specific exemptions as allowed for the Parties listed in the Register in accordance with Part IX of this Annex:
• Parts for use in vehicles specified in paragraph 2 of Part IX of this Annex (see Table A2-B)
• Aircraft for which type approval has been applied for before December 2018 and has been received before December 2022 and spare parts for those aircraft*
• Textile products that require anti-flammable characteristics, excluding clothing and toys
• Additives in plastic housings and parts used for heating home appliances, irons, fans, immersion heaters that contain or are in direct contact with electrical parts or are required to comply with fire retardancy standards, at concentrations lower than 10% by weight of the part
• Polyurethane foam for building insulation

*The specific exemptions for spare parts for aircraft for which type approval has been applied for before December 2018 and has been received before December 2022 shall expire at the end of the service life of those aircraft.

Import/production of EEE and second hand EEE and sales in the local market

Today, for some EEE in particular heating appliances, the use of c-DecaBDE is still exempted and might be produced or imported (see Table A-1B). The major amount of c-DecaBDE has been used until approx. 2016 and is still used at lower volumes in some exempted EEE. Therefore decaBDE is present in selected new EEE but mainly in polymers of second hand EEE in imports or on local markets. Relevant EEE categories are Cathode Ray Tube (CRT) housing from TVs and computers, flat screen TVs, and other flame retarded EEE mainly containing decaBDE. Imported used EEE is, in many countries, subjected to assessment of their functionality to avoid illegal import of WEEE.[290] Therefore, customs are already monitoring used electronics. Within this monitoring, screening of bromine for indication of 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.

Import of waste electrical and electronic equipment (WEEE)

The largest amount of PBDEs of c-OctaBDE (used until 2004) is present in WEEE, in particular Cathode Ray Tube (CRT) housing from TVs and computer monitors and office equipment. C-DecaBDE was used in a wide range of electronics and is used until today for exempted uses (Table A1-B). 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.

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[290] 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.

Depending on further treatment of this WEEE and in particular the treatment of the polymer fraction, this PBDE-containing material can cause environmental pollution (e.g., from the practice of open burning) or hazards if recycled into sensitive products (Box A1-B). 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 *PBDEs BAT/BEP Guidelines*[287]). If the polymer is subjected to further recycling, authority would monitor or ask the companies for monitoring data and assure pollutants like PBDEs are separated according to the recommendations of the COP if no exemption for recycling is granted. If the country has asked for exemption of recycling PBDE (2009) containing materials, it should take care that such polymers are not recycled into sensitive uses (see Box A1-B and *PBDEs BAT/BEP Guidelines*[287]).

WEEE plastic for recycling

The polymer fractions from recycling of WEEE are the most relevant recycling material flow possibly containing PBDEs. Mainly ABS plastic but also mixed WEEE plastic fractions might contain PBDEs at different level depending on the source and separation.[291] 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 PBDEs, other RoHS Directive[292] relevant substances.

Products produced from recycled plastic

Currently no regulation exists on the labelling of products produced from recycled polymers. Therefore, these materials can currently only be controlled by analytical screenings. The main stakeholders to monitor the import and presence of PBDE containing products made from recycled polymers are customs and authorities for market surveillance. Industries using recycled polymers from WEEE or transport would monitor for PBDEs and report to the environmental ministry or NIP coordinator on levels of PBDEs.

The products 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. Possible products for a screening are, for example, those listed in the negative list in particular when made from black plastic (see Box A1-B).

Box A1_B: Examples of sensitive use areas* where PBDE-containing recycled plastic should not be used****[287]**

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.

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[291] Straat M, Nilsson C (2018) Decabromodiphenyl ether and other flame retardants in plastic waste destined for recycling, Contract number: 16128142 Swerea IVF Project Report M-973|20182018.02.23.

[292] Directive on the restriction of the use of certain hazardous substances in EEE 2002/95/EC.

Second hand cars, buses, trains, air planes and other vehicles

c-DecaBDE is the major PBDE used in cars until approx. 2016. Additionally, c-PentaBDE has been used in cars primarily in the United States until 2004.[293] Furthermore minor HBCD have been used in vehicles. From total volume, the major use was/is in backcoated textile for fabric such as rear decks, upholstery, headliners, automobile seats, head rests, sun visors, trim panels, carpets.[294] Furthermore depending on the flammability standard also PUR foam can be flame retarded in cars in particular cars produced in the US[295,296] (see case studies in Annex 2B). Furthermore, a range of small plastic parts of the powertrain like cables and electrical connectors can contain decaBDE (See Table A2-B).

Table A2-B: Specific exemptions for decaBDE parts for use in vehicles

Specific exemption	Application
(a) Parts for use in legacy vehicles, defined as vehicles that have ceased mass production, and with such parts falling into one or more of the following categories:	(i) Powertrain and under-hood applications such as battery mass wires, battery interconnection wires, mobile air-conditioning (MAC) pipes, powertrains, exhaust manifold bushings, under-hood insulation, wiring and harness under hood (engine wiring, etc.), speed sensors, hoses, fan modules and knock sensors; (ii) Fuel system applications such as fuel hoses, fuel tanks and fuel tanks under body; (iii) Pyrotechnical devices and applications affected by pyrotechnical devices such as air bag ignition cables, seat covers/fabrics (only if airbag relevant) and airbags (front and side); (iv) Suspension and interior applications such as trim components, acoustic material and seat belts.
(b) Parts in vehicles specified in paragraphs (a) (i)–(iv) above and those falling into one or more of the following categories:	(i) Reinforced plastics (instrument panels and interior trim) (ii) Under the hood or dash (terminal/fuse blocks, higher-amperage wires and cable jacketing (spark plug wires)); (iii) Electric and electronic equipment (battery cases and battery trays, engine control electrical connectors, components of radio disks, navigation satellite systems, global positioning systems and computer systems); (iv) **Fabric such as rear decks, upholstery, headliners, automobile seats, head rests, sun visors, trim panels, carpets**.

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.

Depending on the phase-out of PBDEs mixtures in the different regions, vehicles produced within a region can be regarded as potentially impacted:

- For all regions DecaBDE has been used until recently.
- For c-PentaBDE (having a high toxicity and exposure potential) and c-OctaBDE
    - In the US: c-PentaBDE have been produced/used until 2004;
    - In Europe: c-PentaBDE have been phase out in 1990s;

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[293] Alcock R.E, Sweetman A.J, Prevedouros K, Jones, K.C. 2003. Understanding levels and trends of BDE-47 in the UK and North America: an assessment of principal reservoirs and source inputs. Environment International 29, 691-698.

[294] 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.Kajiwara

[295] Liu, H.; Yano, J.;Kajiwara, N.; Sakai, S. (2019) Dynamic stock, flow, and emissions of brominated flame retardants for vehicles in Japan. Journal of Cleaner Production, 232: 910-924.

[296] Leslie HA, Leonards PEG, Brandsma SH, Jonkers N () POP STREAM POP-BDE waste streams in the Netherlands: analysis and inventory. A joint IVM-IVAM report. Report R13-16, 17 December 2013

- In Japan: c-PentaBDE stopped 1991 and c-OctaBDE stopped 1995;
- In China: c-PentaBDE has been produced and used until approx. 2004.

Vehicles produced until these dates in these countries/regions can contain the respective PBDEs. Therefore, PBDEs are imported to developing countries with second-hand vehicles containing such treated polymers. Furthermore, other toxic flame retardants have been used such as

Currently there are no data on which producers have used 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 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.

HBB in vehicles (and other products)

Since production and use of HBB stopped in 1976 with only 5400 t produced in the United States, HBB monitoring is not considered relevant. Products which could be flame retarded with HBB are cars and electronics produced in the United States from 1970 to 1976. In particular cars from this time might still be in use or in sale as vintage cars.

Furniture and mattresses containing flexible PUR foam

The use of c-PentaBDE or c-DecaBDE (and other flame retardants) in furniture depends on the flammability standard of a country.[297,298] Due to flammability stands for furniture in the US and UK in particular furniture in North America and UK are often flame retarded including the PUR foam. Therefore, furniture in these region/countries may contain c-PentaBDE (if produced before 2005), c-DecaBDE or other flame retardants. In 2014, the Californian flammability standard TB 117 (now known as TB 117-2013) was updated, eliminating the open flame test and giving manufacturers the option of smoulder-resistant cover fabrics or smoulder-resistant barriers beneath the cover fabrics and need to be labelled if including flame retardants.

Second hand furniture exported from North America or UK for re-use to other regions need to be considered as a possible source for PBDE import to 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 PBDEs BAT/BEP Guidelines). Samples can be taken from mattresses which in field screenings were bromine positive.

These applications can be screened and analysed in end-of-life phase for promoting ESM of waste and for protection of recycling.

Flexible PUR foam in other applications

Also, other PUR-foam applications have partly been treated with c-PentaBDE, c-DecaBDE or other FRs in the past such as various baby products or PUR foam in gymnast training.[299,300]

Rigid PUR foam in construction and other polymers in construction

c-PentaBDE and c-DecaBDE were also used in rigid PUR foam in construction insulation and sealants. c-DecaBDE is still exempted for these uses. Therefore, PUR foams in construction might contain PBDEs. These

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[297] Shaw SD, Blum A, Weber R, et al. (2010) Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks? Reviews on Environmental Health 25(4) 261-305.

[298] Charbonnet J, Weber R, Blum A (2020) Flammability standards for furniture, building insulation and electronics: Benefit and risk. Emerging Contaminants 6, 432-441, https://doi.org/10.1016/j.emcon.2020.05.002

[299] Stapleton HM, Klosterhaus S, Keller A, et al. (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. Environ. Sci. Technol. 45, 5323–5331.

[300] Ceballos DM, Broadwater K, Page E, Croteau G, La Guardia MJ. (2018) Occupational exposure to polybrominated diphenyl ethers (PBDEs) and other flame retardant foam additives at gymnastics studios: Before, during and after the replacement of pit foam with PBDE-free foams. Environ Int. 116, 1-9.

applications can be screened in the end-of-life or use phase. Furthermore, c-DecaBDE has been used in a range of other polymers in construction such as foils and rubber. SCCPs are also used in PUR foam applications and in other polymers in construction (Annex 1-F).

PUR foam for recycling

PUR foam from end-of-life products (furniture, mattresses, ELVs) might be gathered for recycling purposes. Such PUR foam might be recycling in the country, exported or imported from other countries. These might be screened for bromine to evaluate potential contamination.

Articles produced from recycled PUR foam

PUR foam recyclates might be used in different new products which might be screened/analysed:

Carpet rebond: Large scale recycling of PUR foam into carpet padding/rebond is currently practised in the US and Canada (see SC PBDEs BAT/BEP Guidance).[301] Since c-PentaBDE is not intentionally added anymore, the quantity of residual pentaBDE in Canada in rebond carpet cushion is in decline.[302] The extent of this recycling activity for other regions is unknown but appears to be limited.[301] If carpet rebond is imported from this region, it might contain PBDEs. Relevant exposure of workers in PUR recycling and carpet installers has been demonstrated in a first study from the US[303] 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[304]

Regrinding: PUR foam is partly grinded to ultrafine powder and added to the virgin material in the manufacture of new foams. If PBDE-containing PUR foam is used then also new PUR foam can become polluted.

Textiles and recycling of textiles

c-PentaBDE and c-DecaBDE has been used[305] in for the treatment of textiles for uses including back-coating (vehicles and furniture), for curtains and for functional textiles such as tents. Functional textiles might be screened for their bromine content and possibly analysed. If textile fibres are recycled the recyclates can also be screened for bromine and possibly analysed.

Rubber products and recycling of rubber

DecaBDE and before PentaBDE has also been used in rubber for e.g., conveyor belts and other uses. If a country has larger use of rubber conveyor belts also these could be monitored. Also, SCCPs and PCNs were used as additives in rubber and can be included in the assessment.

PBDEs in biosolids, sewage sludge and industrial 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, regulatory limits exist for POPs in sewage sludge and/or biosolids (e.g., PCBs, PCDD/PCDF or PFOS). Also, PBDEs are detected in sewage sludge/biosolids. PBDE contaminated biosolids and sewage sludge might originate from wastewater treatment plants related to

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[301] UNEP (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.

[302] 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.

[303] Stapleton HM, Sjödin S, Jones RS, 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.

[304] UNEP (2010) Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. (UNEP/POPS/POPRC.6/2) and Supporting Document (UNEP/POPS/POPRC.6/INF/6).

[305] C-DecaBDE are still used in the impregnation of textiles.

(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 products are shortly mentioned here. Food and feed can in particular be contaminated with PBDEs in connection with contaminated sites of former 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 sludge or bio-solids have been applied or landfill where PBDE containing materials has been disposed. If a country decides to include feed and food into the monitoring of PBDE containing products then the development of the monitoring concept would best be linked to the development of the inventory of PBDE contaminated sites. A first priority selection of samples can be done based on the findings of the PBDEs contaminated site inventory.

Annex 1-C: HBCD in products and recycling

The major uses of HBCD are described in the HBCD inventory guidance.[306] 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 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 (α-HBCD); 134237-51-7 (β-HBCD); 134237-52-8 (γ-HBCD)). The stop of production in China is terminated for 12/2021; SC Article 25(4) Parties which have not ratified HBCD might continue or start production of HBCD. Chemicals imported or used for flame retarding materials (in particular polystyrene and textiles) could be assessed for HBCD content if the chemical identity is unclear.

HBCD in new polystyrene products 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 production/use exempted under the SC. 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 or certain EPS/XPS applications in construction flame retardants might be used. Some developing countries might not have flammability standards at all. For an overview of the use and presence of HBCD in construction, different EPS and XPS application should be screened in particular if the use of HBCD is unclear in the country. The largest share of HBCD have been used in the past 40 years and is present in insulation in construction and will need management when buildings are demolished or renovated. For the assessment of HBCD in demolition and renovation a screening test has been developed (see also case study in Annex 2-C)[307].

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 EPS packaging in UK and Ireland[308] and food packaging in Korea.[309] HBCD has also been detected in EPS buoy used at fish/muscle farming with associated contamination.[310] 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

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[306] Secretariat of the Stockholm Convention (2015) Guidance for the inventory, identification and substitution of Hexabromocyclododecane (HBCD) (Draft April 2015).

[307] 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

[308] Abdallah MA, Sharkey M, Berresheim H, Harrad S (2018) Hexabromocyclododecane in polystyrene packaging: A downside of recycling? Chemosphere 199, 612-616.

[309] 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.

[310] 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.

The second most important application of HBCD has been in polymer dispersion on cotton or cotton mixed with synthetic blends and synthetic textiles similarly to PBDEs. 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), tents and automobile interior textiles. Therefore, monitoring of HBCD and PBDEs in textile would address such potentially flame retarded textile applications.

HBCD in cars and other vehicles

HBCD has been applied in vehicles in textiles and other synthetic materials such as carpets and floor mats but at lower volumes compared to PBDEs.[311] An screening of car interior has revealed possibly impacted parts and materials.[312] 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 binder 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 should be conducted for polystyrene materials (EPS, XPS and HIPS) used for recycling. The materials can be assessed by screening approach (XRF) combined with confirmation analysis (see Chapter 4). Also, products and recyclates made from recycled EPS/XPS or HIPS. E.g., the assessment of EPS packaging[308,309] and EPS buoy[310] 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.[313] 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 fractions from WEEE for recycling from import or generated in the country could be monitored for HBCD.

HBCD in biosolids, sewage sludge and industrial sludge

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.

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[311] Liu, H.; Yano, J.;Kajiwara, N.; Sakai, S. (2019) Dynamic stock, flow, and emissions of brominated flame retardants for vehicles in Japan. Journal of Cleaner Production, 232: 910-924

[312] 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.

[313] UNEP. (2010). Risk profile on hexabromocyclododecane. UNEP/POPS/POPRC.6/13/Add.2.

Annex 1-D: PCP and its salts and esters in products and recycling

The major uses of PCP and its salts and esters are described in the PCP inventory guidance.[314] 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 PCDD/PCDFs the monitoring for PCP should integrate analysis for PCDD/PCDF as appropriate.

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.[314]

Technical products from Mexico include Dura-Treat 40 Wood Preserver [315] Penta OL Penta Blocks[316]

The production of PCP result in highly PCDD/PCDF contaminated residues.[317] Production residues and landfill leachates where production residues have been disposed can be sampled and analysed for PCP and PCDD/PCDFs.

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.[314]

PCP is currently used in Canada, Mexico and US for utility poles. In India Na-PCP is only allowed as wood preservation purposes-impregnated wood and particle boards.

If the PCP and PCDD/PCDF contamination of the Indian food starch guar gum[318] was a result from treated wood or direct fungicide application could not be clarified.

Since treated wood used the last 70 years in construction/building can have a long service life, these PCP stocks in all world regions are major stocks and PCP and PCDD/PCDF with associated exposure and contamination sources. See detailed case studies in Annex 2-D.

Waste wood reuse and recycling

Waste wood is reused and recycled in a range of products. The reuse of PCP treated wood in children playgrounds, new buildings, gardens and farms might result in human exposure. The recycling of PCP treated wood should be monitored and assessed/monitored and controlled in products produced from recycled wood (e.g. particle boards).

The recycling of PCP treated waste wood into bedding in stables has resulted in PCDD/PCDF and PCP exposure of chicken and resulting PCDD/F contamination in eggs.[319]

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[314] UNEP (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.

[315] KMG (2015) Dura-Treat 40 Wood Preserver. Safety Data Sheet.

[316] KMG (2016) Penta OL Penta Blocks. Safety Data Sheet.

[317] 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

[318] CVUA Freiburg (2007a) Correlation between pentachlorophenol (PCP) and dioxins in contaminated guar gum from India. http://www.cvua-freiburg.de/pdf/dioxine/guar_gum_correlation_270807.pdf

[319] Brambilla G, Fochi I, De Filippis SP, Iacovella N, di Domenico A (2009) Pentachlorophenol and PCDD/PCDF in eggs from hens exposed to contaminated wood shavings. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 26, 258-264.

PCP in leather

PC was used as major preserve in leather treatment. In some countries, PCP might still be used in leather treatment. Leather products produced from 1950s to 1990s have a higher probability to contain PCP and related PCDD/PCDFs. Monitoring can be conducted with assessment of other POPs used in leather (SCCPs, PFOS, PFOA).

Leather is recycled to some extent and PCP (and other POPs) containing leather might impact recycling and should be assessed in this respect.

PCP in textiles

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. The major use was 1950s to 1990s. Assessment can be conducted with other POPs used in textiles (HBCD, PBDEs, PFOS, PFOA). Recycling of textiles might be monitored for PCP and other POPs.

PCP in artwork

PCP and other POP pesticides have been used to treat art work in museum including wood and textiles from 1950s to 1980s.

PCP and related PCDD/PCDF 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.[320,321] In recent years the impact of PCP on sewage sludge has considerably reduced.[320] However countries which are still producing PCP (e.g. India and Mexico) and using PCP (e.g. Canada, India, Mexico, USA) might still have current elevated releases and associated contamination in particular at production sites, formulation sites and the wood treatment sites and associated industrial sludges.

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. Sewage Sludge and related biosolids impacted from runoff from PCP treated agricultural soils[322] or from wood treatment sites[323] might still be contaminated with PCP and PCDD/PCDF.

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[320] 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.

[321] 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.

[322] Yao Y, Masunaga S, Takada H, Nakanishi J. (2002) Identification of polychlorinated dibenzo-p-dioxin, dibenzofuran, and coplanar PCB sources in Tokyo Bay, Japan. Environ Toxicol Chem. 21:991-8.

[323] Aberg A, Tysklind M, Nilsson T et al. (2010) Exposure assessment at a PCDD/F contaminated site in Sweden—field measurements of exposure media and blood serum analysis. Environ Sci Pollut Res 17, 26–39.

Annex 1-E: PCNs (and PCBs) in products and recycling

Details on former production and uses of PCNs are described in the PCN inventory guidance.[324] PCNs were mainly produced and used from 1930 to 1970s with the stop of production for the use in products and articles around 2000. **PCNs were used in most of the uses of PCBs and therefore should be monitored together. SCCPs (Chapter 6 and Annex 1-F) and other CPs have substituted PCNs and PCBs in the major open applications and therefore this three POPs would best be monitored together as appropriate.**

Furthermore, PCNs (and PCBs) are unintentionally produced in certain organochlorine production and in thermal processes and for these sources can be monitored within the screening for UPOPs contamination in chemicals and other products (Chapter 8 and Annex 1-G).

PCNs as chemical in chemical products 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 (PFNs), 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/PFN production and former PCN productions could be analysed for PCN content and contamination including waste disposed in landfills of such productions.

PCNs (and PCBs) in transformers and condensers

A major use of PCNs was in capacitors, particularly in the impregnated paper, since the 1930s.[325] 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.[324] Therefore capacitors produced from 1930 and 1980 can be monitored for PCNs together 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. Therefore pure PCN transformers might not exist or can be considered small. However, PCNs are unintentional by-products in all PCB transformer oils since commercial PCBs contained traces of PCNs (0.01–0.09% of PCB content).[324]

PCNs (and PCBs and SCCPs) in hydraulic oils

PCNs (and PCBs) have been used in hydraulic fluids in the mining sector at least until 1989.[326] Also SCCPs might be used as hydraulic oils.

PCNs (and PCBs and SCCPs) in paints and coatings

PCNs have been used in lacquers and underwater paints and as raw materials for dyes until 1980s[325,327] PCNs has most likely been used similarly to PCBs and SCCPs in paints and coatings as corrosion protection for metal constructions such as bridges, towers, ships, pressure pipes, water sluices, electricity poles, transformers, tanks

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[324] UNEP (2017) Draft guidance on preparing inventories of polychlorinated naphthalenes (PCNs). Draft March 2017. UNEP/POPS/COP.8/INF/19

[325] 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.

[326] 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.

[327] IPCS (2001) Chlorinated Naphthalenes. Concise International Chemical Assessment Document 34 World Health Organization. Geneva, 2001. ISBN 92-4-153034-0.

(outdoor and indoor) and machinery[328,329,330,331,332]. For PCBs it has been described that such additives were mainly used in chloroprene paints and chloroprene lacquers as well as in PVC copolymers.[333] 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%.[333]

Since PCNs, PCBs and SCCPs are used in the same open applications in paints in constructions and equipment, these should be addressed together in the inventory of such applications.

PCNs (and PCBs and SCCPs) in polymers (cables)

The use of PCNs as flame retardants in cables and cable sheaths was a major use of PCNs.[325] Other POPs (PCBs, SCCPs and 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 SCCPs/PBDEs (used since the 1970s) are partly still in use. When screening PCNs in cables, also PCBs, SCCPs and PBDEs could be measured.

PCNs (and PCBs and SCCPs) in sealants

The use of PCNs in sealants and putty has been reported until around 2000.[334] For PCBs, sealants/ caulks and putty in buildings and other constructions have been major open applications[335,332] 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, SCCPs and potentially PCNs are polyurethane, acrylic and butyl sealants. PCBs, PCNs and SCCPs 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% PCBs.[336]

PCNs (and PCBs and SCPPs) in rubber

PCNs have been used in chloroprene rubber until around 2000.[334,337] Such chloroprene rubber has been used in rubber belts, rubber belts for printers and shock absorbing materials.

PCNs and other POPs in treated wood

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[328] Eklund B, Eklund D (2014) Pleasure Boatyard Soils are Often Highly Contaminated. Environ. Management 53, 930–946.

[329] 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.

[330] PCB Elimination Network (2014) PCB Open Application - Identification and Environmentally Sound Management.

[331] 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.

[332] 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

[333] BUWAL (2000) Praxishilfe. PCB-Emissionen beim Korrosionsschutz, Schweizer Bundesamt für Umwelt, Wald & Landschaft,

[334] 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.

[335] USEPA (2015) PCBs in Building Materials—Questions & Answers. July 28, 2015.

[336] Priha E, Hellman S, Sorvari J (2005) PCB contamination from polysulphide sealants in residential areas-exposure and risk assessment. Chemosphere 59, 537-543.

[337] 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.

PCNs have been used as wood preservatives in the past. Higher chlorinated (and toxic) PCN mixtures were used in the 1920s to 1970s while lower chlorinated naphthalenes were used until 1987.[325] 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[338] and inert artillery and mortar projectiles with associated pollution on military training sites.[339,340 ,341]

Former PCN uses not consider 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.[342] High levels of unintentional POPs like HCB and PCNs are formed in the production of chlorinated solvents such as tetrachloroethylene, trichloroethylene and ethylene dichloride.[343,344,345] 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.[342,344]

Unintentional PCNs in commercial chlorinated paraffin products

Chlorinated paraffins are produced by chlorination of C_{10}–C_{30} 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.[346]

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[338] Generalstab Schweizer Armee (1945) Bericht des Chefs des Generalstabes der Armee an den Oberbefehlshaber der Armee über den Aktivdienst 1939-1945. Pp 322-326.

[339] 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.

[340] 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.

[341] Falandysz J (1998) Polychlorinated naphthalenes: an environmental update. Environ Pollut 101, 77–90

[342] 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

[343] 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).

[344] 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.

[345] 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

[346] Takasuga T, Nakano T, Shibata Y (2012) Unintentional POPs (PCBs, PCBz, PCNs) contamination in articles containing chlorinated paraffins and related impacted chlorinated paraffin products. Dioxin 2012, 26-31. August, Cairns/Australien.

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 PCDFs.

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.[347,348] 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[349] and similar levels in fly ash.[347]

PCNs in waste fractions

Since PCNs have been produced and used between 1920 to approx. 2000, most products 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.[350]

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 A-1E.

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[347] Imagawa T, Lee CW (2001) Correlation of polychlorinated naphthalenes with polychlorinated dibenzofurans formed from waste incineration. Chemosphere. 44(6), 1511-1520.

[348] 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.

[349] 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.

[350] 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.

Annex 1-F: SCCPs and other CPs containing SCCPs as products and as additives in products

The major uses of SCCPs are described in the SCCP inventory guidance.[351] If new uses would be discovered then they can be reported to the BRS Secretariat that they can be considered in the update of guidance documents.

SCCPs as chemical product and SCCPs in other CP mixtures

SCCPs and other CP mixtures containing SCCPs are currently still produced. Most of the SCCP major applications are exempted by the Stockholm Convention and therefore SCCP production can continue. **The main challenge and larger amount are CP mixtures that contain >1% SCCPs and are also considered POPs** (but it is possible to produce MCCPs with <1% SCCPs, as required by the SC to not meet the POP criteria).[352]

CAS numbers synonyms and tradenames of SCCP and other CPs potentially containing SCCPs are listed below which can be used to trace CP mixtures for assessing SCCP content.

The following Chemical Abstract Service (CAS) numbers are used for CPs which might contain SCCPs[351]

CAS numbers indicative for SCCPs:

- 85535-84-8 (Alkanes C10-C13, chloro); • 71011-12-6 (Alkanes, C12-13, chloro);
- 85536-22-7 (Alkanes, C12-14, chloro); • 85681-73-8 (Alkanes, C10-14, chloro);
- 108171-26-2 (Alkanes, C10-12, chloro); • 68920-70-7 (Alkanes, C6-18, chloro);
- 84082-38-2 (Alkanes, C10-21, chloro); • 97659-46-6 (Alkanes, C10-26, chloro);
- 84776-06-7 (Alkanes, C10-32, chloro).

CAS numbers without defined chain length which might contain SCCP>1%:

- 61788-76-9 (Alkanes, chloro);
- 63449-39-8 (Paraffin waxes and hydrocarbon waxes, chloro);
- 97553-43-0 Paraffins, normal C>10, chloro)

CAS numbers of MCCPs and LCCPs which might be contaminated with SCCP>1%:

- 85535-85-9 Alkanes, C14-17, chloro (MCCPs)
- CAS 63449-39-8; Paraffin waxes (C18 and longer), chloro (LCCPs)

SCCP Synonyms (Some synonyms are general in nature, but might guide to CPs contaminated by SCCPs >1%)**:**

Alkanes, chlorinated; alkanes (C10-13), chloro (60%); alkanes (C10-13), chloro (50-70%); chlorinated alkanes; chlorinated alkanes, chlorinated paraffins; chloroalkanes; chlorocarbons; paraffin, chlorinated; paraffins, chloro; paroils, chlorinated; polychlorinated alkanes; polychloroalkanes.

Tradenames for CPs, potentially containing SCCPs[351]

The following generic trade names are usually accompanied by a suffix indicating a specific product (IARC, 1990): A 70; A 70 (wax); Adekacizer E; Arubren; Cereclor; Chlorinated paraffins (CPs); Chlorcosane; Chlorez; Chlorofin; Chloroflo; Chlorparaffin; Chlorowax, Chlorowax 500AO; Chlorowax 45AO, Chlorowax 52AO; Cloparin; Cloparol; Clorafin; CP F; CW; Diablo; Derminolfett; Derminolöl; EDC-tar; Electrofine; Enpara; FL X; Hordaflam; Hordaflex; Hordalub; Hulz; KhP; Meflex; Monocizer; Paroil; Poliks; Tenekil; Toyoparax; Unichlor.

SCCPs in lubricants and metal working fluids

According to the Stockholm Convention exemptions, SCCPs can be still used as additives in lubricants, in particular for engines of automobiles, electric generators and wind power facilities, and for drilling in oil and

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[351] UNEP (United Nations Environment Programme) (2019). Detailed Guidance on Preparing Inventories of Short-Chain Chlorinated Paraffins (SCCPs), Draft of 2019.

[352] Guida Y, Capella R, Weber R. (2020) Chlorinated paraffins in the technosphere: A review of information and data gaps demonstrating the need to support Stockholm Conv. implementation. Emerg. Contam. 6, 143–154.

gas exploration and petroleum refining to produce diesel oil. The SCCP/CP content in lubricants can reach up to 70% of the product weight. Lubricant oils are generally used as engine oils, transmission oils, gear oils and coolant oils. Open applications of lubricants can lead to higher releases of SCCPs into the environment than lubricant use in closed systems with sound waste management. Another problematic application of SCCP/CP-based lubricants are in the machinery used in the food & beverage sector, where the contamination of these products can lead to a direct human exposure through ingestion.[351]

Metal working fluids (MWF) are also industrial lubricants for manufacturing of metal parts (e.g., cutting, grinding, forming). Due to the specific listing of MWF in the exemptions and the specific use of CPs they are specifically addressed here:

Metalworking fluids are liquids, which are supplied to a manufacturing process of a metal in a way that allows for increased productivity based on lubricating and cooling effects. By their lubricating and cooling properties. Liquids which are included in the term MWFs have been classified based on different criteria. According to DIN 51385, MWFs are classified following their composition as oil-based or water-based MWFs. They can also be categorized according to the manufacturing process as cutting fluid, grinding oil or forming oil.[351]

Major applications of lubricants that might contain CP mixtures containing SCCPs are[351]:

- Metalworking fluids; Coolant oils; Engine oils; Transmission oils; and Gear oils.

Major sectors that might use SCCP/CP-based lubricants are:

- Industrial machinery; Industrial automotive; passenger automotive;
- Power generation;
- Drilling in oil and gas exploration; other rock drilling and petroleum refinery.

Screening of lubricants with XRF could guide to CP mixture.

Lubricant and MWF recycling and reuse

Waste lubricants might in particularly be reused in developing countries in external lubrication of gears and metals.

SCCPs in PVC

According to the Stockholm Convention exemptions, SCCPs can be still used as secondary plasticizers in flexible PVC, except in toys and children's products. SCCP application as secondary plasticizers is a major use of SCCPs and other CP mixtures containing SCCPs. In PVC primary plasticizers (phthalates or phosphate esters) are used to increase softness and elongation properties of polymers. Secondary plasticizers are generally used in combination with primary plasticizers to enhance the plasticizing effect, thus, they are also called extenders. The SCCP/CP content in PVC can reach up to approx. 10% of the product weight. Major products and applications of PVC that might contain SCCPs or other CP mixtures containing SCCPs are e.g.:

- General soft PVC; PVC pellets (masterbatch);
- Toys; inflatable products;
- Artificial leather;
- Sport equipment; Yoga/exercise mats; stickers; flip flops;
- Cables and cords; Electrical cable sheathing;
- Conveyor belts;
- Flooring; roofing and roof cladding; Plumbing;
- Products or tubes for outdoor decoration bulbs;
- Signage; and Phonograph records.

PVC recycling and waste management

Currently, in many countries PVC waste is mostly burned or landfilled. However, PVC is recycled to some extent according to the country and the purity and volume of PVC waste. It is important to highlight that the recycling of SCCP-containing products is not exempted in the Stockholm Convention. Therefore, the content of SCCPs must be assessed in PVC products to prevent that such products containing SCCPs are dumped or burned in the open sky or even recycled, resulting in releases to the environment and human exposure. Moreover, PVC can contain other hazardous chemicals including POPs (PCBs, PCNs) or heavy metals (lead, cadmium). PVC may also contain problematic softeners such as DEHP (Diethylhexyl phthalate). BBP (Benzyl butyl phthalate), DBP (Dibutyl phthalate), DIDP (diisodecyl phthalate), DINP (diisononyl phthalate), or DNOP (di-n-octyl phthalate) which are regulated in some regions and are prohibited e.g., in the EU in toys or medical devises.[353]

SCCPs in rubber

According to the Stockholm Convention exemptions, SCCPs can be still used as additives in the natural and synthetic rubber industry, in the production of transmission belts and also spare parts of rubber conveyor belts in the mining and forestry industries. SCCPs are added to rubber products as flame retardants and/or plasticizers. The SCCP/CP content in rubber products can reach up to 17% of the product weight. It is expected that SCCPs or CP mixtures containing SCCPs are mainly applied in elastomers of poor flame resistance, such as natural rubber (NR), styrene and butadiene rubber (SBR), polybutadiene rubber (BR), acrylonitrile and butadiene rubber (NBR), butadiene or isoprene rubber (IR) and ethylene propylene diene monomer (EPDM), when they are required to meet flammability standards (e.g., conveyor belts – ISO 340:2013). However, chlorobutadiene rubber (CR – or chloroprene, also known as neoprene) has inherent flame resistance – like PVC for which CPs are used as secondary plasticizer – but it may also take SCCP/CP additives when used mining conveyor belt compounding

The use of SCCPs and other flame retardants in rubber applications depends on the individual uses and the related safety and in particular flammability standards. Major products and applications of rubber that might contain SCCPs or other CP mixtures containing SCCPs are:

- Fire resistant rubber products; Rubber cables; and
- Rubber conveyor belts; Rubber transmission belts;
- Industrial roller coverings; Industrial sheeting;
- Rubber in sealants in buildings and pipe seals;
- Rubber applications in the transport sector (cars, busses, trains, airplanes);
- Rubber carpets (mainly automotive) and flooring; Shoe soles;

An overall assessment SCCP use in rubber products might be conducted considering that companies might have difficulties to distinguish exempted and not-exempted uses in the rubber industry and that CPs mixtures not listed are added to rubber products as flame retardants (e.g. non-specified CPs) that might contain >1% of SCCPs.

Please note: For rubber tires normally no flame retardants are added and therefore tyre production is not considered as a use of SCCPs. However, SCCPs were detected in a first assessment of car tires recyclates, such as rubber granulates and playground tiles, in the Netherlands at low levels <50 mg/kg.[354]

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[353] Weber R, Fantke P, Ben Hamouda A, Mahjoub B (2018) 20 Case Studies on How to prevent the use of toxic chemicals frequently found in the Mediterranean Region. Report of the Regional Activity Centre for Sustainable Consumption and Production (SCP/RAC) an EU SwitchMed

[354] Brandsma SH, Brits M, Groenewoud QR, van Velzen MJM, Leonards PEG, de Boer J. 2019. Chlorinated Paraffins in Car Tires Recycled to Rubber Granulates and Playground Tiles. Environ Sci Technol. 53:7595-7603.

Rubber recycling and waste management

Rubber products can be recycled and rubber belts are increasingly being recycled by reduction to powder. The European Chemicals Agency (ECHA) suggests that it is possible that also articles other than conveyor belts could be made of it (for example mats, building materials, paving materials) and so this could result in an additional source of widespread use of, and hence diffuse exposure from, SCCPs.[355] Companies recycling rubber belts inform in their approach of repurposing: "*Once conveyor belts can no longer be used as conveyor belts, rather than being cut or shred into raw materials, they can be reused as gym floors, cow mats, dock bumpers, etc. When the belts can no longer be used for those purposes they can be reused as gasket materials and thin rubber sheeting. And finally, once the belt can no longer be used in these applications it can then be shredded and used as a rubber mulch material*."[356] Moreover, SCCPs have been measured in main feedstocks (rubber granulates and adhesives) for rubber products, in rubber products and in recycled products made out of rubber.[357,358].

SCCPs in paints and coatings

According to the Stockholm Convention exemptions, SCCPs can be still used as waterproofing and flame-retarding agents in paints. Moreover, SCCPs can also be used as plasticizers in paints and coatings. The SCCP/CP content in paints and coatings can reach up to 20% of the product.

The main types of paints that are likely to contain chlorinated paraffins are those based on chlorinated rubber, vinyl copolymers and acrylic based coatings.[355] SCCPs may also be used in crosslinkable polyester systems for the production of long-term road markings.[359]

Chlorinated rubber-based paints are typically used in aggressive environments such as marine, industrial applications or liquid manure pit. Vinyl copolymer-based paints are used mainly for exterior masonry.[355]

The major applications of SCCPs or other CP mixtures containing SCCPs in paint and coating formulations include:

- Road marking paints;
- Anti-corrosive coatings for metal surfaces;
- Swimming pool coatings, fishpond coatings and water tank coatings;
- Decorative paints for internal and external surfaces;
- Masonry paints;
- Intumescent coatings; and
- Textile printing inks.

While only waterproofing and fire-retardant paints are listed as exemptions (Table 1-1), other manufacturers of paints might not be aware of this and use SCCPs or other CPs containing >1% SCCPs. Therefore, productions of all paints and coatings potentially using these CP mixtures can be assessed for the use of SCCPs and CPs containing >1% of SCCPs.

A particular interesting paint application are waterproof paints for coating of fishponds and swimming pools and water tanks. These applications might present direct exposure to humans via food or skin contact.

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[355] ECHA (2008) Data on manufacture, import, export, uses and releases of alkanes, C10-13, chloro (SCCPs) as well as information on potential alternatives to its use. Technical report, European Chemicals Agency, 2008.

[356] EZA Recycling Solutions (2020) How do we recycle materials? http://ezarecyclingsolutions.com/our-process

[357] C. Wang, W. Gao, Y. Liang, Y. Wang, G. Jiang (2018) Concentrations and congener profiles of chlorinated paraffins in domestic polymeric products in China. Environ. Pollut., 238 (2018), pp. 326-335,

[358] Xu C, Gao L, Zheng M (2019) Short- and medium-chain chlorinated paraffins in commercial rubber track products and raw materials. Journal of Hazardous Materials 380, 120854.

[359] Risk & Policy Analysts Limited (2010) Evaluation of Possible Restrictions on Short Chain Chlorinated Paraffins (SCCPs). Final Report, Non-Confidential Version prepared for National Institute for Public Health and the Environment (RIVM) The Netherlands July 2010

Paint and coating recycling and waste management

While paints and coatings are not directly recycled, painted or coated materials might be recycled without their removal. Also, such paintings might be removed by sand blasting and distributed into the environment as documented for PCB painted bridges.[329,331] Therefore, in addition to monito-ring of recycling of painted products, also renovation of painted products should be monitored.

SCCP in adhesives and sealants

According to the Stockholm Convention exemptions, SCCPs can be still used as adhesives. SCCPs and other CP mixtures that might contain SCCPs are used as plasticizer and flame retardant in adhesive and sealant manufacturing. Adhesives and sealants are often considered together because they can have similar applications and they are difficult to define and differentiate as one or another. In broad terms, adhesives are used to transfer loads and are typically designed with much higher tensile and shear strength than sealants, while sealants are used to into a gap or joint to prevent water, wind, dirt or other contaminants from passing through the joint or crack.[351] There is no particular exemption for SCCP application in sealants. However, as sealants may be used as adhesives, SCCPs could still be used in sealant production. Moreover, other CP mixtures, such as MCCPs and LCCPs (possibly containing >1% of SCCPs) might be used to replace SCCP applications in both adhesives and sealants. Therefore, SCCP content needs to be assessed in both adhesive and sealant productions. The SCCP/CP content in adhesives and sealants can reach up to 30% of the product weight and their major uses are adhesive and sealants including: Polysulphide; Polyurethane; Butyl; and Acrylic materials.

SCCP/CP containing adhesives and sealants are mainly used in the construction industry. Furthermore, SCCPs and MCCPs were measured in adhesive feedstocks used in rubber track production and SCCPs and MCCPs in commercial rubber track products were shown to be more related to the use of adhesives than with the use of granulate rubber.[358]

Adhesives and sealants in recycling and waste management

Adhesives and sealants applied in the construction industry finally become part of buildings and demolition waste and can be monitored if such waste is recycled for landscaping or other uses.

***Please note:** The screening of adhesives and sealants in the construction industry and in buildings and in construction and demolition waste might also include PCBs (major open use) and PCNs used until 1980s[360,332] and up to 2000[361] respectively.

SCCPs in fatliquors (leather production)

The use of SCCPs in the leather industry, in particular fatliquoring in leather, has been exempted by the Stockholm Convention. Fatliquors are applied as the last step, before drying, in leather preparation. The SCCP/CP content in formulated fatliquors can reach up to 20% of the product weight, but is typically around 10%.[351] In this step, fatliquors are added to leather in a proportion of around 7–12% of pre-treated leather. Therefore, considering the typically 10% of the fatliquors is CPs, it can be assumed that 7 to 12 g of CPs are used per kilo of leather.[362]

Leather recycling

In the recycling of leather different POP used in the leather production in the past might need to be considered and monitored including SCCPs, PCP and PFOS/PFOA.

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[360] USEPA (2015) PCBs in Building Materials—Questions & Answers. July 28, 2015.

[361] 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.

[362] U.K. Environment Agency. 2009. Environmental risk assessment: long-chain chlorinated paraffins. Science Report

SCCPs in textiles

The use of SCCPs in textiles is not exempted but textile producers might still use SCCPs in flame-retarding, water repelling and rot-preventing textile finishes. In addition, other CP mixtures containing SCCPs might also be used for the same purposes.

In addition to SCCPs, other POP flame retardants (decabromodiphenyl ether (c-DecaBDE) and hexabromocyclododecane (HBCD)) are/were used in the backcoating in textiles for furniture upholstery, seating upholstery in transport applications, and interior textiles such as blinds and curtains as well as industrial protective clothing. SCCPs were also used for the production of tent fabrics which have been substituted with rot-flame-water proofing based on a combination of MCCPs, c-DecaBDE and biocide in a formulation based on aqueous dispersions.[363]

In the assessment of such textiles, all POPs chemicals used as flame retardants should be assessed. In the assessment of textiles with water repellent properties, the use of PFOS/PFOA and related chemicals should be assessed in addition to SCCP use.

Textile recycling

In the recycling of textiles different POP used in the textile production in the past might need to be considered and monitored including SCCPs, HBCD, PBDEs, PCP and PFOS/PFOA.

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[363] RPA (Risk & Policy Analysts Limited). 2010. Evaluation of Possible Restrictions on Short Chain Chlorinated Paraffins (SCCPs). Final Report, Non-Confidential Version prepared for RIVM Institute. The Netherlands July 2010

Annex 1-G unintentional POPs (HCBD, HCB, PeCB, PCNs, PCDD, PCDF, and PCBs) as unintentional trace contaminants in products

PeCB, PCNs and HCBD were added to Annex C (unintentional production) at the 4th COP (2009), 5th COP (2015) and 6th COP, respectively. Similar to HCB, they are also listed as intentionally produced POPs in SC Annex A and are not produced anymore with minor remaining stockpiles (for PCNs see Chapter 5 and Annex 1-E). Today, the relevance of PeCB, HCB, PCNs and HCBD are rather as unintentionally formed POPs (UPOPs) in products and processes.

Since the different UPOPs are normally formed in most processes at the same time, it is reasonable not to solely address new listed PeCB, PCN and HCBD in suspected chemicals and products, but to also address in such monitoring all listed UPOPs. The necessity to e.g., screen PCDD/PCDF in products has been highlighted by discovery of extreme high levels of PCDD/PCDF in Chinese chloranil with PCDD/PCDF levels 35 and 520 times above the provisional low POPs limits of the Basel Convention and a total yearly release in product of 1044 g TEQ[364] which is about 10% of China's total PCDD/PCDF inventory and 1% of total global inventory, but for chloranil present directly in treated consumer products like textiles. PeCB, HCB, and PCBs were also detected in chloranil in high concentration.[364]

UPOPs in chemicals, mixtures, and products can be addressed by assessing lists of chemicals, mixtures, and products which, from past analysis, have been found to contain these chemicals or are suspected to contain UPOPs. Such a lists of chemicals is included in Part II of the UNEP Toolkit in Source Group 7 with identified PCDD/PCDF emission factors.[365] Additional lists of chemicals that potentially contain UPOPs are compiled in Annex 2 of the UNEP Toolkit in the "Guidance on Identifying Sources of PCDD/PCDF[366] in Table A on "Commercial chemicals recently associated with PCDD/PCDF formation and release", and Table B on "*Currently-used pesticides recently associated with PCDD/PCDF formation and release*".[366] Since other unintentional POPs are formed to different levels in parallel to PCDD/PCDFs, these lists can be used as an initial list to select chemicals and products for monitoring other unintentional POPs.

Review on new information on unintentional POPs in chemicals[367]

The UNEP BAT/BEP group published a review on new information on formation and release of UPOPs from production processes for pesticides and industrial chemicals. This is compiled for reducing or preventing releases and related information gaps from UPOPs in chemicals. The document is an attempt to gather monitoring information on relevant individual processes of chemical production with respect to the formation and presence of UPOPs.[482] Information gaps for chemicals are highlighted[482] to stipulate monitoring and screening of UPOPs in chemicals.

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 can be screened in the internet and a snap-shot were listed 2017 in the Annexes of the POPs Customs Control Guidance.[368] Some suppliers are listed here for HCB with a maximum sales volume of 10 t/month[369] but also fine chemicals and standards.

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[364] 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.

[365] UNEP (2013) Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention on POPs. http://toolkit.pops.int/Publish/Main/II_07_Chemicals.html

[366] UNEP (2013) http://toolkit.pops.int/Publish/Annexes/A_02_Annex02.html

[367] 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

[368] Stockholm Convention (2017) Guidance for the control of the import and export of POPs (Draft).

[369] https://www.guidechem.com/cas/118-74-1.html

HCBD as product

Although the production of HCBD is banned it might be separated from the raw product and possibly still marketed (see SC HCBD inventory guidance). In 03/2021 for HCBD 18 suppliers are offering HCBD with a capacity of up to 100 t/year.[370] This indicates that HCBD formed in the production of chlorinated solvents tetrachloroethylene

Unintentional POPs in chlorinated solvents and production

HCBD, HCB, PCBs, PCNs[344,345,371;372] are unintentionally generated during the production of certain organochlorine solvents, particularly tetrachloroethene (CAS: 127-18-4), trichloroethene (CAS: 79-01-6), and tetrachloromethane (CAS: 56-23-5)[373,374]. In addition to HCBD, wastes and possibly products from the production of these organochlorine solvents can contain and lower levels of PCDD/PCDFs.[344]

There is a lack of data on HCB, PeCB and HCBD in chlorinated solvents (UNEP 2010[375]. Therefore solvents like tetrachloroethylene, trichloroethylene or tetrachloromethane/carbon tetrachloride[376,377] and possibly other organochlorine solvents and hexachlorocyclopentadiene might be sampled and analysed for UPOPs content. Samples for monitoring at organochlorine solvent productions for UPOPs are the raw products, the solvents, the heavy end after distillation of the solvents and other products marketed from these processes.

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). These include ethylene dichloride, vinyl chloride monomer, chloroprene and possibly allyl chloride and epichlorohydrin[378]. HCBD might also be formed during the production of chlorine.[373] 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[379], products and wastes from the production of these chemicals an also be analysed for other unintentional POPs.

PeCB, HCB, PCDD/PCDF and PCB in pesticides and related organochlorine chemicals

Some pesticides are known to contain or form high 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).[373,380]

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[370] https://www.guidechem.com/cas/87-68-3.html

[371] Dow Chemical. 1990. Waste Analysis Sheet: Heavy Ends from the distillation of Ethylene Dichlorine in Ethylene Dichloride Production. Plaquemine, LA, February 21.

[372] Thornton J (2001) Environmental Impacts of Polyvinyl Chloride Building Materials. A Healthy Building Network Report.

[373] 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).

[374] Lecloux A (2004) Hexachlorbutadiene – Sources, environmental fate and risk characterization. Science Dossier, EuroChlor.

[375] 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.

[376] BUA (1991) Hexachlorobutadiene. BUA Report 62. GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA).

[377] Environment Canada 2004.Risk Management Strategy - Update 2004 Hexachlorobutadiene (HCBD).

[378] In a dossier for Eurochlor the presence of HCBD in these processes was considered unlikely from a chemical point of view (LeCloux 2004)[374].

[379] UNEP (2017) Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with hexachlorobutadiene. UNEP/CHW.13/6/Add.2.

[380] 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.

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[381] and Chloranil in China[364] revealed that PCDD/PCDF were present in all tested products and that some products contained high levels of PCDD/PCDF.

In the updated UNEP toolkit[365,366] a range of chemicals are listed which are known or suspected to contain PCDD/PCDF. Since UPOPs are normally formed in parallel, these chemicals can be suspected to also contain PeCB, HCB, and PCBs. This list might therefore be used for monitoring of PeCB and other UPOPs in products. Samples might be gathered from stakeholders or purchased from the market.

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 (COP3) 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[382] and 2007[383]). Pigments reported to contain HCB could be monitored for PeCB and other unintentionally produced POPs (Table A-1G).

Table A1-G: Pigments known to contain HCB, and possibly PeCB or other UPOPs

Pigment/chemical	***CAS Registry Number***
Pigment Yellow 110	5590-18-1
Pigment Yellow 138	30125-47-4
Pigment Green 7[384]	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 consumer products

Consumer products where chemicals and mixtures are added or included known or suspected to contain UPOPs 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, paper and paints. Potentially UPOPs containing biocides are used for treatment of wood or leather (e.g., PCP) or in soap and toothpaste (e.g. triclosan).

Another source of Dioxin contamination of consumer products including toys stem from PBDD/PBDF in PBDE treated plastic[385] including recycling of this plastic[386].

Unintentional POPs in biosolids/sewage sludge

Sewage sludge/biosolids are sinks for UPOPs. 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

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[381] 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.

[382] 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.

[383] 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.

[384] 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.

[385] Sindiku O, Babayemi JO, Tysklind M, Osibanjo O, Weber R, Schlummer M, Lundstedt S (2015) Polybrominated Dioxins and Furans (PBDD/Fs) in e-waste plastics in Nigeria. Environ Sci Pollut Res Int. 22, 14462-14470.

[386] Budin C, Petrlik J, Strakova J, et al. (2020). Detection of high PBDD/Fs levels and dioxin-like activity in toys using a combination of GC-HRMS, rat-based and human-based DR CALUX® reporter gene assays. Chemosphere. 251:126579.

organic fertilizers are also traded at the international level and control of POPs and heavy metals could be addressed with respect to imports, exports, and trade.

In a survey of sewage sludge in Germany, levels of PeCB and HCB were relatively low (< 10 ng/g) and much lower compared to their brominated analogues hexabromobenzene and pentabromobenzene detected at an average conc. of 330 ng/g and 45 ng/g respectively.[387]

Formerly the use of PCP was the main source of PCDD/PCDF in sewage sludge.[388] Today elevated levels of PCDD/PCDF are e.g. associated with industries such as the textile industry.[389]

Another product containing UPOPs are soil amendments from ashes from thermal processes. The use of any ashes from waste incineration has too high PCDD/PCDF values to be used on soils or any purpose in the environment. The use of ashes from biomass incineration might be used for soil amendments but should be monitored for its PCDD/PCDF content.[390]

Unintentionally produced POPs in feed additives and food

Feed additives such as ZnO, CuSO4 or CuCl2 can be contaminated with PCDD/PCDFs and other UPOPs. Food and feed can also be contaminated with PCDD/PCDF and other UPOPs in connection with historic releases of PCDD/PCDF, intentionally and unintentionally PCBs and other UPOPs from industries, contaminated pesticides, or application of contaminated sludge.[391,392] This includes, for example, fish from lakes and rivers or the sea with former PCDD/PCDF, PCBs or other unintentionally produced POPs input.[393] Floodplains of such rivers can also be impacted by PCDD/PCDF and other UPOPs with contamination of grazing cattle and related milk and meat.[394] Furthermore, also relevant contamination are eggs and milk from areas where formerly PCDD/PCDF, PCBs or other UPOPs contamination has occurred.

If a Party decides to include food and feed into the monitoring of U POPs, the development of the monitoring concept would be linked to the development of the inventory of PCDD/PCDF, PCBs and other UPOPs contaminated sites. A first priority selection of samples can be made based on such an inventory. Monitoring could also include feed[395] and imported food and feed.[396]

Fish and other biota in surface waters impacted from organochlorine industry and related landfills might have increased levels of HCBD (and other UPOPs).[397] In particular industries producing organochlorine solvents and

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[387] 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.

[388] 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.

[389] Fuentes MJ, Font R, Gomez-Rico MF, Molto J (2007) Multivariant statistical analysis of PCDD/FS in sewage sludges from different areas of the Valencian Community (Spain). Chemosphere 67, 1423–1433.

[390] Lopes H, Proença S (2020) Insights into PCDD/Fs and PAHs in Biomass Boilers Envisaging Risks of Ash Use as Fertilizers. Applied Sciences 10(14):4951. https://www.mdpi.com/2076-3417/10/14/4951/pdf

[391] Weber et al. (2008) Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. Env Sci Pollut Res. 15, 363-393.

[392] 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.

[393] Assmuth T, Jalonen P (2005) Risks and management of dioxin-like compounds in Baltic Sea fish: An integrated assessment. TemaNord 2005:568

[394] 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.

[395] 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.

[396] Hussain A, Dashti B, Gevao 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.

[397] 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.

related landfills and potential releases to surface water and associated accumulation in biota including edible fish would be assessed.

HCBD in ground water and drinking water around organochlorine disposal sites

HCBD is moderately water soluble (3.2 mg/L at 25°C) while the aromatic UPOPs have lower water solubility. Therefore, in particular HCBD can contaminate ground- and drinking water and such contamination has been discovered close to landfills from the organochlorine industry along with other pollutants.[398,399] Health assessment found likely health impact in humans[398] 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.

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[398] 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.

[399] 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.

ANNEX 2 Case studies of POPs in products and recycling

Annex 2-A Case studies of PFOS, PFOA and related compound screening in products and recycling

Monitoring project of PFOS/PFOA 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 PFASs in Norway in industrial manufacturing and applications used by the Norwegian population in daily life.[400]

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.[401] These products were all within the leather or carpet product groups: The two leather samples had the highest concentrations of PFASs: Office furniture leather; (pool of 3) and black shoe, leather, showed PFOS levels of 38 and 21 µg/m^2, exceeding the EU regulation of 1 µg/m^2. Carpets were around the regulation of 1 µg/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 PFASs 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/PFOA and other PFASs 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 PFASs (Teflon table cloth, AFFF, water proofing agents) or
    - by information from literature that production of these products may include perfluorinated chemicals (epoxy resin board, semiconductor fabrication etc.).

  A number of product types were identified as potential PFASs containing groups and several samples were collected in each group distributed as
- Good analytical coverage: 29 different PFASs 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, PFOA and other PFASs in selected consumer products[402]

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.

The study did not find high levels of PFASs 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,

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[400] 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

[401] 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.

[402] Blom C, Hanssen L Analysis of per- and polyfluorinated substances in articles. http://norden.diva-portal.org/smash/get/diva2:808634/FULLTEXT04.pdf

6:2 FTOH, PFOA, PFBA, PFHpA and PFHxA. However, for the latter three the levels were mainly very low. Only PFOA, 8:2 FTOH and 6:2 FTOH were found in amounts at or above 1 µg/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[403]

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.[403] As screening methods sliding spark spectroscopy, wave length dispersive x-ray fluorescence and HS-GC-EPED were applied. 47 fluorine-positive samples were identified und subjected to a detailed analysis for PFOS and other perfluorinated sulfonates (PFSA), fluorotelomer alcohols (FTOH), and perfluorinated carboxylates (PFCA) including PFOA. 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, PFHxS and other perfluorinated sulfonates (PFSA) were not detected in any sample at levels above 1 ng/g. Instead, 6:2 FTOH, and the PFOA precursor 8:2 FTOH and 10:2 FTOH were identified in all fluorine positive samples at levels ranging from 9 to 39500 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, e.g., 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; and Pattern C: clearly dominated by PFHxA.

In the 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)[404]

In a 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^2 each were combined in 60 ml 50% ethanol/water and extracted for 24 hrs at 60 °C. The extracts/migrates were filtered through 0.2 µm nylon/PP filters and analysed by an UHPLC-ESI$^-$-MS/MS (Waters Quattro Ultima) method in single reaction monitoring (SRM also called SIR) mode for the compounds. An C_{18} CSH column (1.7 µm*2.1 mm*150 mm, Waters) was used with a 35 min gradient program, with MeOH/water (+NH_4OH) 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 compounds on this instrument, which only has 20 Hz data sampling

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[403] 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

[404] Danish Veterinary and Food Administration (2012) Danish Technical University Report (not published).

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+PFSAs+PFOSA+FTMAPs, 2) Un-even PFCAs+FTOHs, 3) monoPAPs and diPAPs. ^{13}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 PFASs, possibly due to ion suppression by co-eluting salts. The previous d_4-6:2/6:2 diPAPs was found to contain considerable amounts of d_2-6:2 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 PFSAs, and only two of these contained PFOS but in low levels (< 10 ppb). The other samples contained FTOH based PFASs 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/confirmed with the pattern of detected PFASs 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.

Monitoring of fast food wrapping paper[405]

Total fluorine were measured in approx. 400 samples of food contact papers, paperboard containers, and beverage containers from fast food restaurants throughout the United States using particle-induced γ-ray emission (PIGE) spectroscopy. PIGE can rapidly and inexpensively measure total fluorine in solid-phase samples.[406] The study found that 46% of food contact papers and 20% of paperboard samples contained detectable fluorine (>16 nmol/cm^2). LC/HRMS analysis of a subset of 20 samples found perfluorocarboxylates, perfluorosulfonates, and other known PFASs and/or unidentified polyfluorinated compounds (based on nontargeted analysis). Six of the 20 samples contained PFOA while no PFOS has been detected. The total peak area for PFASs was higher in 70% of samples (10 of 14) with a total fluorine level of >200 nmol/cm^2 compared to six samples with a total fluorine level of <16 nmol/cm^2. The study concluded that the prevalence of fluorinated chemicals in fast food packaging demonstrates their potentially significant contribution to dietary PFAS exposure and environmental contamination during production and disposal.[405]

Screening PFASs in firefighting foams[407]

A systematic evaluation of 3M and fluorotelomer-based AFFFs, commercial products, and AFFF-impacted groundwaters from 15 U.S. military bases was conducted to identify new PFASs. Liquid chromatography quadrupole time-of-flight mass spectrometry was used for compound discovery.[407] Nontarget analysis utilized Kendrick mass defect plots and a “nontarget” R script. Suspect screening compared masses with those of previously reported PFASs. Forty classes of novel anionic, zwitterionic, and cationic PFASs were discovered, and an additional 17 previously reported classes were observed for the first time in AFFF and/or AFFF-impacted groundwater. All 57 classes received an acronym and IUPAC-like name derived from collective author knowledge. Major PFASs contained C4 and C6 moieties and only some contained C8 moieties, which could degrade to PFOA or PFOS.[407]

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[405] Schaider LA, Balan,SA, Blum A et al. (2017) Fluorinated Compounds in U.S. Fast Food Packaging. Environ Sci Technol Lett.;4(3), 105-111

[406] Ritter EE, Dickinson ME, Harron JP, et al. (2017) PIGE as a screening tool for Per- and polyfluorinated substances in papers and textiles. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 407, 47-54.

[407] Barzen-Hanson KA, Roberts SC, Choyke S, et al. (2017). Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater. Environ Sci Technol. 51(4):2047-2057.

Screening of PFASs in firefighting foams with TOP-Assay[408]

Quantification of PFASs and their precursors by total oxidisable precursor assay (TOP-Assay) in fluorosurfactants used for the preparation of aqueous film-forming foams in China demonstrated that perfluorooctanesulfonate and perfluorooctanoate were still significantly present in 2019 in certain domestic products.[408] However, such compounds, as well as the other long chain homologues, were not detected in alternative products (produced in China for use abroad). In particular, such products are based on telomerization and seem to evolve toward smaller amounts of fluorinated chemicals and shorter chain fluoroalkyl compounds.[408]

Screening of PFASs in textile finishing agents with TOP-Assay[409]

Textile finishing agents (TFA) products were investigated by the Kendrick mass defect method. The quantification results demonstrated a significant presence of PFOS (0.37 mg/L) in TFAs manufactured by electrochemical fluorination technology.[409] The products obtained by short-chain PFAS-based telomerization were dominated by perfluorooctanoic acid (mean concentration: 0.29 mg/L), whose values exceeded the limits stated in the European Chemical Agency guidelines (0.025 mg/L). Moreover, the total oxidisable precursor assay indicated high levels of indirectly quantified precursors with long alkyl chains (C7–C9). The study concluded, that there is currently a certain of environmental and health risks in China that originates from the utilization of TFAs, and a better manufacturing processes are required to reduce risks of PFOS and PFOA related compounds.[409]

Non-analytical screening of PFOS, PFOA and other PFASs on the Danish market[410]

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 PFASs in consumer products in Denmark.

Approaches of the Danish market survey of PFOS/PFASs 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.
- 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.

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[408] Mumtaz M, Bao Y, Liu L, et al. (2019) Per- and Polyfluoroalkyl Substances in Representative Fluorocarbon Surfactants Used in Chinese Film-Forming Foams: Levels, Profile Shift, and Environmental Implications. Environ. Sci. Technol. Lett. 6(5), 259–264.

[409] Mumtaz M, Bao Y, Li W, et al. (2019) Screening of textile finishing agents available on the Chinese market: An important source of PFASs to the environment. Front. Environ. Sci. Eng. 13(5): 67

[410] 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. http://www2.mst.dk/udgiv/publications/2008/978-87-7052-845-0/pdf/978-87-7052-846-7.pdf

Monitoring of ground and drinking water in the United States[411]

Drinking water contamination with PFOS and PFOA 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.[411] 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[411] (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, PFOA 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.[411]

As of July 2020, several PFASs, including PFOA and its cousin, PFOS, had been found in drinking water samples collected at 2,230 sites in 49 U.S. states.[412] A recent study[413] estimated that more than 200 million Americans, or over 60 percent of the population, could be exposed to PFOA and PFOS in their drinking water at levels exceeding 1 ng/L, which has been recommended as a maximum safe level for exposure by some toxicologist[414] and corresponds to the Tolerably Weekly Intake (TWI) of the European Food Safety Authority (EFSA)[415] (considering 10% of PFAS intake from drinking water).

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[411] Hu XC, Andrews DQ, Lindstrom AB et al.(2016) Detection of 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.

[412] https://www.ewg.org/interactive-maps/pfas_contamination/

[413] Andrews DQ, Naidenko OV (2020) Population-Wide Exposure to Per- and Polyfluoroalkyl Substances from Drinking Water in the United States Environ. Sci. Technol. Lett. 7, 12, 931–936

[414] Grandjean P, Budtz-Jørgensen E (2013) Immunotoxicity of perfluorinated alkylates: calculation of benchmark doses based on serum concentrations in children. Environmental Health 12, 35

[415] EFSA (2020) Risk to human health related to the presence of perfluoroalkyl substances in food. EFSA Journal 2020;18(9):6223, https://doi.org/10.2903/j.efsa.2020.6223

Annex 2-B Case studies of PBDEs screening in products, and recycling

Some countries/institutes or NGOs have performed screening of PBDE in products, recycling and wastes. These case studies already give a good insight into 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[416]

The largest and most relevant substance flow of 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 and decaBDE[416]. The report on the study can be downloaded here[416]. Specific features of EMPA's case study 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[416]. 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 PBDEs content of the polymer fractions of WEEE categories in Europe around 2010.
- The study further gives an overview on other critical RoHS relevant pollutants which might be relevant today for other regions too.

Determination of PBDEs and BFRs in WEEE plastics in France[417]

Data of bromine (n = 4283) and BFR concentrations (n = 98) in plastics from EEE and WEEE processing facilities before and after sorting for bromine in four sites in France have been studied for chemical composition and for regulatory classification. The WEEE was analysed by handheld XRF, and the waste was sorted after shredding, by on-line X-ray transmission for total bromine content (< or > 2000 mg/kg) in small household appliances (SHA), CRTs and flat screens plastics.

In equipment (n = 347), 15% of the items had no bromine, while 46% had at least one part with bromine, and 39% had all plastic parts brominated. The bromine concentration in plastics is very heterogeneous, found in high concentrations in large household appliance (LHA) plastics, and also found in unexpected product categories.[417]

In waste (n = 65), PBDEs, PBBs, HBCD and TBBPA were analysed. The most concentrated BFRs was decaBDE (3000 mg/kg) and TBBPA (8000 mg/kg). The bromine concentration of regulated brominated substances was identified in 2014 and 2015 to be up to 86% of total bromine in ''old'' waste (SHA, CRT), 30–50% in ''younger'' waste (flat screens), and a mean of only 8% in recent products (2009–2013). Regulated substances are a minority of all the brominated substances and the only practical way to sort is to measure total bromine on-line. The sorting reduces the mean bromine concentration in the ''Low Br'' fraction in all sites, and reduces the decaBDE concentration to levels below 1000 mg/kg. After sorting, the concentration in the ''High Br'' fractions exceeds all present or future regulatory limits.[417]

In conclusion, sorting of small household appliances, cathode ray tubes and flat screen plastics is necessary to avoid uncontrolled dispersion of regulated substances in recycled raw material. Other categories (large household appliances, electric and electronic tools, lighting equipment) should also be considered, since their total bromine content (unweighted mean concentration) is high for some of these products.[417]

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[416] Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. Final Report. https://resource-recovery.net/sites/default/files/empa_2010_rohs_substances_in_mixed_plastic.pdf

[417] Hennebert P, Filella M (2018) WEEE plastic sorting for bromine essential to enforce EU regulation. Waste Manage 71, 390-9

PBDEs in plastics from WEEE and ELVs after separation[418]

A Swedish study assessed plastic samples from WEEE and ELVs after separation into a low PBDE/bromine fraction and a high bromine/PBDE fraction from facilities from 6 European countries.[418] The low BFR fraction on plastic from WEEE/ELV intended for recycling (ABS, ABS/PS, PP/PE and PP) which all met the CENELEC Standard TS 50625-3-1 (CENELEC 2015) for bromine of <2000 mg/kg plastic was measured for PBDEs. In most cases total bromine content was <1000 ppm and PBDE content <200 mg/kg and therefore were below the two provisional Basel Convention low POPs content for PBDEs of 1000 mg/kg and 500 mg/kg (Table A2-B1).[418] However non of the fraction could meet the provisional Basel Convention low POPs content for PBDEs of 50 mg/kg due to decaBDE contents (see Table A2-B1).

Table A2-B1 POP-PBDEs in plastic from recycling after bromine separation (Swerea 2018)[418]*

Recycled polymers from WEEE/ASR after separation of bromine rich fraction	Average* PBDE-209 content (mg/kg)	Average* ΣPOP-PBDE (2009)** content (mg/kg)	Average* bromine content (mg/kg)	Share of samples above 250 mg Br/kg
ABS	77	6	696	63 % (5/8)
PS	81	< 5	695	56 % (5/9)
PS / ABS	119	< 5	916	80 % (4/5)
PP / PE	76	< 5	795	50 % (1/2)
PP	130	<5	685	– (1/1)

* Since only 65% of samples (n'=17 out of n=26) which exceeded 250 mg/kg bromine were analysed for PBDEs (Swerea 2018) the overall average content of PBDEs and bromine in the total samples studied are lower (average maybe 70%) than those listed in the table.

** PBDEs listed 2009 in Annex A of the Stockholm Convention, including tetra-, penta- hexa-, hepta-PBDEs.

Determination of PBDEs and BFRs in WEEE plastics in Nigeria[419,420]

The largest PBDEs share within EEE/WEEE are casings of Cathode Ray Tubes (CRTs) (see *PBDEs Inventory Guidance*). In a monitoring study of PBDEs listed 2009 in Nigeria the two major CRT categories (TVs and computers) were monitored. 382 single housings of computer and TV CRTs were sampled at WEEE storage sites in Nigeria.[419,420] Furthermore, the recycling of the plastic of these appliances is of particular interest from an economic perspective.

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^2 sizes were cut from each sample. Dismantling and cutting were done with simple tools (Figure A2-1a). A hole was made on the cut samples through which a metal tag (Figure A2-1b) was attached with the aid of a safety pin (Figure A2-1c). These were transferred to the workshop where 40 mm X 40 mm squares were cut (Figure A2-1d), and the cut squares packaged in labelled drug envelops (Figure A2-1e) for further analysis and stored 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 c-OctaBDE as their use is thought to have been stopped in about 2004.

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[418] Hennebert P, Filella M (2018) WEEE plastic sorting for bromine essential to enforce EU regulation. Waste Manage 71, 390-9

[419] Sindiku O, Babayemi JO, Osibanjo O, Schlummer M, Schluep M, Weber R (2012) Assessing PBDEs and BFRs in E-waste polymers in Nigeria. Organohalogen Compounds 74, 1320-1323.

[420] 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 and detailed Supporting Information.

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 A2-1a: Sampling tools

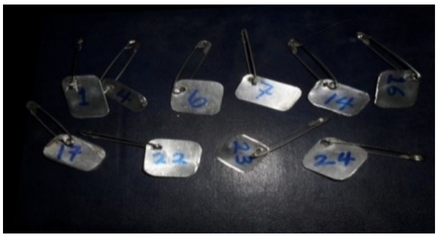

Figure A2-1b: Labelling tags

Fig. A2-1c: Labelled field sample **Fig. A2-1d:** Cut squares **Fig. A2-1e:** packaged samples

Table A2-1: 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
Total	**224**	**158**	**382**

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 than selected for GC/ECD and GC/MS analysis.

In case of high bromine levels, GC-ECD provides typical fingerprint of technically applied BFRs. However, in case of lower bromine concentrations (below 1000 mg/kg) and unclear ECD results the aliquots of the sample extracts were fortified with ^{13}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 keys (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 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 PBDEs/BFRs content in the CRTs products specific.
- With the generated data set PBDEs impact factors for plastic of TV CRTs (11 kg ∑c-OctaBDE+decaBDE per tonne TV CRT plastic) and computer CRTs (1.3 kg ∑c-OctaBDE+decaBDE per tonne PC CRT plastic)

in Nigerian. Based on the EEE/WEEE inventory of Nigeria[421] these impact factors have been used for developing the PBDE inventory for Nigerian EEE/WEEE.

Monitoring of BFRs in polymers of electronics on Swiss market[422]

The Swiss relevant authorities monitored in 2000 consumer products the presence of brominated flame retardants including electrical devices, building materials and lighting equipment.[422] The aim of the survey was to evaluate the compliance of commercial products 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 products 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 PBDEs and commonly used flame retardants
    - Scanning of bromine positive samples where the BFR were not those commonly used for new brominated flame [423]
- The study gives an insight on BFRs used in electronic products imported to the European market. The study shows that the PBDE content in current products on the Swiss (and likely 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.

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 (HBBz) or pentabromobenzene (PeBBz) while their chlorinated analogues (HCB and PeCB) are listed POPs.

Monitoring of PBDEs and other BFRs in plastics in consumer products[424]

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[424].

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[421] 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.

[422] 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.

[423] Zennegg M (2011) Identification of "Novel" Brominated flame retardants in new products of the Swiss market. Organohalogen Compounds 73, 1238-1241.

[424] 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.

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 extracted plastic shows promise in predicting not only the types of BFRs present but also estimating the concentrations.[424]

Monitoring PBDEs in carpet rebond from recycled PUR foam[425]

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 PBDEs in carpet rebond was performed with XRF for bromine screening and 26 samples were analysed for PBDEs by GC/MS analysis.[425]

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 PBDE-containing materials.
- The study was planned and performed from an NGO working on POPs (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 PBDEs and other flame retardants in baby products[426]

PUR foam samples collected from 101 commonly used US baby products were monitored for PBDEs and other flame retardants.[426] From these products:

- Five samples contained PBDE congeners commonly associated with c-PentaBDE, suggesting that such products were still in-use in sensitive use areas although production of c-PentaBDE is considered to have stopped in 2004.[427]
- 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.
- 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.

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[425] DiGangi J, Strakova J, Watson A (2011) A Survey of PBDES in Recycled Carpet Padding. Organohalogen Compounds 73, 2067-2070.

[426] Stapleton MH, Klosterhaus S, et. al. (2011) Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products. Env. Sci. Technol. 45. 5323-5331.

[427] With some uncertainties for the c-PentaBDE production in China which might have stopped later.

- For the first time a wide range of polyurethane baby products were sampled, screened and analysed for 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 standards[428] in a country can result in high levels of flame retardant in sensitive products with high exposure to vulnerable groups like infants.

Monitoring of PBDEs/BFRs in children's toys in China[429]

A Chinese research group assessed the presence of PBDEs and other BFRs (including PBBs, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and DBDPE) in children's toys purchased from South China.[429] In all samples PBDE or other BFRs were detected. The median BFR concentrations in the hard plastic toys were notably higher than values in other toys. The PBDE concentrations were below the 1000 mg/kg RoHS directive limit in all of the toys, except for one hard plastic toy with a total PBDE concentration of 5344 mg/kg. The BFR profiles in the toys were consistent with the patterns of their current production and consumption in China, where PBDEs, specifically c-DecaBDE, were the dominant BFR, followed by the emerging DBDPE. The relatively high concentrations of octa- and nonaBDEs in the foam toys suggest the decomposition of decaBDE during the manufacturing processes of the toys and/or further exposure to light/UV.

Specific feature of the study analysing 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 a broad use of recycled WEEE plastic in the sensitive use area "children's toys".
- The study highlighted that because of extended play, mouthing behaviour, and frequent hand-to-mouth contact, toys may pose a significant pathway of BFR exposure for children.
- Together with a second study of the group on PBDE/BFR screening in household goods[430], the research reveals that the recycling of WEEE plastics were largely uncontrolled in this region.

Monitoring of PBDE and other FRs and plasticisers in consumer/children's products[431]

A Belgium study investigated the occurrence and profiles PBDEs and phosphate FR (PFRs) as well as plasticisers (phthalate esters) in 106 toys samples.[431] Low levels and detection frequencies of congeners of c-PentaBDE and c-DecaBDE were found, with BDE209 being the dominant PBDE in all samples (maximum value was 0.14 mg/g). The levels of PFRs and phthalates were up to 10,000 times higher than those of the PBDEs, with triphenyl phosphate and diethylhexyl phthalate being the major representatives of these classes. Maximum values were 1.3 and 6.9%, respectively.[431] The detection frequencies were up to 50% for PFRs and 98% for phthalates. All but one of the toys produced after the REACH regulation went into force complied with its provisions.[431] Using models in the literature, exposure to these chemicals was tentatively assessed. It is clear that at the levels found in the investigated toys may pose a health hazard to the children in some cases. Since these additives do

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[428] 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.

[429] 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.

[430] 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.

[431] Ionas AC, Dirtu AC, Anthonissen T, Neels H, Covaci A. Downsides of the recycling process: harmful organic chemicals in children's toys. Environ Int. 2014 Apr;65:54-62.

not contribute to the intended characteristics of the materials, it is most likely that recycling was the source of these additives in toys.[431]

Monitoring of PBDE and other FRs in consumer/children's products[432]

The Washington State Department of Ecology assessed in 2012-2013 the presence of PBDEs, HBCD and other flame retardant in general consumer and children's products.[432] 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.[432] The majority of samples tested (94%) did not contain PBDEs above a reporting limit of 100 mg/kg of this study, which supports the conclusion that manufacturers have moved away from using PBDEs in products available to Washington State consumers.

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).[432] The majority of these samples were foam and many were children's products. A subset of samples was 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.[432] 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.[432]

Monitoring of PBDE and other FRs in consumer/children's products[433]

To investigate the extent to which kitchen utensils are contaminated with BFRs and the potential for resultant human exposure, we collected 96 plastic kitchen utensils and screened for Br content using a hand-held XRF spectrometer. Only 3 out of 27 utensils purchased after 2011 contained detectable concentrations of Br (≥ 3 mg/kg). In contrast, Br was detected in 31 out of the 69 utensils purchased before 2011. Eighteen utensils with Br content higher than 100 mg/kg, and 12 new utensils were selected for GC–MS analysis of BFRs. BFRs targeted were PBDEs and novel BFRs (NBFRs) pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and decabromodiphenyl ethane (DBDPE). The ability of XRF to act as a surrogate metric of BFR concentration was indicated by a significant (Spearman coefficient = 0.493; $p = 0.006$) positive relationship between Br and ΣBFR concentration. Measurements of ΣBFRs were always exceeded by those of Br. This may be due partly to the presence of BFRs not targeted in our study and also to reduced extraction efficiency of BFRs from utensils. Of our target BFRs, BDE-209 was the most abundant one in most samples, but an extremely high concentration (1000 mg/kg) of BTBPE was found in one utensil. Simulated cooking experiments were conducted to investigate BFR transfer from selected utensils ($n = 10$) to hot cooking oil, with considerable transfer (20% on average) observed. Estimated median exposure via cooking with BFR contaminated utensils was 60 ng/day for total BFRs. In contrast, estimated exposure via dermal contact with BFR-containing kitchen utensils was minimal.

Monitoring of PBDEs, HBCD and PBDD/PBDF in vehicles[434]

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

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[432] Washington State Department of Ecology (2014) Flame Retardants in General Consumer and Children's Products. https://fortress.wa.gov/ecy/publications/publications/1404021.pdf

[433] Washington State Department of Ecology (2014) Flame Retardants in General Consumer and Children's Products. https://fortress.wa.gov/ecy/publications/publications/1404021.pdf

[434] 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

each material/component was conducted by using a handheld XRF analyser with RoHS/WEEE mode and analytical time was set at 30 seconds. The 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.[434]

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 c-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 c-PentaBDE technical mixture. High HBCD contents were found in only 2 floor covering samples (none of seat fabric).[434]

Monitoring of PBDEs in major PBDE containing waste streams in the Netherlands[435]

The Dutch authorities investigated how waste materials that possibly contain 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. PBDEs have been used mainly in the electronics and the automotive sectors. For both 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 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 PBDEs, such as the automotive and electronic waste stream materials (especially PUR and ABS). 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 PBDEs. The method can be used to screen samples for PBDEs, so that the more laborious solvent extraction procedures are only done when quantifiable amounts are present.

In general, 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 PBDE hot spot in ELVs, with up to 25,000 µg/g in PUR 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 PBDEs in WEEE is expected to end up in recycled plastics. In the automotive sector, 14% of the 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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[435] 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).

Annex 2-C Case studies of HBCD screening in products and recycling

A few countries/institutes have performed screening of HBCD in articles and wastes. Some are presented in Annex 2-B under PBDEs[432,434] and others are shortly described below.

Monitoring of HBCD in EPS and XPS packaging and food contact materials in Korea[436]

Rani et al. (2014)[436] 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 products relatively high concentration of HBCD was detected including an ice box (960 µg/g) and disposable tray (8.4 µg/g) used in fish market. HBCD was also detected in buoy used in aquaculture (53.5 µg/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 EPS and XPS packaging in Ireland[437]

50 samples of PS packaging materials from the UK and 20 from Ireland were collected to evaluate uncontrolled recycling of HBCD into EPS/XPS. HBCD was detected in 63 (90 %) of samples, with concentrations in 4 samples from Ireland exceeding the EU's low POP concentration limit (LPCL) of 0.1 % above which articles may not be recycled. Moreover, 2 further samples contained HBCD >0.01 %. The data suggest that continued monitoring is required to assess compliance with this limit value and uncontrolled recycling. Ratios of α- vs γ-HBCD in the EPS packaging samples (average = 0.63) exceeded significantly (p=0.025) those in EPS building insulation material sample (average = 0.24) reported previously for Ireland. This shift towards a-HBCD in packaging EPS is consistent with the additional thermal processing experienced by recycled PS and suggests the source of HBCDD in PS packaging is recycled PS insulation foam.[437]

Monitoring of HBCD in Buoy in aquafarms and related oysters[438]

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.[438]

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.[438] The study concluded that the presence of HBCDs in aquaculture buoy demonstrate the lack of proper control for the use of HBCDs in manufacturing EPS products.[438]

Rapid distinction between EPS/XPS containing HBCD and brominated polymeric alternatives[439]

Schlummer et al. (2015)[439] 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

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[436] 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.

[437] Abdallah MA, Sharkey M, Berresheim H, Harrad S (2018) Hexabromocyclododecane in polystyrene packaging: A downside of recycling?Chemosphere 199, 612-616.

[438] 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

[439] 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

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.[439]

Monitoring of HBCD in textile[440,441]

Kajiwara et al. (2008[440], 2009[441]) screened curtains and other textiles on the Japanese market with a handheld 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 possibly 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 DCM.

Monitoring of HBCD in WEEE plastic in EU[442]

HBCD has also been used as a minor use BFR in high impact polystyrene (HIPS) in electronics.[443] Therefore, HIPS plastic casings or parts and WEEE plastic fractions from recycling might contain HBCD. 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.[442]

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 200 mg/kg.[442] 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 mg/kg.

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[440] Kajiwara N, Sueoka M, Ohiwa T, Takigami H (2008) Determination of flame-retardant hexabromocyclododecane diastereomers in textiles. Organohalogen Compds 70, 1414-17. http://dioxin20xx.org/wp-content/uploads/pdfs/2008/08-569.pdf

[441] Kajiwara N, Sueoka M, Ohiwa T, Takigami H. (2009) Determination of flame-retardant hexabromocyclododecane diastereomers in textiles. Chemosphere 74, 1485-1489.

[442] Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. Final Report September 17, 2010.

[443] UNEP (2010), Risk profile on hexabromocyclododecane. UNEP/POPS/POPRC.6/13/Add.2.

Annex 2-D Case studies of PCP screening in products and recycling

Some institutes have performed screening of PCP in products, recycling 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[444]

In Germany PCP, DDT and HCH has been extensively used as wood preservative including art works. The applicability of energy-dispersive μ-XRF spectrometry for the monitoring of chlorine-containing wood preservatives in art objects was tested. Since largely these POPs has been used for treatment and since HCH was largely evaporated over time, the detection of high chlorine content was specific for DDT and PCP.[444] The use of μ-XRF technique combines the advantages of high spatial resolution (about 100 μm spot size), needed in studies of penetration profiles of cut sections, and the ability to analyse larger areas in a relatively short time.[444] 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).[444]

Screening of PCP and other POPs in wooden museum artwork and remediation[445]

In the second half of the 20th century, many wooden museum artworks were massively treated with POP 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 object's surfaces forming a white layer of crystals or they are emitted into the indoor air of storage rooms or exhibitions.[445] In order to prevent the conservators as well as the visitors from health risks, it is important to decontaminate these objects. Two projects were conducted in Switzerland to evaluate suitable decontamination methods and to investigate their influence on the wooden microstructure.[445] In a first step, the pesticides distribution was investigated by GC/MS and μ-XRF on wooden dummies. In a second step, the penetration behaviour of the pesticides was investigated by GC/MS and μ-XRF and, additionally, the distribution in the wood microstructure was determined by μ-XRF. In a third step, the efficiency of the two above mentioned decontamination methods was tested by GC/MS and μ-XRF.[445] This method can be used for screening of PCP, DDT and other chlorinated POPs in wood.

Screening of POP and other pesticides and pollutants in textiles in a museum[446]

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 were discovered by GC/MS analysis.[446] 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.[446] It was concluded that such knowledge is a crucial prerequisite to proper risk prediction.

Monitoring PCP and PCDD/F in Guar Gum[447]

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

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[444] 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.

[445] 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.

[446] 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.

[447] 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

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 PCDD/F and PCP in guar gum:

- PCP in guar gum exceeding 0.01 mg/kg taking into account the measurement uncertainty is considered as un-acceptable.
- PCDD/Fs 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 in the EU.

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. two times 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.[448] Fries et al. (2002)[449] analysed the PCP and PCDD/PCDF levels in the wood samples of these stables (Table A2-2) and found a good correlation between PCP levels and PCDD/F concentration (Figure A3-2; Table A2-2).[449] PCDD/F 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[449] (Table A3-2). PCDD/F 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[449] (Table A2-2). This demonstrates the relevance of PCDD/PCDF contamination in PCP treated wood and the need for environmentally sound management of PCP treated wood.

Table A2-2: Concentrations of pentachlorophenol (PCP) and total PCDD/PCDF expressed as toxic equivalents (TEQs) in wood samples (Fries et al. 2002)[449]

PCP level	Number 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

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[448] Huwe JK, Davison K, Feil VJ, Larsen G, Lorentzsen 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.

[449] 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.

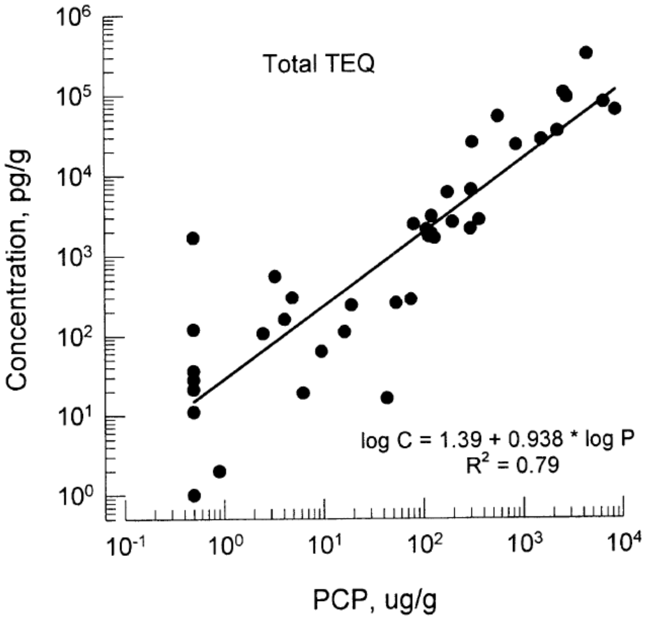

Figure A2-2: Concentrations of PCDD/PCDF (TEQ) in wood of beef stables as functions of concentrations of PCP (Fries et al. 2002)[449]

PCP treated wood as feed additive and PCDD/PCDF contamination in wood and meat[450]

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.

PCP treated wood as source for PCDD/PCDF contamination in eggs[451,452]

Chicken eggs in farms in Germany and Poland were recently contaminated from PCP-treated wood or contaminated soil.[451,452] PCDD/PCDF from former PCP use is a major source of PCDD/PCDF contamination of free range eggs.[452]

PCP treated wood used as animal bedding source for PCDD/PCDF in eggs[319]

In Italy, eggs were contaminated above the regulatory limit due to wood shavings from PCP-treated wood used for animal bedding.[319] Animal bedding from wood recycling was also a source for PCB and lead exposure due to recycled painted wood.[452]

Incineration of PCP treated wood as source for PCDD/PCDF contamination in meat[453]

The incineration of PCP-treated wood for drying of feed also resulted in PCDD/PCDF contaminated feed and meat from cattle fed with this feed.[453]

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[450] Llerena JJ1, Abad E, Caixach J, Rivera J. (2003) An episode of dioxin contamination in feeding stuff: the choline chloride case. Chemosphere. 53(6), 679-683.

[451] Piskorska-Pliszczynska J, Strucinski P, Mikolajczyk S, Maszewski S, Rachubik J, Pajurek M (2016) Pentachlorophenol from an old henhouse as a dioxin source in eggs and related human exposure. Environ Pollut 208:404–412.

[452] Weber R, Herold C, Hollert H, et al. (2018) Reviewing the relevance of dioxin and PCB sources for food from animal origin and the need for their inventory, control and management. Environ Sci Eur. 30:42. https://rdcu.be/bax79

[453] 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, 30.09.2000.

Annex 2-E Case studies of PCN screening in products and materials

A few countries or institutes have performed screening of PCN in products and recycling. 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 for United Kingdom to Japan[454]

Technical polychlorinated naphthalene formulations were illegally imported from the United Kingdom into Japan and were assessed for detailed content and congener profile.[454] The PCN composition was compared to known technical Halowax mixtures (Halowax 1000, 1001 and 1031). Principal component analysis and cluster analysis of PCN 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.[454] 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.[454]

Monitoring of PCNs in Neoprene FB rubber[455]

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.

Monitoring of PCNs and selected other POPs in waste wood[456]

The National Institute for Environmental Studies of Japan screened POPs (chlordanes (CHLs), PCP, PCA, and PCNs) in waste timber (n = 55) and its recycled products (woodchip, n = 42; particle board, n = 3). In the recycled products, the highest concentrations detected were 0.86 mg/kg CHLs, 3.0 mg/kg PCP, 1.1 mg/kg PCA, and 2.6 mg/kg PCNs, which were lower than the low POP content limits for the environmentally sound management of wastes defined under the Basel Convention.[456]

Analysis of unintentional PCNs in PCBs[457,458]

Yamashita et al. (2000)[457] 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.[457,458] analysed the major Chinese PCB formulation (PCB3) and detected relatively high PCN levels (1307 mg/kg). [458]

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[454] 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.

[455] 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.

[456] Koyano S, Ueno D, Yamamoto T, Kajiwara N (2019) Concentrations of POPs based wood preservatives in waste timber from demolished buildings and its recycled products in Japan. Waste Management 85, 445-451.

[457] 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.

[458] 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.

Analysis of PCN and other UPOPs in by-product of chloromethane production[459]

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, HCBD, HCB, and PeCB were found in the carbon tetrachloride by-product of the methanol-based production of chlorinated methanes.[498] The total emission amounts during the production of chlorinated methanes in China of PCNs in 2010 was estimated to 427 kg.[459] Furthermore large amounts hexachloro-cyclopentadiene, HCBD, PCBz, octachlorostyrene, and PCB release were estimated to be 10080, 7350, 5210, 212, and 167 kg, respectively.[459] 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.[459]

Monitoring of PCNs in rubber and different waste fractions[460]

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 was found in the Neoprene FB rubber.

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[459] 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.

[460] 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 2-F Case studies of screening SCCPs in products and recycling

A few countries or institutes have performed screening of SCCPs in products and recycling. These case studies give an initial insight into SCCP presence in products and recyclates. The case studies are shortly described below with reference to the reports/publications.

Monitoring of SCCPs in consumer products at national markets

SCCPs have been screened in consumer products marketed in the European Union and Norway. The Rapid Exchange of Information System of the European Union (RAPEX), reported that a wide range of consumer products, assessed from 2013 to 2017, exceeded the limit of 1500 mg kg^{-1} limit. These products included toys, sport equipment, clothing and others.[461] Moreover, European countries informed to the POPRC, in the Annex F submission, that SCCPs were measured in consumer products at their respective national markets.[462] Austria reported that SCCPs were measured in mats at concentrations of 4,000–69,000 mg/kg Germany reported that SCCPs were measured in 19 of 84 plastic products at concentrations of 440–50,000 mg/kg Norway reported that SCCPs were measured in children's products at concentrations of 1,600–107,000 mg/kg. The Swedish Chemicals Agency reported that of 62 household articles tested, SCCPs were measured in high concentrations in 16 articles and in lower concentrations (probably from manufacturing contamination) in 11 articles.[462]

McGrath et al. (2021)[463]assessed the SCCP and MCCP content in PVC and rubber consumer products and toys purchased on the Belgian market in 2019. The authors reported that SCCPs were detected in 27 of 28 (<LOD–130,000 µg g^{-1}; median of 2.5 µg g^{-1}) while MCCPs were detected in only five samples (<LOD–3500 µg g^{-1}). However, despite of one sample, SCCP concentrations were below the European Union's limit of 1500 mg kg^{-1} (0.15%). The low concentrations of both SCCPs and MCCPs were attributed to unintentional incorporation to the polymeric materials during manufacturing or recycling. Moreover, the SCCP homologue pattern was different from major commercial formulations but MCCP patterns were similar to known industrial mixtures. This study suggests that that unintentional sources of both SCCPs and MCCPs contaminate polymer products on the European market.[463]

The International Pollutants Elimination Network (IPEN), has also reported that SCCPs were measured in PVC products and toys intended to children from different countries.[464] Chemical analysis showed that 27 of 60 (45%) toys and other children's articles from 10 countries (Brazil, Canada, China, Czech Republic, India, Japan, Kenya, Netherlands and Russia and United States) contained SCCPs at concentrations ranging from 8.4 to 19,808 mg/kg. Despite of the United States' samples, SCCPs were found in PVC products from all other countries. Most of the labelled products containing SCCPs were manufactured in China (n=12) but products manufactured in Germany (n=1), Kenya (n=1) and Russia (n=1) also contained SCCPs. Six products (10%) exceeded the EU regulatory limit of 1500 mg/kg (0.15%) and one of the two provisional low POP contents (100 mg/kg, or 0.01%) defined by the Basel Convention[465], with concentrations of 4,376 mg/kg (a baby bib purchased in India), 4,866 mg/kg (baby bib purchased in Kenya), 6,918 (beach ball purchased in Kenya), 9,715 mg/kg (gym ball purchased in the Czech Republic), 13,973 mg/kg (plastic duck purchased in Brazil), and 19,808 mg/kg (jump rope purchased in Japan). Moreover, the last two products, (plastic duck purchased in Brazil and jump rope purchased in Japan), also exceeded the higher provisional low POP content (10,000 mg/kg, or 1%) of the Basel Convention.

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[461] UNEP (United Nations Environment Programme) (2019). Detailed Guidance on Preparing Inventories of Short-Chain Chlorinated Paraffins (SCCPs), Draft of 2019

[462] UNEP (2016) Risk Management Evaluation on Short-Chain Chlorinated Paraffins. Persistent Organic Pollutants Committee (POPRC). UNEP/POPS/POPRC12/11/Add.3.

[463] McGrath TJ, Poma G, Matsukami H, Malarvannan G, Kajiwara N, Covaci A. (2021). Short- and Medium-Chain Chlorinated Paraffins in Polyvinylchloride and Rubber Consumer Products and Toys Purchased on the Belgian Market. Int. J. Environ. Res. Public Health. 18, 1069.

[464] Miller P and DiGangi J. (2017). Toxic industrial Chemical recommended for global prohibition contaminates children's toys. International Pollutants Elimination Network (IPEN).

[465] UNEP (2019). Technical guidelines, Addendum - General Technical Guidelines on the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Persistent Organic Pollutants, 2019. UNEP/CHW.14/7/Add.1/Rev.1

In China, SCCPs and MCCPs were measured in 108 domestic polymeric products collected from markets and waste tire recycling stations in Beijing.[466] The average concentrations of SCCPs in polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE) and food packaging were 234, 3,968, 150 and 188 ng/g, respectively MCCP concentrations were 37, 2,537, 208 and 644 ng g^{-1}, respectively. SCCP and MCCP concentrations were up to two orders of magnitude higher in Rubber (614 µg/g) and PVC samples (40,770 µg/g), suggesting their intentional application during the manufacturing of these products. The co-occurrence of both SCCPs and MCCPs in all polymers is noteworthy. Moreover, the authors highlighted that $C_8H_{11}Cl_7$, $C_9H_{13}Cl_7$ and $C_9H_{15}Cl_5$ CPs were found in several PVC and PP samples.

In a following study, it was shown that both SCCPs and MCCPs can migrate from food packaging into food simulants.[467] Using hydrophilic, lipophilic and dry food simulants, the migration of SCCPs and MCCPs from packaging into food was assessed in storage conditions (40 °C over 10 days) and the results evidenced that CPs of shorter chain-lengths (C_{10}) and lower chlorine content (Cl_6 and Cl_7) had higher migration efficiencies. Therefore, SCCPs had significantly higher average migration efficiencies (12.15%) than MCCPs (1.51%), except in hexane food simulants, which suggests that both SCCPs and MCCPs can migrate and accumulate into fatty food. Besides, the results suggested that food packaging can be a considerable source of CPs into food but the average estimated dietary intakes did not represent an immediate risk to human health.

Monitoring of SCCPs in household kitchen devices

Despite of the CP occurrence in the environment, leading to food contamination and the above-mentioned potential contamination of food from food packaging, kitchen devices can also be a considerable source of CPs into food with potential exposure risks to humans.[468,469] A study of CP leaching from handheld food blenders purchased in Sweden in 2014 and 2016 reported that 75% of the devices released elevated levels (from 0.10 to 120 mg) of CP mixtures of all chain lengths (C6–C22) during simulated food preparation, with potential exposure risks to humans.[468] MCCP releases were on average higher (35–92%; average of 70%), but all CP mixtures detected had a SCPP content significantly above 1% (4–59%; average of 28%), resulting that the used mixtures should also be classified as POPs according to the Stockholm Convention limit for other CP mixtures containing SCCPs. The amounts of CPs released did not decrease even after using the handheld blenders 20 times, indicating release from a reservoir like plastic parts containing additives. The study authors warned that CP leakage may continue even after the hand blender is used several hundred times. Moreover, using those food blenders once a day could increase human exposure by a factor of up to 26 and, if considering the 95th percentile intake of CPs, the TDI for infants (body weight < 7.2 kg) would be exceeded.

CPs were found in baking ovens from German kitchens.[469] High levels of MCCPs (up to 100,000 mg g^{-1}) were measured inside 10 out of 21 (48%) domestic baking ovens. In seven of these ovens the SCCP content was below the limit of quantification meeting the Stockholm Convention requirement of a SCCP content of less than 1% in CP mixtures. However, in 3 cases the SCCP content was 2.8%, 5.0% and 14.4% of the total CP content. One baking oven was dismantled and the polymeric components were analysed. Since the authors did not detect SCCPs in this particular oven in the initial assessment with the wipe test inside the oven, only MCCP, PBDE and PCB concentrations were reported for the oven components. In any case, the authors assumed that SCCPs in the other ovens might also stem from the polymer parts of the baking oven itself, due to their high concentrations. SCCP concentrations inside the baking oven doors were one order of magnitude higher than

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[466] Wang C, Gao W, Liang Y, Wang Y, Jiang G. (2018). Concentrations and congener profiles of chlorinated paraffins in domestic polymeric products in China, Environ. Pollut. 238, 326-335.

[467] Wang C, Gao W, Liang Y, Jiang Y, Wang Y, Zhang Q, Jiang G. (2019) Migration of chlorinated paraffins from plastic food packaging into food simulants: concentrations and differences in congener profiles, Chemosphere 225, 557-564.

[468] Yuan B, Strid A, Ola P, De Wit CA, Nyström J, Bergman A. (2017). Chlorinated paraffins leaking from hand blenders can lead to significant human exposures, Environ. Int. 109, 73-80.

[469] Gallistl C, Sprengel J, Vetter W, (2018). High levels of medium-chain chlorinated paraffins and polybrominated diphenyl ethers on the inside of several household baking oven doors. Sci. Total Environ. 615, 1019-1027.

those reported in indoor dust in Germany (6000 ng g^{-1})[470] and in Sweden (7500 ng g^{-1})[471]; and at least 40 times higher than those reported in cooking oils.[472] Moreover, CPs emitted from baking ovens may contribute to their frequent detection in fat deposits, such as kitchen hoods (100% detection frequency; mean CP level of 3500 ng g^{-1} fat)[473] and dishcloths (58% detection frequency; mean CP level of 4900 ng g^{-1} fat).[474]

Monitoring of SCCPs in cutting fluids and lubricants

Cutting/metalworking fluids and lubricants are products that might contain a relevant share of CPs. Randegger-Vollrath (1998)[475] and Koh et al. (2000)[476] reported the presence of SCCPs, MCCPs and LCCPs in several cutting fluids and lubricants. 21 of 37 cutting fluid and lubricant samples (57%) contained CPs. The SCCP content in 1998 study ranged from 1 to 70% in eight samples (21%), while MCCPs with a chlorination degree of about 50% were measured in 11 samples (30%) and LCCPs were measured in only two samples (5%).[475] In 2000 CPs were measured in five cutting fluids provided by two German manufactures. MCCPs and LCCPs were quantified in two cutting fluid samples each, while SCCPs were quantified in only one. The authors reported that the CP content found (2–30%) corresponded with the manufacturer's specifications for each product.[476]

Monitoring of SCCPs in rubber products

Some of the products included in the section "Monitoring of SCCPs in consumer products at national markets" above were also rubber products. More specific studies are presented here.

SCCPs, MCCPs and LCCPs were measured in an assessment of car tires and its recyclates, such as rubber granulates and playground tiles, in the Netherlands.[477] Total CP (C_{10}–C_{30}) concentrations ranged from 1.5 to 67 µg g^{-1} in car tires, 13−67 µg g^{-1} in rubber granulates, and 16−74 µg g^{-1} in playground tiles. The similar concentration ranges in car tires and recycled products suggested that CPs were not introduced during shredder or moulding processes but were already present in car tires. Moreover, the authors suggested that the low CP content (maximum of 67 mg/kg) detected in car tires could indicate rather a contamination during the manufacturing process than an intentional CP application. Nevertheless, they estimated that tire wear particle (TWP) releases can be responsible for an annual input of 2–89 tons of CPs into the environment in the European Union. On the other hand, higher concentrations of SCCPs (up to 106 µg g^{-1}) and MCCPs (up to 442 µg g^{-1}) had been previously reported in car tires from China.

Besides of the CP content in car tires, the Chinese study of CPs in domestic polymeric products[466] also reported CP concentrations as high as 338 µg g^{-1} (SCCPs) and 3095 µg g^{-1} (MCCPs) in rubber tracks and 13,144 µg g^{-1} (SCCPs) and 22,774 µg g^{-1} (MCCPs) in conveyor belts.[466]

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[470] Hilger B, Fromme H, Völkel W, Coelhan M. (2013). Occurrence of chlorinated paraffins in house dust samples from Bavaria, Germany. Environ. Pollut. 175, 16-21.

[471] Fridén UE, Mclachlan MS, Berger U. (2011). Chlorinated paraffins in indoor air and dust: concentrations, congener patterns, and human exposure, Environ. Int. 37, 1169-1174.

[472] Cao Y, Harada KH, Liu W, Yan J, Zhao C, Niisoe T, Adachi A, Fujii Y, Nouda C, Takasuga T, Koizumi A. (2015). Short-chain chlorinated paraffins in cooking oil and related products from China. Chemosphere 138, 104.111.

[327] Wang C, Gao W, Liang Y, Wang Y, Jiang G. (2018). Concentrations and congener profiles of chlorinated paraffins in domestic polymeric products in China, Environ. Pollut. 238, 326-335.

[473] Bendig P, Hägele F, Vetter W. (2013). Widespread occurrence of polyhalogenated compounds in fat from kitchen hoods. Anal. Bioanal. Chem. 45, 7485-7496.

[474] Gallistl C, Lok B, Schlienz A, Vetter W. (2017). Polyhalogenated compounds (chlorinated paraffins, novel and classic flame retardants, POPs) in dishcloths after their regular use in households. Sci. Total Environ. 595, 303-314.

[475] Randegger-Vollrath. (1998). Determination of chlorinated paraffins in cutting fluids and lubricants. Fresenius' J. Anal. Chem. 360, 62-68.

[476] Koh IO, Rotard W, Thiemann WH. (2000). Analysis of chlorinated paraffins in cutting fluids and sealing materials by carbon skeleton reaction gas chromatography, Chemosphere 47, 219-227.

[477] Brandsma SH, Brits M, Groenewoud QR, van Velsen MJM, Leonards PEG, De Boer J. (2019) Chlorinated paraffins in car tires recycled to rubber granulates and playground tiles. Environ. Sci. Technol. 53, 7595-7603.

SCCPs and MCCPs were also later monitored in commercial rubber tracks and raw materials from China.[478] However, unlike the study from Netherlands[477], which found similar CP concentrations in rubber granulates and playground tiles, this study[478] found significantly higher concentrations of SCCPs (3.64 x 10^3 µg g^{-1}) and MCCPs (4.14 x 10^4 µg g^{-1}) in rubber track than SCCPs (2.78 µg g^{-1}) and MCCPs (2.51 µg g^{-1}) in rubber granulates. The CP content and CP congener profile in rubber tracks were similar to the adhesives used as raw material for rubber track manufacturing. The SCCP content in almost half of the rubber track samples exceeded the Chinese standard (GB 36246-2018) and the European Union limits of 0.15%.

Monitoring of SCCPs in adhesives and sealants

Adhesives were assessed in a previously mentioned study as raw material for rubber track production The SCCP and MCCP concentrations in adhesive samples were 62.5–7.14 x 10^3 and 43.4–2.20 x 10^5 µg g^{-1}, respectively. In four of five adhesive samples, the SCCP content exceeded the Chinese standard (GB 36246-2018) and the European Union limits of 0.15%.

Sealants were also assessed in a previously mentioned study, together with cutting fluids.[337] In that study six sealing products were purchased on the open market and ten products were collected in office buildings. Organochlorine compounds were already prohibited in commercial sealing materials in Germany at that time, thus, CPs were not measured in samples purchased at local markets. However, SCCPs were measured in 5 sealing samples applied in doors and windows of two offices and a university building and MCCPs were measured in only one sample applied in a door of a university building. SCCPs concentrations ranged between 9% and 12% and MCCPs showed a concentration of 16% of the product mass. The SCCPs found in sealing products were associated with the use of two commercial products (CP 56 and Hordalub 500) before its restriction in Germany. The MCCP content could not be further identified due to the lack of a reference CP.

Monitoring of SCCPs in plastic waste

Wastes containing SCCPs at concentrations above the Basel Convention low POP content values must be destroyed or irreversibly transformed in an environmentally-sound manner. Matsukami et al. (2020)[479], developed a novel LC-ESI-MS^2 method to determine SCCP concentrations in mixed plastic wastes. Seven samples were prepared using mixed plastic waste (60–70% plastics, 20–30% papers and <5% fabrics) from seven industrial waste-processing facilities in Japan. The results suggest that mixed plastic waste currently undergoing disposal may be contaminated with SCCPs. However, the SCCP contents in mixed plastic wastes (<LOD–2,700 ng g^{-1}) were lower than those in domestic solid waste previously analysed in Japan (7,600 ng g^{-1})[480] and two orders of magnitude lower than the two provisional limits of low POP contents (100 or 10,000 mg/kg) adopted by the Basel Convention.

Monitoring of SCCP release from thermal treatment of PVC flooring

A simulated thermal processing of PVC plastics demonstrated that SCCPs can be abruptly released during PVC thermal treatment.[481] It was estimated that within the initial 1h treatment of PVC flooring, the overall release of SCCPs was equivalent to approximately 2%, 7% and 11% of the product mass at heating temperatures of 100 °C, 150 °C and 200 °C, respectively. In an 8 h long treatment the SCCP release could reach 43% of the product mass. However, increasingly heating time gradually decreased the release rates of SCCPs. The highest release rates were observed to shorter chain length SCCPs and they were mostly in

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[478] Xu C, Gao L, Zheng M, Qiao L, Cui L, Wang K, Huang D. (2019) Short- and medium-chain chlorinated paraffins in commercial rubber track products and raw materials, J. Hazard Mater. 380, 120854.

[479] Matsukami H, Takemori H, Takasuga T, Kuramochi H, Kajiwara N. (2020). Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes. Chemosphere. 244, 125531.

[480] Matsukami, H, Kajiwara, N. (2019). Destruction behavior of short- and medium-chain chlorinated paraffins in solid waste at a pilot-scale incinerator. Chemosphere. 230, 164-172.

[481] Zhan F, Zhang H, Wang J, Xu J, Yuan H, Gao Y, Su F, Chen J. (2017). Release and gas-particle partitioning behaviors of short-chain chlorinated paraffins (SCCPs) during the thermal treatment of polyvinyl chloride flooring, Environ. Sci. Technol. 51, 9005-9012.

the gas-phase during the thermal treatment of PVC flooring at 100 °C, while at 150 °C and 200 °C SCCPs tended to be released in the particle-phase. The high concentrations of SCCPs emitted to air (63–183 µg m^{-3}) during the thermal treatment of PVC plastics was comparable to real conditions for PVC processing and recycling plants. Therefore, PVC processing and recycling could result in a considerably high risk for occupational inhalation exposure to SCCPs.[339] Moreover, unintentional thermal stresses of PVC plastics, such as PVC melting in recycling, open burning of solid waste or from fire accidents and short circuit current of PVC cables could release even more SCCPs into the environment and lead to higher risk of inhalation exposure

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Annex 2-G Case studies of unintentional POPs in products and other matrices

Review on new information on unintentional POPs in chemicals[482]

The UNEP BAT/BEP group published a review on new information on formation and release of UPOPs from production processes for pesticides and industrial chemicals.[482] This is compiled for reducing or preventing releases and related information gaps from UPOPs in chemicals. 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 UPOPs. One aim was to help to assess and improve these processes where systematic BAT/BEP is not yet applied and to help in developing better inventories of UPOPs in these processes and chemicals.[482] Information gaps for individual chemicals are included[482] to stipulate monitoring/screening of UPOPs in chemicals.

Screening of unintentionally POPs in chloranil[483]

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 and 1% of global dioxin inventory[224], but present directly in treated consumer products. PeCB, HCB, and PCBs were also detected in these chemicals in high concentrations[483].

Monitoring of pesticides for unintentionally POPs[484,485]

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 and above regulatory limits established in other countries.

In another study current used pesticides in Australia were screened for PCDD/PCDF. PCDD/PCDF were detected in all pesticide formulation with high levels in PCNB.[484,485] PeCB and HCB were not screened in this study but it was stressed that PCNB degrades to PeCB in the environment (approx. 3%). POPRC acknowledged that this is the largest source of unintentional PeCB larger than all other sources combined.[486]

Monitoring of pesticides for dioxin-like toxicity[487]

Chlorinated pesticides commonly used in the Red River Valley of Minnesota were collected and assayed for dioxin-like activity by a reporter gene bioassay (CALUX). Of the twelve pesticides assayed, ten had measurable dioxin toxic equivalency (TEQ) and four had TEQs of over 1 µg TEQ/kg (above the lower provisional Basel Convention low POP content). In order to confirm the presence of PCDD/Fs and provide a congener profile of dioxins in these pesticides, GC/HRMS analysis on several of these same pesticides. For six of the samples, the TEQs from both methods correlated quite well, although the CALUX TEQs tended to be higher than the HRGC-

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[482] 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

[483] 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.

[484] 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.

[485] 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.

[486] 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.

[487] Huwe JK, Clark GC, Chu AC, Garry V (2003) CALUX and high resolution GC/MS analysis of dioxin-like compounds of chlorphenoxy pesticides. Organohalogen Compd, 60, 227-230. http://dioxin20xx.org/wp-content/uploads/pdfs/2003/03-58.pdf

MS results by 1.3−3 fold (Table A2-G-1). Two pesticide samples (Bronate and Assure II) differed greatly in the response of the CALUX bioassay and the HRGC-MS. This divergence is most likely due to dioxin-like compouds other than PCDD/PCDFs. The CALUX bioassay measure all dioxin-like compounds including e.g. brominated dioxins or other dioxin-like compounds. Therfore the bio-assay result indicate the entire dioxin-like risk of a pesticide or other product. The active ingredients in Bronate and Assure II contain halogenated aromatic moieties that possess some affinity for the aryl hydrocarbon receptor and elicit a CALUX respons. These substance are unfortunately not yet regulated. And in many countries also PCDD/PCDFs in pesticides are not yet regulated.

Table A2-G-1: Composition and TEQs (pg/g) of screened chlorophenoxy pesticides. 2,4-D = 2,4-dichlorophenoxyacetic acid; MCPA = 4-chloro-2-methylphenoxyacetic acid; EH = ethylhexyl.

Pesticide	Collection Year	Active Ingredients	CALUX TEQ (n=3)	HRGC-MS TEQ
2,4-D Amine	1993	2,4-D dimethylamine, 46.9%	26.2 ± 0.5	8.7
See 2,4-D	1993	2,4-D isooctylester, 61.7%	1637 ± 212	731
2,4-D LV4	1993	2,4-D isooctylester, 66.2%	3392 ± 257	2627
2.4-D LV6	1993	2,4-D isooctylester, 88.8%	1882 ± 311	1379
Weedone LV4	1998	2,4-D isooctylester, 67.2%	45.7 ± 4.1	27.7
Tiller	1998	MCPA-2EH ester, 32.1% 2,4-D isooctylester, 10.4% Fenoxaprop-p-ethyl, 4.4%	34.2 ± 4.1	19.8
Bronate	1998	Bromoxynil octanoic acid ester, 31.7% MCPA isooctyl ester 34%	800 ± 180	0.3
Assure II	1998	Quizalofop-p-ethyl, 10.3%	1668 ± 419	4.1

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Monitoring of dioxin-like toxicity of releases of the chlorine industry (Netherlands)[488]

A governmental institute in The Netherlands screened industrial processes and products of the chlorine chain industries for dioxin-like toxicity. The main objectives of the study were: 1) to assess whether and if so, to what extent unknown chlorinated compounds with PBT properties (accepted or potentially persistent, bioaccumulative and/or toxic compounds) or groups of compounds with PBT properties are emitted from the Dutch chlorine chain and 2) to contribute to the assessment of the environmental impact of these emissions.[488]

The toxicological assessment of wastewater effluents included both *in vivo* testing and *in vitro* bioassays for compounds with dioxin-like or estrogenic modes of action. Toxicity screening for impurities in products and incinerator emissions was limited to the DR-CALUX *in vitro* bioassay. Where relevant, the presence of dioxins (PCDD/Fs) was confirmed with instrumental analysis. The results of the present study indicate that chlorinated substances with potential PBT properties are present (and are probably being formed and emitted) as impurities in some production processes in the chlorine chain. Dioxins and some other chlorinated compounds with known or potential PBT properties, as well as tentatively identified and partially characterised chlorinated compounds were found to be present in various samples, especially in some product samples.[488] Dioxins (PCDD/Fs) were found in three of the eleven products sampled with elevated levels in chloroprene rubber. Moreover HCB and PeCB were identified in some products and PCP in one product. A substantial number of other chlorinated compounds were tentatively identified in various products which may have P and B characteristics.[488] The bio-assay showed in several samples much higher dioxin-like TEQ compared to instrumental analysis[488] highlighting that other dioxin-like compounds were present in some processes in high concentration.

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[488] van Hattum B, Senhorst H, Tukker A, Lamoree M, Sanderson T, de Koning A (2004) Evaluation of current emissions of chlorinated microcontaminants from the Dutch chlorine chain: Final Technical Report. IVM Report E-04/08, Vrije Universiteit, Amsterdam. http://www.ivm.vu.nl/en/Images/OVOC_final_technical_report_tcm234-189202.pdf

Monitoring of dioxin-like toxicity of feed additives (Chile)[489]

It is known from several that mineral premixes supplement in feed such as zinc oxide could be a source of PCDD/PCDF exposure. The Chilean government carried out a surveillance program for PCDD/PCDF and dl-PCBs in mineral feed additives by DR CALUX for food safety purpose.[489] The results confirmed that zinc oxide and mineral clay are main mineral ingredients which can cause higher Total-TEQ levels (Figure A2-G1). From 92 tested minerals, 5 (5.4%) were higher than the EU limit for PCDD/PCDF-DL-PCB-TEQ of 1.5 ng/kg and 7 (7.6%) samples were higher than the EU limit for PCDD/PCDF-TEQ of 0.75 ng/kg (Figure A2-G1).[489] Contaminated zinc oxide from a smelting process was the primary source of dioxins.

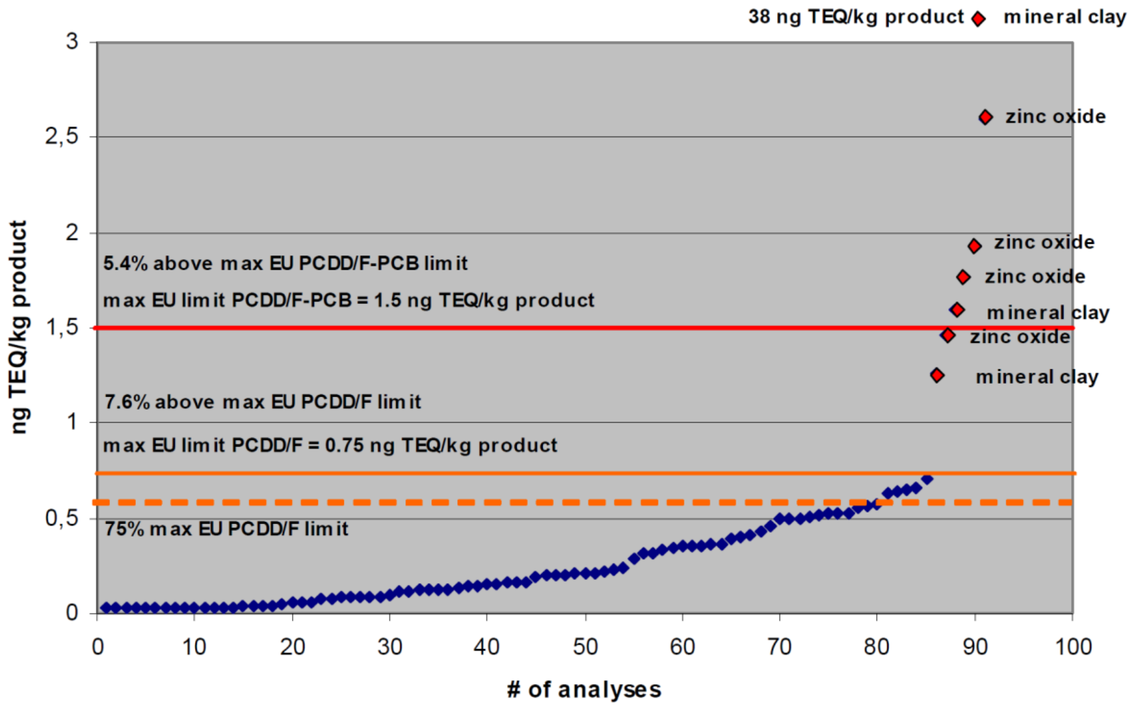

Figure A2-A-1: Distribution of Total PCDD/PCDF/dl-PCB-TEQ data analysed by DR CALUX▯▯from several mineral items from Chile (Behnisch et al. 2010)[489]

Monitoring of dioxin-like toxicity in plastic children toys[490]

6 toys were selected from a larger toy screening[491] which contained a total PBDE content (>500 ppm) and DecaBDE content (>250 ppm) in their black component. All toys were made in China but purchased in different countries. Sample 1 was a puzzle cube from Argentina, Sample 2 was a hair clip from Czech Republic, Sample 3 a key fob puzzle cube, Sample 4 and 5 were puzzle cubes from India and Nigeria respectively, Sample 6 was a toy guitar from Portugal.[490] GC-HRMS-based TEQ calculated using PCDD/F TEF were up to 3821 pg TEQ/g. CALUX activities were found in all samples tested and, the total dioxin-like activity ranged from 230 to 1520 pg 2,3,7,8-TCDD BEQ/g for the DR CALUX and from 640 to 2550 pg 2,3,7,8-TCDD BEQ/g for the DR$_{\text{human}}$ CALUX. The PBDD/PBDF concentration were 5.6 ng/g to 386 ng/g total PBDD/PBDF and 41 to 3821 pg TEQ/g calculated from instrumental analysis.[490] Differences between TEQs/BEQT and the total BEQ values may be explained by the presence of other, compounds in the mixtures, acting as agonists and antagonists of the AhR in particular PBDEs present in the samples at much higher concentration.[490] Such agonistic and antagonistic activities are known from PCBs. An estimate was made of the daily ingestion of TEQs from PBDD/Fs-contaminated plastic

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[489] Behnisch PA, Gras N, Guerrero P, et al (2010) First surveillance monitoring results of feed/food items from Chile by DR CALUX®. Organohalogen Compounds 72, 1715-1718 http://dioxin20xx.org/wp-content/uploads/pdfs/2010/10-1649.pdf

[490] Budin C, Petrlik J, Strakova J, et al. (2020). Detection of high PBDD/Fs levels and dioxin-like activity in toys using a combination of GC-HRMS, rat-based and human-based DR CALUX® reporter gene assays. Chemosphere. 251:126579.

[491] Strakova, J., Digangi, J., K Jensen, G., Petrlik, J., Bell, L., 2018. Toxic Loophole: RecyclingHazardous Waste into New Products. Report of the International POPs Elimination Network, https://doi.org/10.13140/RG.2.2.21990.68164.

toys by child mouthing habits. It was observed that the daily ingestion of PBDD/Fs from contaminated plastic toys may significantly contribute to the total dioxin daily intake of young children.[490]

Total PBDD/PBDF in plastic and other polymers from the approx. 1.5 million tonnes of PBDEs produced was estimated in another study to 1000 tonnes [385] and is one of the larges reservoir of dioxin-like compounds.

Screening of unintentionally POPs in HCl[492]

Wang et al. (2014)[492] screened HCl from different production processes. The secondary by-product HCl from the production of chlorinated paraffins (n=2) had an average concentration of PCDD/PCDF in HCl of 8.95 ng/L with consistent levels in both samples. For HCl from other chlorinated organic compounds in the chlor-alkali industry (n=8) the PCDD/PCDF were 0.78 ng/L. Furthermore 8 HCl samples from printed circuit etching processes were measured with average PCDD/PCDF amount of 82.9 ng/L (1.26 ng TEQ/L) and maximum values of 540 ng L-1 (20.6 ng TEQ/L).[492] The origin and respective processes of these 8 HCl samples was not clarified in this study. The use of such HCl in the recovery of copper was the PCDD/PCDF source in the production of thousands of tonnes of $CuSO_4$ per year for feeding of pigs.[492]

Monitoring of HCB in pigments[493,494]

The Japanese government submitted two reports on HCB in Tetrachlorophthalic acid (TCPA, tetrachloro-1,2-benzenedicarboxylic acid)[495] 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[493] and 2007[494]). 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 mg/kg and the suggested BAT levels for TCPA and pigments were in mg/kg range (up to 200 mg/kg).

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[496]

A first assessment of UPOPs 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 analysed, had lower-bound PCDD/PCDF concentrations that ranged from 133 to 545 µg TEQ/t.[496] LCCPs produced from an East Asian country were found to have total PCB concentrations ranging from 140 to 210 mg/kg, with a mean of 165 mg/kg, as well as HCB concentrations ranging from 6.1 to 8.9 mg/kg, with a mean of 7.7 mg/kg. Considerable lower levels of PCB (0.04 mg/g) and HCB (0.007 mg/kg) were detected in a CP sample from another East Asian country with legislation in place limiting UPOPs in chemicals and products.[496]

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[492] Wang P, Zhang Q, Lan Y, Xu S, Gao R, Li G, Zhang H, Shang H, Ren D, Zhu C, Li Y, Li X, Jiang G (2014) Dioxins contamination in the feed additive (feed grade cupric sulfate) tied to chlorine industry. Sci Rep. 4:5975. doi:10.1038/srep05975.

[493] 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.

[494] 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.

[495] The dimethyl ester of tetrachlorophthalic acid is used as an herbicide, Dachtal.

[496] 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 HCB, PCB, PCDD/PCDF in chlorinated paraffins[497]

The production of chlorine by the chlor-alkali process using graphite electrodes was one of the largest sources of PCDD/PCDFs in history with estimates in the kg TEQ range for individual factories. Chlorination of foal tar used as pitch binder for electrodes in the chlor-alkali process and was the major source for formation of PCDD/PCDFs and other UPOP. The complex PAH mixture in the tars which were chlorinated in the processes contained approx. 1% dibenzofuran. The full range of chlorinated aromatic and heteroaromatic compounds in contaminated soils from former chlor-alkali plants in Germany and Japan using GC-HR-TOF-MS. At all investigated sites the full range of UPOPs (PCDFs, PCDDs, PCBs, PCNs, HCB, HCBD and PeCBz) were present at high ppb levels and TEQ was up to several 100,000 ng/kg soil in hot spot areas. Additionally, a wide range of other polychlorinated (PC-) PAHs (PC-phenanthrene/anthracene, PC-pyrene/fluoranthene, PC-benzo(a)anthracene/chrysene) were detected. Some of these compound classes were present in one to two order of magnitude higher concentrations compared to PCDFs. Furthermore, polychlorinated methyl-dibenzofurans, polychlorinated dimethyl-/ethyl-dibenzofurans, and polychlorinated carbazoles – the N-analogue of dibenzofuran - were detected at levels comparable to PCDFs at all three sites. Polychlorinated benzonitriles were detected in addition to chlorobenzenes as monoaromatic pollutant. Since the factories have stopped production 50–120 years ago, all detected chlorinated (hetero)aromatics can be regarded as very persistent. The technologies have been used in several hundred locations globally. The study concluded that these (former) chlorine production sites should be assessed for contamination and their contemporary threat to humans and the environment considering the overall risk of the UPOPs and additional mixture of chlorinated (hetero)aromatic compounds.

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[497] Takasuga T, Takemoria H, Yamamoto T, Higashino K, Sasaki Y, Weber R (2020) Comprehensive monitoring of chlorinated aromatic and heteroaromatic pollutants at sites contaminated by chlorine production processes to inform policy making. Emerging Contaminants 6, 133-142. https://doi.org/10.1016/j.emcon.2020.03.001.

Annex 2-G2 Case studies of HCBD screening in products and materials

A few countries or institutes have performed screening of HCBD in 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.

HCBD and other UPOPs in by-product of chloromethane production[498]

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, HCB, and PeCB were found in the carbon tetrachloride by-product of the methanol-based production of chlorinated methanes.[498] The total emission amounts during the production of chlorinated methanes in China of HCBD in 2010 was estmimated to 7350 kg.[498] Furthermore large amounts hexachloro-cyclopentadiene, PCBz, PCNs, octachlorostyrene, and PCB release were estimated to be 10080, 5210, 427, 212, and 167 kg, respectively.[498] Also PCDD/Fs were detected in the by-product.[498]

Monitoring of unintentional HCBD and HCB in industrial processes[499]

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, perchloroetylene, 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[499]. 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).[499]

Table A2-3: Estimated total quantity of HCBD and HCB contained in U.S. industrial wastes, by-products, and products in 1972 (Mumma and Lawless 1975)[499]

	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	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)
Total	6,538.5 (14,530)	3,276 (7,280)	2,198 (4,884)	1,093 (2,429)

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[498] 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.

[499] 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).

Analysis of HCBD in drinking water close to organochlorine landfills in the US[500]

Ground water that was used as a source of potable water by residents of a small community became contaminated by leachate from a waste dump of 300,000 pesticide/organochlorine barrels. High levels of HCBD and carbon tetrachloride was detected in the drinking water.[500] 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.[500] 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.[500]

Analysis of HCBD in drinking water close to organochlorine landfills in Switzerland[501]

In 2006, Greenpeace Switzerland analysed this drinking water by GC/MS screening and found a range of chemicals including HCBD and tetrachlorobutadiene.[501] 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.[501] Also the water supplier "Hardwasser AG" had already detected HCBD and tetrachlorobutadiene in the drinking water in 1980 and 2005 without publishing the results.[501] 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[502] and the authorities forced the drinking water supply company to treat the drinking water.[501]

Analysis of HCBD in fish around landfills from organochlorine production[503,504]

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.[504]

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[500] 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.

[501] 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.

[502] Swiss Federal Office of Public Health (2010) Toxikologische Beurteilung von polychlorierten Butadienen im Trinkwasser. Faktenblatt, Bern, 27.4.2010.

[503] U.S. EPA (2004) HRS Documentation Record Devil's Swamp Lake (LAD981155872). EPA Region 6 (214) 665-7436 Superfund Site Assessment Section (6H-MA).

[504] 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 Examples for instrumental analysis

Acknowledgement: The analytical conditions and chromatograms were mainly provided by Prof. Dr. Dr. Takumi Takasuga (Shimadzu Techno Research, Kyoto, Japan), and some by Drs. Sachi Taniyasu, Eriko Yamazaki, Nobuyoshi Yamashita (National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan); Dr. Natsuko Kajiwara, (National Institute for Environmental Studies (NIES); Tsukuba, Japan); Dr. Kerstin

Annex 3-A: GC/MS analysis of PBDE (instrumental setting and chromatogram)

GC/MS conditions for PBDE analysis (example)

An example of instrumental setting for the GC/MS analysis of PBDEs are given in Table A3-A1 and the exact masses of native and ^{13}C-labled HBB in Table A3-A2.

A chromatogram of PBDEs from GC/MS analysis is shown in Figure A3-A1.

Table A3-A1: 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}C-labelled PBDE homologues are listed in Table A3-A2

Table A3-A2: 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[$^{13}C_{12}$]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[$^{13}C_{12}$]diphenylether	577.6598	575.6618
Hexabromo[$^{13}C_{12}$]diphenylether(M-2Br)	495.7357	493.7377
Heptabromo[$^{13}C_{12}$]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[$^{13}C_{12}$]diphenylether(M-2Br)	573.6462	575.6442
Perfluorokerosene	566.9665	
Octabromodiphenylether (M-2Br)	641.5145	639.5165
Octabromo[$^{13}C_{12}$]diphenylether(M-2Br)	653.5546	651.5567
Perfluorokerosene	642.9601	
Nonabromodiphenylether (M-2Br)	719.4250	721.4230
Nonabromo[$^{13}C_{12}$]diphenylether(M-2Br)	731.4651	733.4631
Perfluorokerosene	730.9537	
Decabromodiphenylether (M-2Br)	799.3335	797.3355
Decabromo[$^{13}C_{12}$]diphenylether(M-2Br)	811.3737	809.3757
Perfluorokerosene	804.9505	

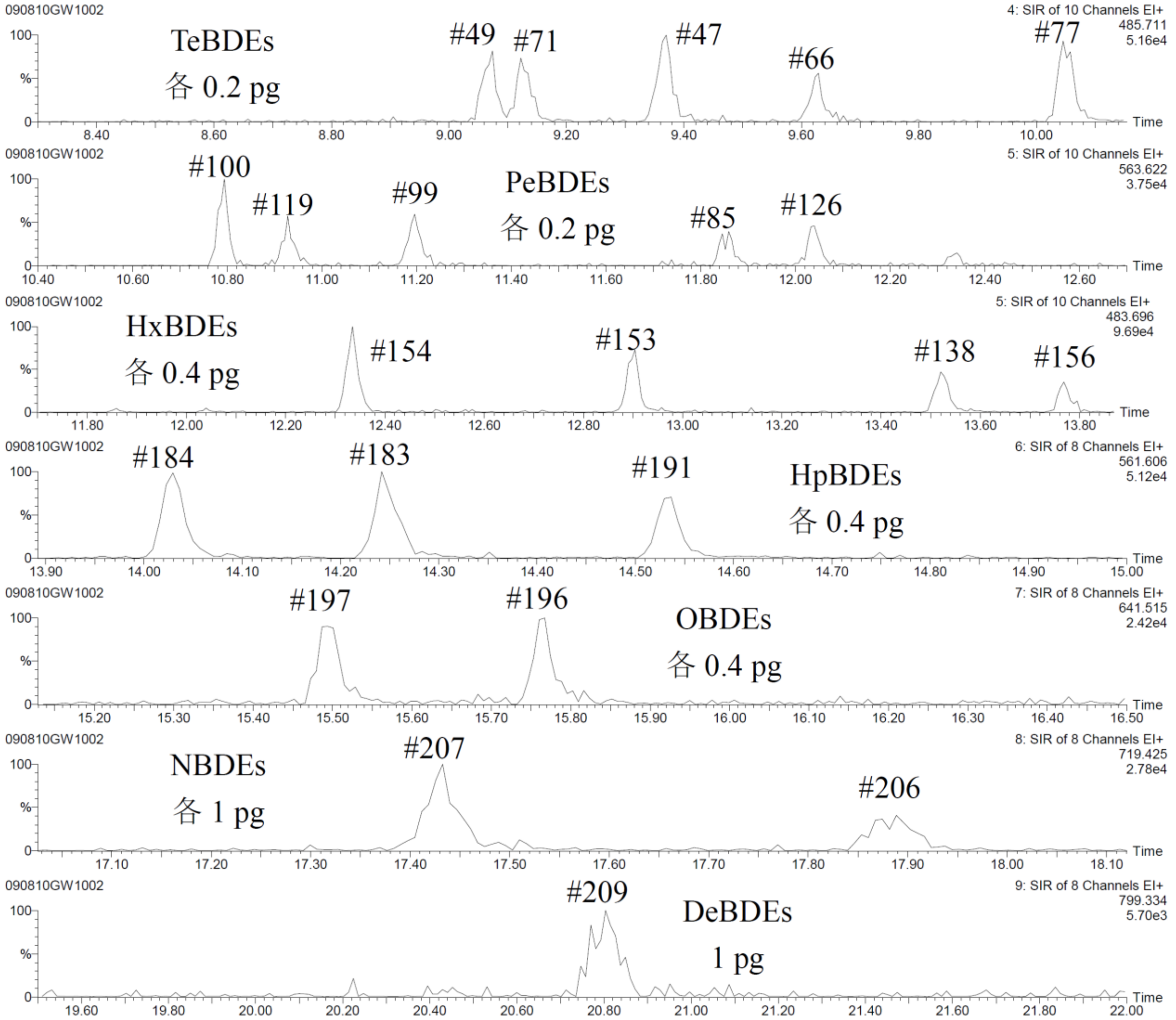
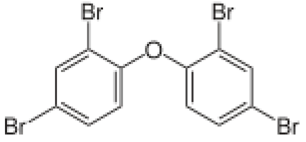
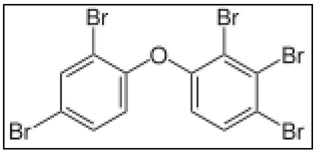
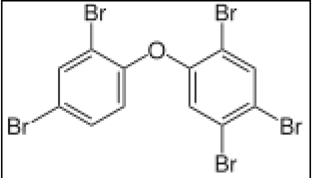
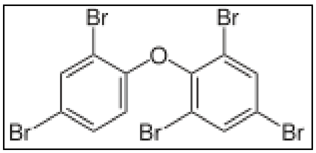
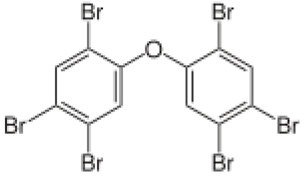
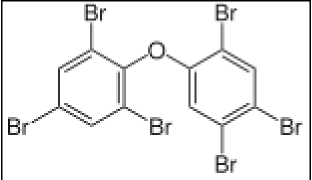


Figure A3-A-1: Chromatogram of tetraBDE to decaBDE (Please note that only tetraBDE, pentaBDE, hexaBDE and heptaBDE are listed as POPs)

Major PBDE congeners in commercial mixtures

Table A3-A-3 and A3-A-4 list the major PBDE in c-PentaBDE and c-OctaBDE present in products where these mixtures have been applied[505]

Table A3-A-3: Major PBDEs in commercial PentaBDE[445]

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

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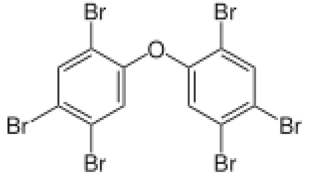
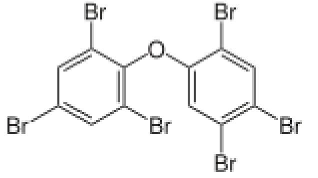
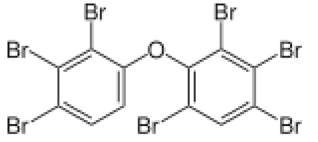
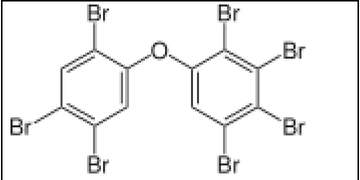
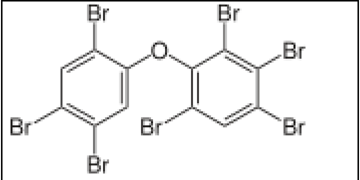
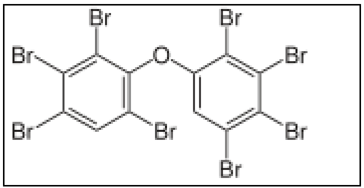
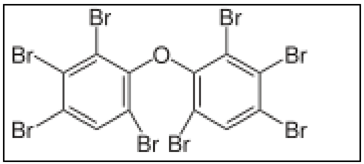
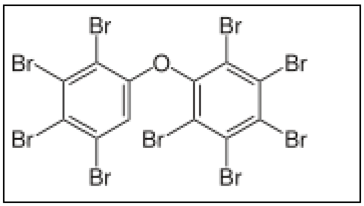
[505] La Guardia MJ, Hale RC, Harvey E (2006) Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-retardant Mixtures, Environ. Sci. Technol. 40, 6247–6254.

Table A3-A-4: Major PBDEs and other PBDE congeners in c-OctaBDE in treated products[505]

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 3-B: GC/MS and GC-ECD analysis of PBDE and HBCD (instrumental setting and chromatogram)

Example of PBDEs GC/MS and ECD conditions (Eguchi et al., 2021)[506]

An example of instrumental setting for the rapid analysis of PBDEs and HBCD by GC/MS and GC-ECD are given in Table A3-B-1. Chromatograms of PBDE homologues and HBCD from GC/MS and GC-ECD analysis are shown in Figure A3-B-1 and A3-B-2, respectively.

Table A3-B-1: Instrument settings for PBDE and HBCD analysis

Gas chromatograph	
Injection method	Splitless (1 min)
Injector temperature	300°C
Liner/insert	without glass wool
Injection vol.	0.5 µL
Oven temperature	High-power oven: 100°C (1 min) – 65°C/min-175°C (0min) – 45°C/min – 300°C (0 min) – 35°C/min – 320°C (0.5 min) 100V oven: 150°C (1 min) – 40°C/min-200°C (0min) – 15°C/min – 320°C (1 min)
Column	DB-5ht (5 m × 0.25 mm, 0.1 µm) (Agilent J&W)
Carrier gas	Helium
Velocity	High-power oven: 2.2 mL/min (Constant flow) 100V oven: 1.87 mL/min (Constant flow)
Mass spectrometer	
Ion mode	Selected ion monitoring (SIM)
Interface temperature	300°C
Ion source temperature	230-300°C
Ionization energy	70 eV
Target ions	
TetraBDE (M^+)	*m/z* 485.7
$^{13}C_{12}$-TetraBDE (M^+)	*m/z* 497.7
PentaBDE (M^+)	*m/z* 563.6
$^{13}C_{12}$-PentaBDE (M^+)	*m/z* 575.6
HexaBDE ($[M-2Br]^+$)	*m/z* 483.7
$^{13}C_{12}$-HexaBDE ($[M-2Br]^+$)	*m/z* 495.7
HeptaBDE ($[M-2Br]^+$)	*m/z* 561.6
$^{13}C_{12}$-HeptaBDE ($[M-2Br]^+$)	*m/z* 573.6
OctaBDE ($[M-2Br]^+$)	*m/z* 641.5
$^{13}C_{12}$-OctaBDE ($[M-2Br]^+$)	*m/z* 653.5
NonaBDE ($[M-2Br]^+$)	*m/z* 719.4
$^{13}C_{12}$-NonaBDE ($[M-2Br]^+$)	*m/z* 731.4
DecaBDE ($[M-2Br]^+$)	*m/z* 799.4
$^{13}C_{12}$-DecaBDE ($[M-2Br]^+$)	*m/z* 811.4
HBCD ($[M-Br]^+$)	*m/z* 560.8
$^{13}C_{12}$-HBCD ($[M-Br]^+$)	*m/z* 572.8
Electron capture detector	
Detector temperature	330°C
Makeup gas	Nitrogen
Flow rate of makeup gas	20 mL/min

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[506] Eguchi A, Matsukami H, Takahashi A, Kajiwara N (2021) Simultaneous determination of polybrominated diphenyl ethers and hexabromocyclododecane in plastic waste by short-column gas-chromatography-quadrupole mass spectrometry and electron capture detector. Chemosphere 277, 130301.

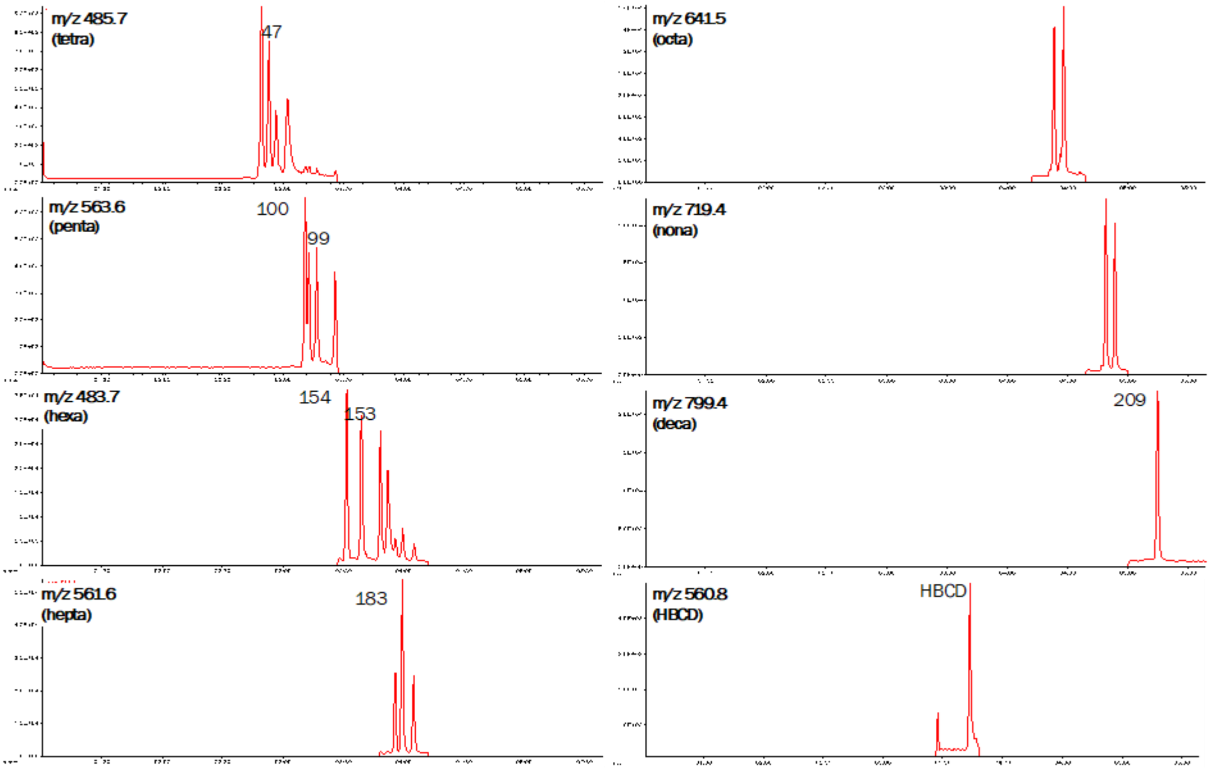


Figure A3-B-1: GC/MS chromatograms of PBDE and HBCD

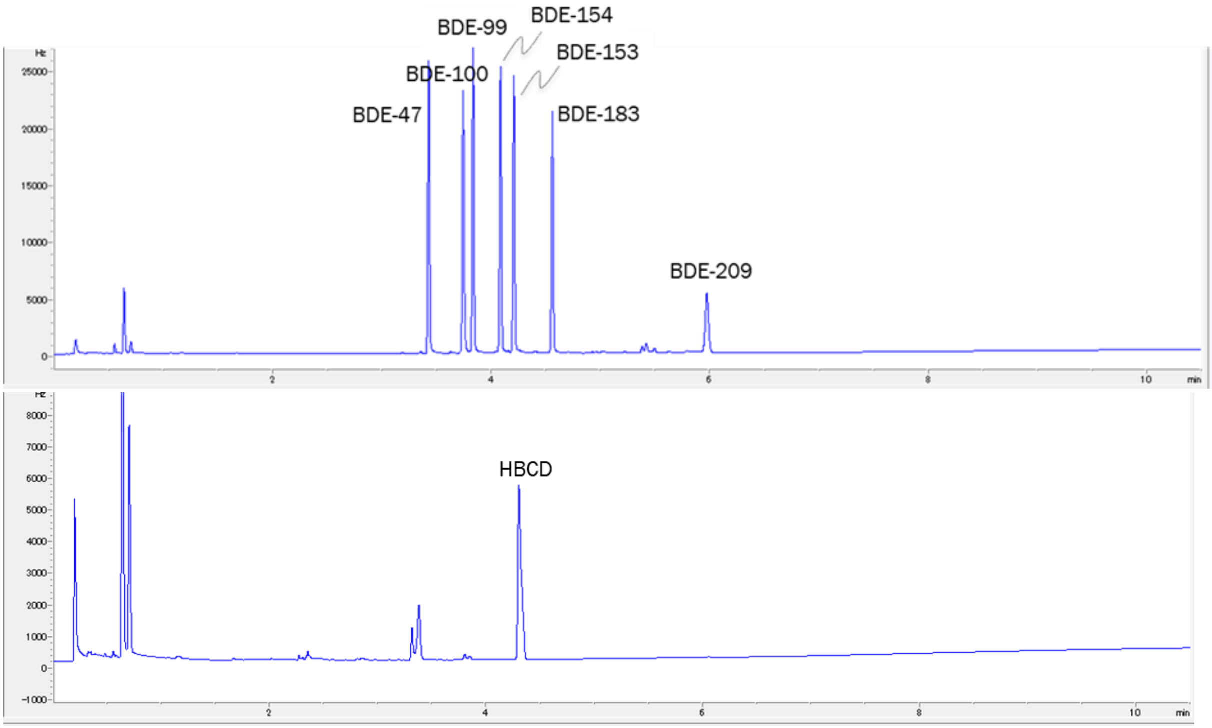


Figure A3-B-2: GC-ECD chromatograms of PBDE and HBCD

Annex 3-C: 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 A3-C-1 and the exact masses of native and ^{13}C-labled HBB in Table A3-C-2.

A chromatogram of HBB from GC/MS analysis is shown in Figure A2-2 and A2-3.

Table A3-C-1: 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 A3-C-2: Masses of detected ions (*m/z*'s) for HBB

	Quant.	Confirm.
Hexabromobiphenyl	**627.5352**	**625.5372**
Hexabromo[13*C*12]biphenyl	**639.5754**	**637.5775**
Hexabromo[13*C*12]diphenylether	**655.5703**	**653.5723**
Perfluorokerosene	**642.9600**	

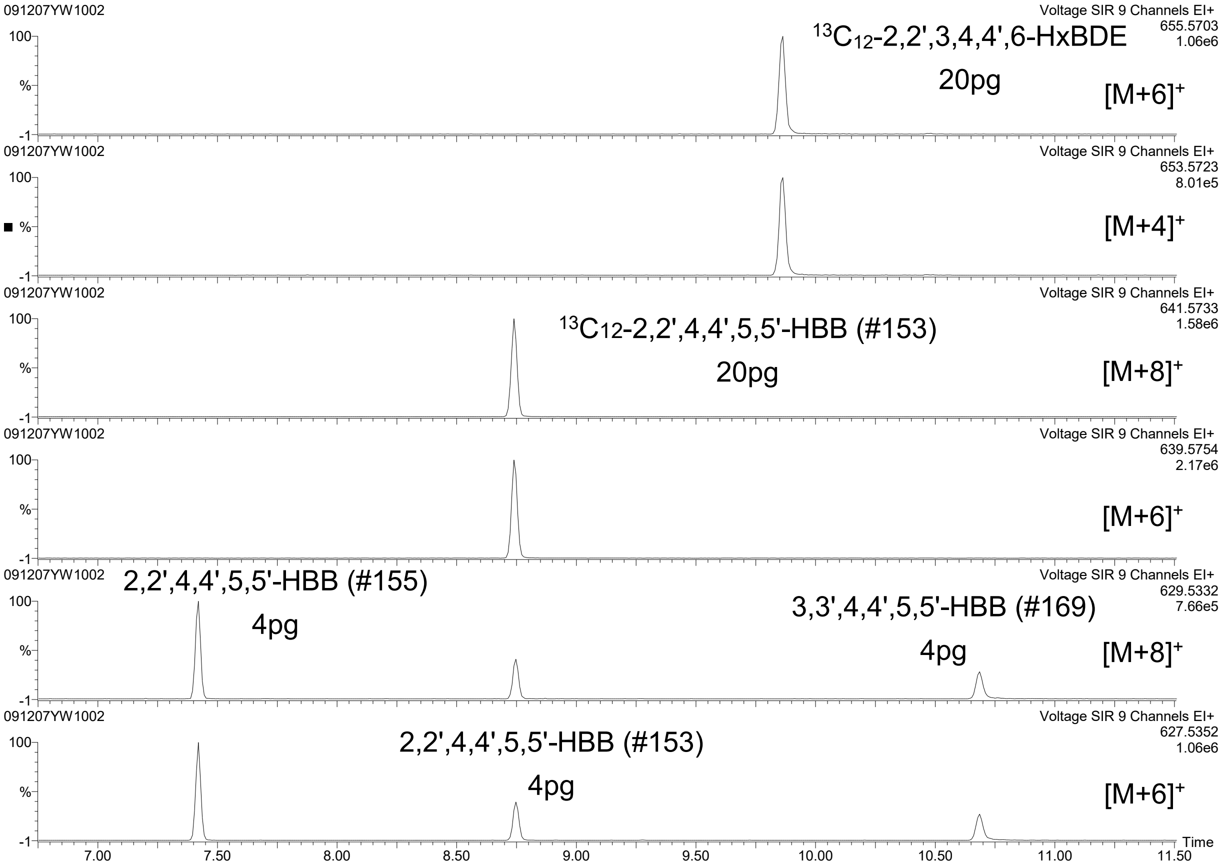


Figure A3-C-1: Chromatogram of native HBB congeners and $^{13}C_{12}$-HBB

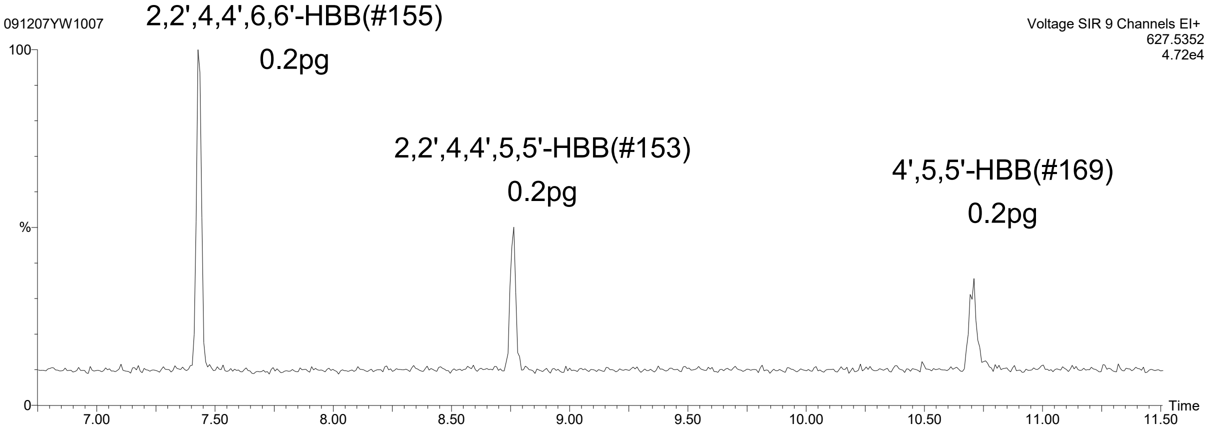


Figure A3-C-2: Chromatogram of native HBB congeners

Annex 3-D: 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}C-labled PCP is given in Table A3-D-1.

A chromatogram of PBDEs from GC/MS analysis is shown in Figure A3-D1.

Table A3-D-1: PCP GC/MS conditions (example)

GC condition	
Instrument	GC
GC column	Restek Rtx-5MS 30 m×0.25 mm×0.25 µm
Column Temp.	40°C (2 min) → 10°C /min →290°C (2 min)
Injection	split less
Injector Temp.	250°C
Injection volume	1 µL
MS condition	
Instrument	LRMS or HRMS
Ionization	EI
Interface Temp.	230°C
Ion source Temp.	230°C
PCP-TMS	m/z 323; 325
$^{13}C_6$-PCP-TMS	m/z 329

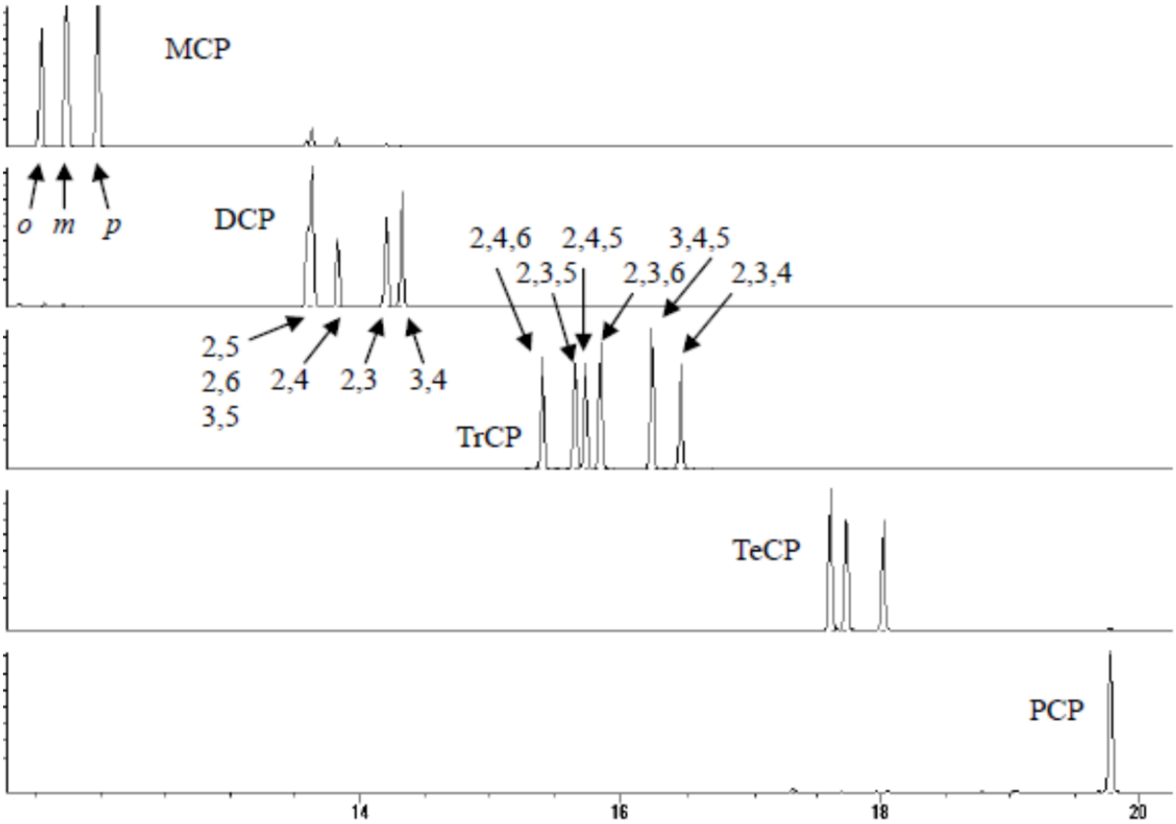


Figure A3-D-1: Chromatogram of PCP and other chlorinated phenols (not listed in the convention); (Chloropenols TMS derivatization. GC column; Rtx-5MS 30 m)

Annex 3-E: 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 A3-E-1 and the exact masses of native and ^{13}C-labled PCNs in Table A3-E-2.

A chromatogram of PCN homologues from GC/MS analysis is shown in Figure A3-E-1.

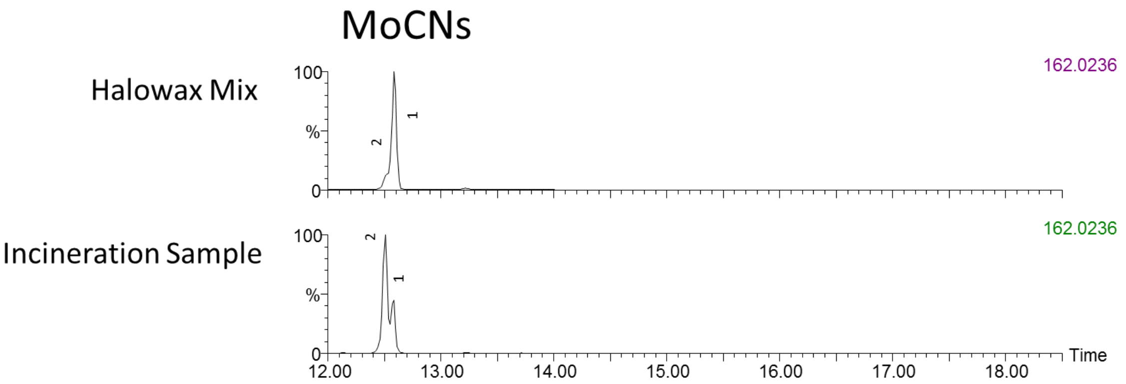
Table A3-E-1: PCP GC/MS conditions (example)

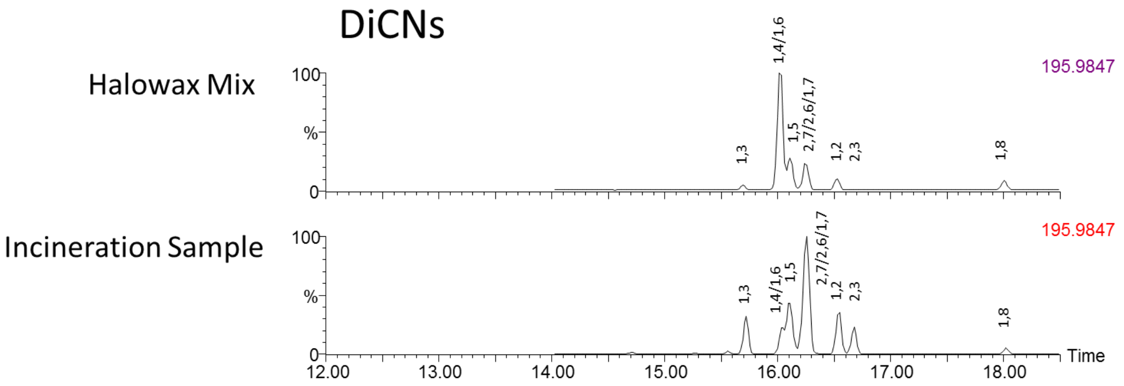
GC column	DB-5MS（Agilent Technologies/J&W）fused silica capillary column ID 0.32 mm, length 60 m, thickness 0.25 µm
Oven Temp.	90°C (2 min hold) - (20°C/min)→160°C - (3°C /min) →245°C -(5 C/min) →310°C（2 min hold）
Injection	On-column or Split less
Injector Temp. (On-column)	90 C(1 min hold)－（100 C/min）→300 C
Injection volume	1～2 µL
HRMS condition	Autospec Ultima （Waters/Micromass）
Ionization	EI
Ionization voltage	35 V(35～70 V)
Ionization current	500 µA
Accelerating voltage	8 kV
Ion source Temp.	290～300 °C
Interface Temp.	290～300 °C
MS resolution	10 000

Table A3-E-2: Masses of detected ions (*m/z*'s) and isotope ratio for PCNs

	CL degree	M^+	$(M+2)^+$	$(M+4)^+$
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	$^{13}C_{10}$-DiCN	206.0183(100)	208.0152(64.0)	
	$^{13}C_{10}$-TeCNs	273.9402(78.2)	275.9373(100)	
	$^{13}C_{10}$-PeCNs		309.8983(100)	311.8954(64.0)
	$^{13}C_{10}$-HxCNs		343.8593(100)	345.8564(80.0)
	$^{13}C_{10}$-HpCN		377.8204(100)	379.8174(95.9)
	$^{13}C_{10}$-OcCN		411.7814(89.4)	413.7785(100)
	$^{13}C_{12}$-DiCB*,**	234.0406(100)	236.0376(65.6)	
	$^{13}C_{12}$-TrCB*	268.0016(100)	269.9986(98.0)	
	$^{13}C_{12}$-TeCB**	301.9626(78.2)	303.9597(100)	
	$^{13}C_{12}$-PeCB*		337.9207(100)	339.9177(65.3)
	$^{13}C_{12}$-HxCB*		371.8817(100)	373.8788(81.5)
	$^{13}C_{12}$-OcCB*		439.8038(87.8)	441.8008(100)

Up to now, not sufficient of $^{13}C_{10}$-PCN for internal standard, so alternatively used $^{13}C_{12}$- PCB


MoCNs
Halowax Mix
Incineration Sample
162.0236
162.0236
100
%
0
2
1
Time
12.00
13.00
14.00
15.00
16.00
17.00
18.00


DiCNs
Halowax Mix
Incineration Sample
195.9847
195.9847
100
%
0
1,3
1,4/1,6
1,5
2,7/2,6/1,7
1,2
2,3
1,8
Time
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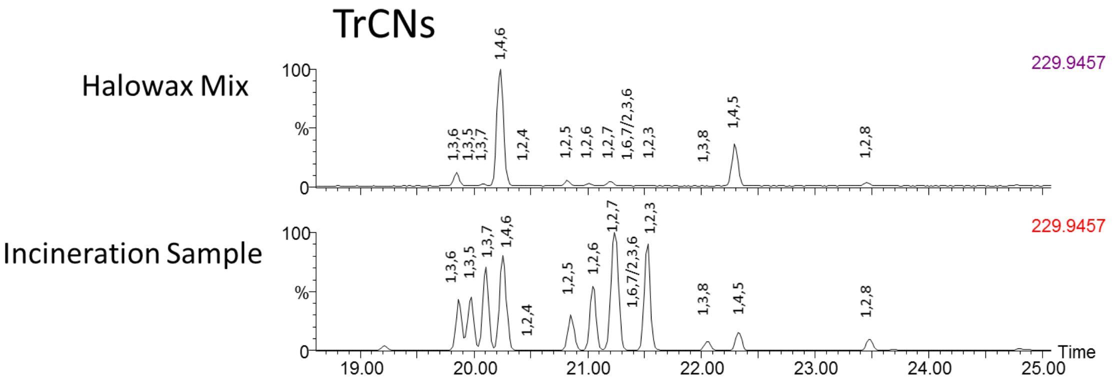
13.00
14.00
15.00
16.00
17.00
18.00


TrCNs
Halowax Mix
Incineration Sample
229.9457
229.9457
100
%
0
1,3,6
1,3,5
1,3,7
1,4,6
1,2,4
1,2,5
1,2,6
1,2,7
1,6,7/2,3,6
1,2,3
1,3,8
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1,2,8
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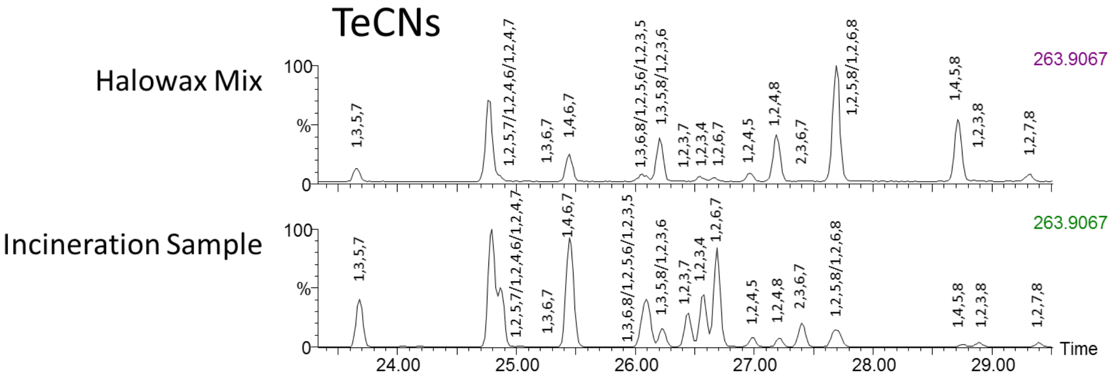
21.00
22.00
23.00
24.00
25.00


TeCNs
Halowax Mix
Incineration Sample
263.9067
263.9067
100
%
0
1,3,5,7
1,2,5,7/1,2,4,6/1,2,4,7
1,3,6,7
1,4,6,7
1,3,6,8/1,2,5,6/1,2,3,5
1,3,5,8/1,2,3,6
1,2,3,7
1,2,3,4
1,2,6,7
1,2,4,5
1,2,4,8
2,3,6,7
1,2,5,8/1,2,6,8
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Time
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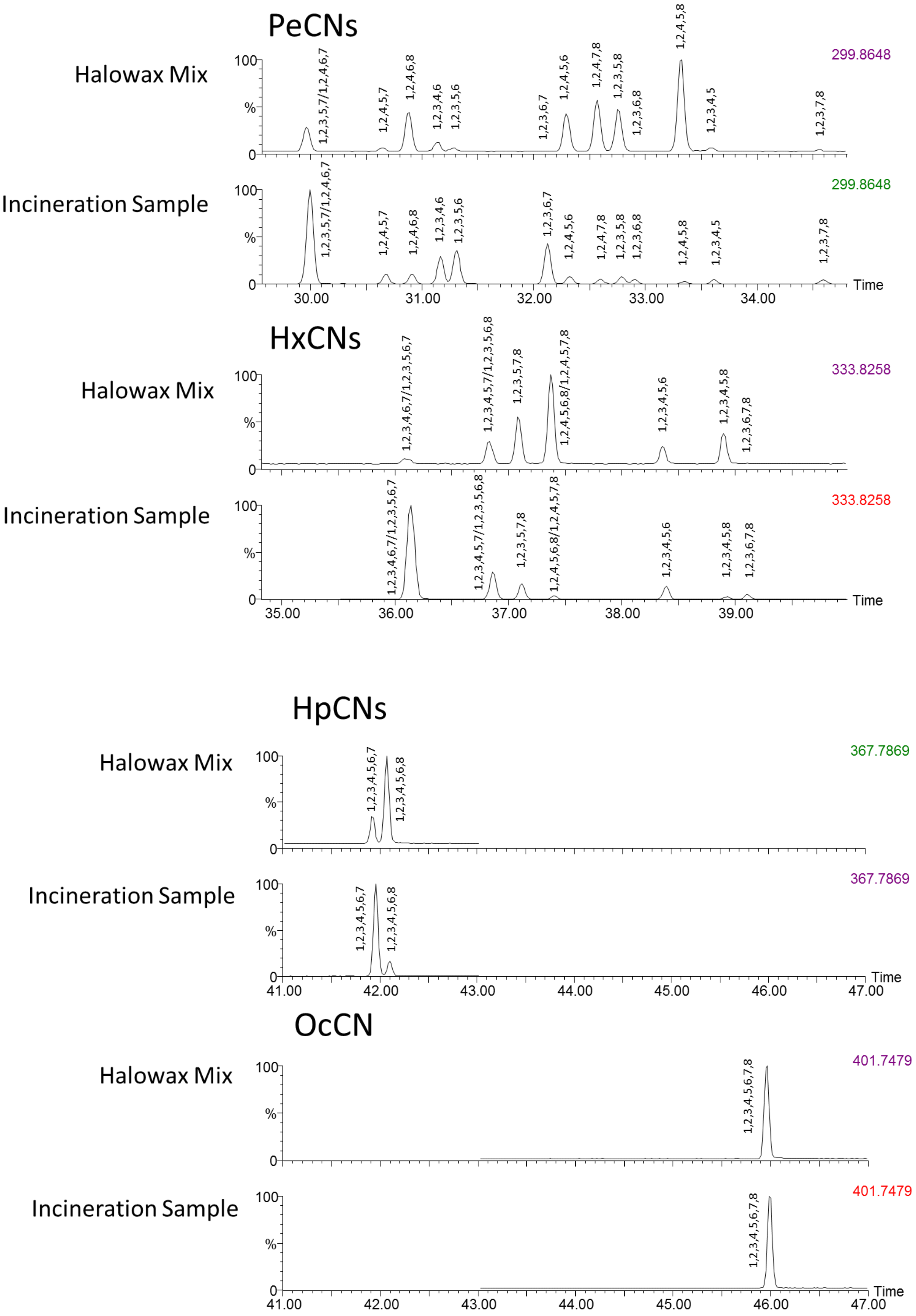
25.00
26.00
27.00
28.00
29.00



※Halowax Mix： Halowax 1000,1001,1013,1014,1031,1051,1099 mixture

Incineration sample：flue gas sample

Figure A3-E-1: Chromatogram of PCN congeners from technical mixtures and waste incineration.[507]

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[507] 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 3-F: 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 HCBD is given in Table A3-F-1 and the exact masses of native and ^{13}C-labled HCBD in Table A3-F-2.

A chromatogram of HCBD from GC/MS analysis is shown in Figure A3-F-1.

Table A3-F-1: HCBD GC/MS conditions (example)

GC condition	
Instrument	HP 6890 （HEWLETT PACKARD）
GC column	DB-5（5%-phenyl-95%-dimethylsiloxane） （J&W) 30 m x 0.25 mm I.D. (0.25 µm)
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 µL
Interface temperature	300°C
Ion source temp.	300°C
MS condition	LRMS or HRMS
Ionization current	300 µA
Ionization	EI
Ionization voltage	35 eV
Trap Current	600 µA
Accelerated Voltage	8 kV
Ion source Temp.	300 °C
Interface Temp.	290～300 °C
Detection mode	SIM

Table A3-F-2: Masses of detected ions for Hexachloro-1,3-butadiene, ^{13}C4- Hexachloro-1,3-butadiene and ^{13}C6-Fluoranthene

		Quant.	Confirm
		$[M-Cl]^{+}$	$[M-Cl]^{+2}$
Target substance	Hexachloro-1,3-butadiene	222.8443	224.8413
		$[M-Cl]^{+4}$	$[M-Cl]^{+6}$
Surrogate material	$^{13}C_4$- Hexachloro-1,3-butadiene	230.8518	232.8488
Internal standard substance	$^{13}C_6$-Fluoranthene	208.0984	

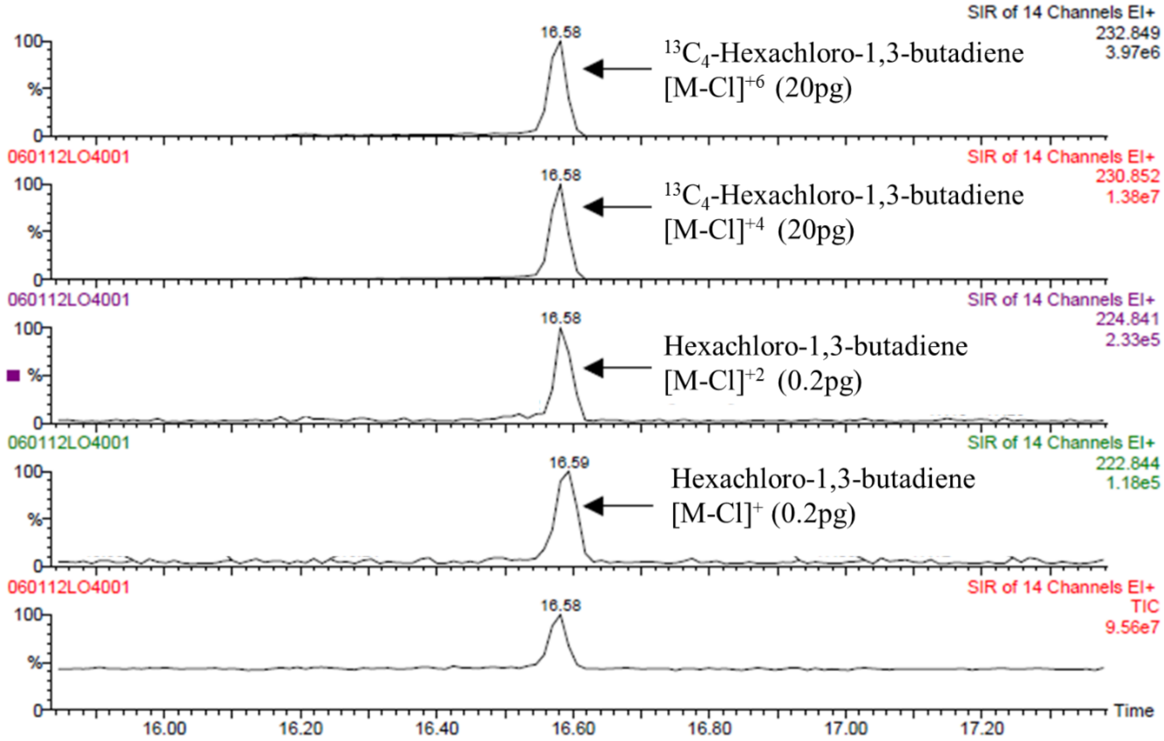

Figure A3-F-1: Chromatogram of native and ^{13}C-labeled HCBD

Annex 3-G: GC/MS analysis of PeCB and HCB within POPs-pesticides (instrumental setting; chromatogram)

GC/MS conditions for PeCB and basic POP pesticides (example)

An example of instrumental setting for the GC/MS analysis of PeCB within POPs pesticide analysis is given in Table A3-G-1 and the exact masses of native and ^{13}C-labled PeCB and HCB in Table A3-G-2.

A chromatogram of PeCB and POPs pesticides from GC/MS analysis is shown in Figure A3-G-1.

Table A3-G-1: GC/MS conditions for PeCB, HCB and POPs pesticides (example)

MS Instrument	LRMS or HRMS
GC	HP 6890 (Agilent)
Column	DB-17HT 30 m x 0.32 mm I.D. (0.15 μm) （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℃/min-300°C (3 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	30～40eV
Trap Current	500 μA
Accelerated Voltage	8 kV
Interface temp.	300°C
Ion source temp.	300°C
Detection	SRM (e.g. SIM)
Resolution	M/ΔM > 10,000 (10% Valley)

Table A3-G-2: Masses of detected ions (m/z) for native and ^{13}C-labelled PeCB and HCB

	Quantification	Confirmation
PeCB	249.8492	251.8462
$^{13}C_6$-PeCB	255.8693	257.8663
HCB	283.8102	285.8072
$^{13}C_6$-HCB	289.8303	291.8273

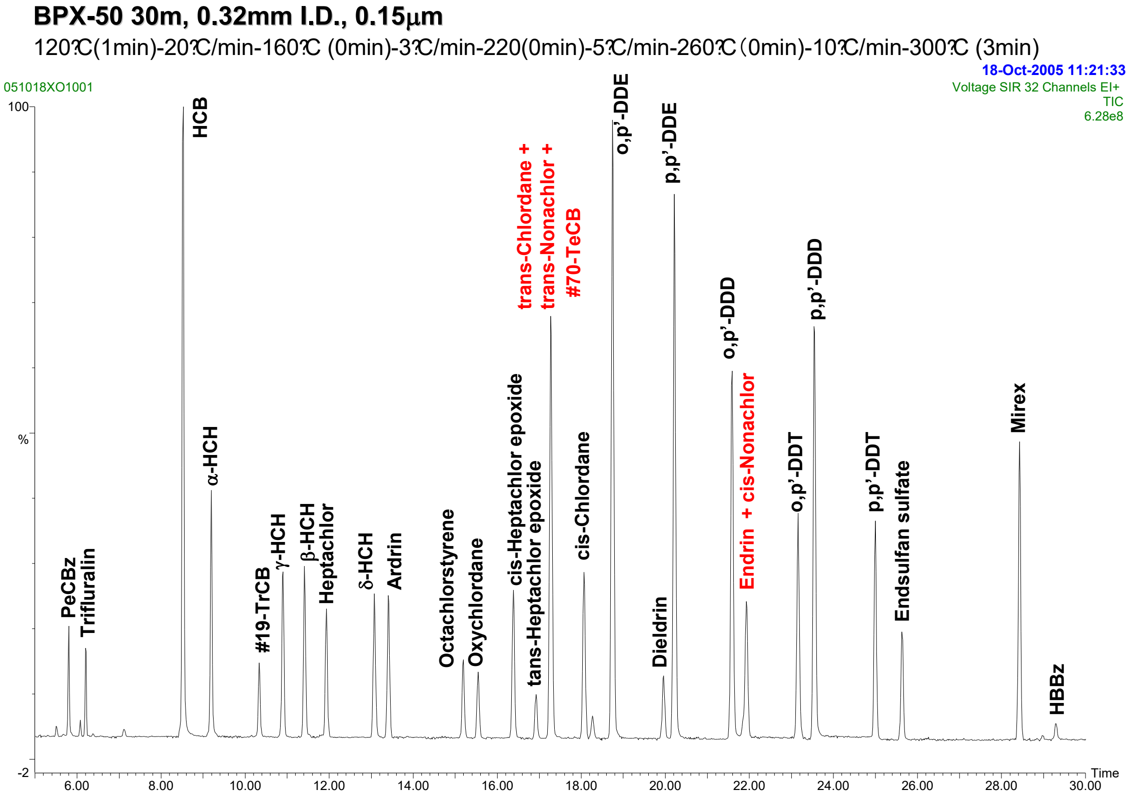

Figure A3-G-1: Chromatogram of PeCB, HCB and POPs pesticides (Column BPX-50; 30 m)

Annex 3-H1: GC-MS analysis of SCCPs and MCCPs (instrumental setting; chromatogram)

Despite of the above-mentioned (section 6.6; quantification) limitations in CP determination by GC/ECNI-LRMS, this is still the most widely used instrument and probably the most accessible one for determining SCCPs and MCCPs. Therefore, the following method is recommended for SCCP/MCCP screening and/or semi-quantitative analysis using the select ion monitoring mode (SIM):

Exemplar instrument setup: GC/ECNI-LRMS-SIM

Injector: Pulsed Splitless; temperature 280 °C

Column: 30 m x 250 µm x 0,25 µ column with DB-5 phase (or equivalent)

Pressure: 9,7853 psi

Flow: 1,2 mL/min

Oven: Temperature program: 50°C (for 1 min) then 10 °C/min to 300 °C (for 14 min)

Run time: 40 min

Transfer line: Temperature 300 °C

Ion source: Temperature 150 °C maximum 300 °C;

Quadrupole: Temperature 150 °C maximum 200 °C;

CPs can be quantified by monitoring the two most abundant isotopes of the $[M\text{-}Cl]^-$ ions of CPs in the SIM mode. All m/z values used for CP-analysis are listed in Table A3-H-1. It is necessary to make a SIM run for each CP chain-length. Thus, a total of 8 SIM runs will be necessary to quantify SCCPs and MCCPs by GC/ECNI-LRMS-SIM.

Table A3-H-1: *m/z* values monitored in GC/ECNI-SIM runs.

	Used for	measured ions (*m/z*)	Dwell time [ms]
SIM 01	C_{10}-CP quantification	243; 245; 279; 277; 313; 315; 347; 349; 381; 383; 417; 415; 451; 449 ***+ ISTD ions****	28
SIM 02	C_{11}-CPs quantification	257; 259; 293; 291; 327; 329; 361; 363; 395; 397; 431; 429; 465; 463 ***+ ISTD ions****	28
SIM 03	C_{12}-CPs quantification	271; 273; 307; 305; 341; 343; 375; 377; 409; 411; 445; 443; 479; 477 ***+ ISTD ions****	28
SIM 04	C_{13}-CPs quantification	285; 287; 321; 319; 355; 357; 389; 391; 423; 425; 459; 457; 493; 491 ***+ ISTD ions****	28
SIM 05	C_{14}-CPs quantification	299;301; 335; 333; 369; 371; 403; 405; 437; 439; 473; 471; 507; 505 ***+ ISTD ions****	28
SIM 06	C_{15}-CPs quantification	313; 315; 349; 347; 383; 385; 417; 419; 451; 453; 487; 485; 521; 519 ***+ ISTD ions****	28
SIM 07	C_{16}-CPs quantification	327; 329; 363; 361; 397; 399; 431; 433; 465; 467; 501; 499; 535; 533 ***+ ISTD ions****	28
SIM 08	C_{17}-CPs quantification	341; 343; 377; 375; 411; 413; 445; 447; 479; 481; 515; 513; 549; 547 ***+ ISTD ions****	28

**Internal/Injection standard (ISTD) m/z values must be set according to the available ISTD.*

Within the above instrument setups, trace SCCPs and MCCPs can be screened with a higher sensitivity than in full-scan setup. However, a single full-scan (m/z from 30–700) run can be performed to an overall CP screening as a first step for each sample.

Please note: The full-scan mode is less sensitive than the SIM mode and it will result in a single hump where different chain-length-CPs contributions are not distinguishable.

For semi-quantitative analysis it is recommended to use at least five different chlorine content CP standards (e.g. SCCPs 51.5%, 53.3%, 55.5%, 59.25%, 63% and MCCPs 42%, 47%, 52%, 54.5% 57%). Intermediary chlorine contents can be achieved by mixing standards with different chlorine contents.

It is noteworthy that several injections will be necessary for SCCP and MCCP determination. Each standard solution (with different Cl content) has to be injected in their four respective chain-length SIM runs. Therefore, the 5 SCCPs with different Cl% have to be inject four times each, being one in each method (SIM runs 01, 02, 03 and 04; according to Table A2-9) and the 5 MCCPs with different Cl% have to be inject four times each, being one in each method (SIM runs 05, 06, 07 and 08; according to Table A3-H-1). Samples will be injected in the four SIM methods for SCCPs and MCCPs, just like the standards.

For chromatogram integration, the selected ions (m/z) will be extracted from each chromatogram and integrated. The computed area of each ion will be used for CP quantification as described by Sprengel & Vetter (2019)[508] based on (Reth & Oehme, 2004[509]; Reth et al., 2005[510]).

It is extremely important, especially for setups using LRMS, to ensure a precise integration of the correct CP humps. Therefore, it is elementary to get to know the typical hump shapes of CPs, especially as they appear on your system. Be careful if you have any peak which do not match the standard chromatogram. If there is any clearly discernible peak on top of the CP hump, the interference must be integrated separately afterwards and its area have to be deducted from the integration of the total area (CP + interference). Starting with the standards will make you familiar with CP chromatograms, which is necessary to recognize any interference afterwards. For some examples of CP shapes, please check the chromatograms in Figure 1.

Additionally, one has to consider the interferences between the CPs themselves. On LRMS systems, especially CPs which are 2 and 5 carbon atoms apart can lead to big interferences. On a 30 m column, CPs which are 5 C apart can be separated via retention time. By comparing the retention times of the samples with the respective standards, the overlapping hump peak in the sample can generally be sharply separated between the two CP species. However, overlaps between CPs that are 2 C apart cannot be separated via retention time. Here, it is important to know which CP chain length (+2 or -2) is causing the interference. In that case, the peak area contribution of the desired chain length can be calculated from the measured isotope ratio, and the theoretical isotope ratios of the desired CPs and the interference. Generally, one can say:

- If **$C_{(x+2)}$-CPs are much more abundant**, than the **Cl_{8-10} homologs** of C_X-CP are affected and need correction
- If **$C_{(x-2)}$-CPs are much more abundant**, the **Cl_{5-7} homologs** of C_X-CPs are affected and need correction

Be careful, as sometimes additional interferences of another origin can occur in your sample that also need arithmetic correction.

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[508] Sprengel J & Vetter W. Synthesis and characterization of eight single chain length chlorinated paraffin standards and their use for quantification. Rapid Commun Mass Spectrom. 2019; 33: 49-56. doi: 10.1002/rcm.8310.

[509] Reth M & Oehme M. Limitations of low-resolution mass spectrometry in the electron capture negative ionization mode for the analysis of short- and medium-chain chlorinated paraffins. Anal. Bioanal. Chem. 2004; 378 (7): 1741–1747.

[510] Reth M, Zencak Z, Oehme M. New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. J. Chromatogr. A 2005; 1081 (2): 225–231. doi: 10.1016/j.chroma.2005.05.061

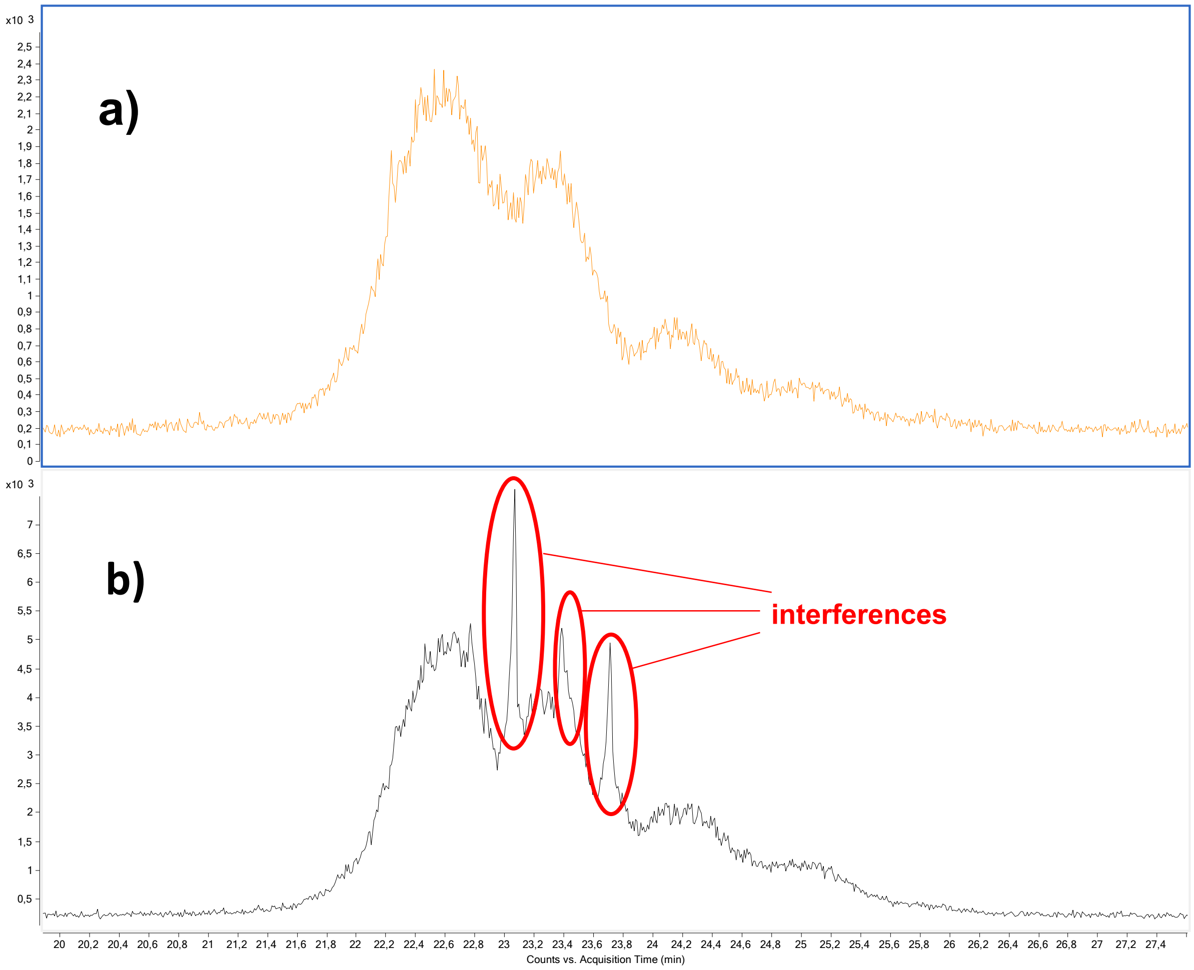

Figure A3-H-1: examples of **a)** CP-only hump and **b)** CP hump with interference peaks.

Annex 3-H2: GC-MS analysis of SCCPs and MCCPs (instrumental setting; chromatogram)

Some of the drawbacks of the method described in Annex 3-H1 can be compensated by using high resolution MS instruments, e.g., Orbitrap-MS, Time-of-fight (TOF)-MS or Fourier-transform ion cyclotron resonance (FT-ICR)-MS. For NCI or ECNI, target ions are $[M\text{-}Cl]^-$ and, for isomer groups/homologues with low overall chlorination degree, $[M\text{-}HCl]^-$.

Further information might also be found in the EURL POPs Guidance Document on CP analysis in food and feed (LINK available 05-2021##), where several LRMS, HRMS methods for GC and LC are described along with chromatograms and possible quality criteria.

For quantification purposes, the use of chain-length specific standards of at least three different chlorination degrees is recommended to determine instrument-specific but chlorination degree-independent response factors for all target ions.[285,511] They can also be used, if preferred, to further specify results calculated based on peak deconvolution.[512]

Only one injection is necessary for scanning all relevant mass traces. Differences in instrument response due to external influences can be compensated for by using an additional (non-CP) injection standard. Quantification itself is then done with a mixture of the chain-length specific standards as calibration curve using linear or weighted regression.[285]

Table A3-H2-1: Example method parameters for GC-ECNI-Orbitrap-HRMS[513]

Instrument	TRACE 1310 GC system coupled to a Q-Exactive mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA)
Column	15 m × 0.25 mm, 0.25 µm HP-5MS UI capillary column connected to 1 m of an uncoated pre-column (Agilent Technologies, Santa Clara, CA, USA)
GC oven programme	60 °C (2 min), increase at 50 °C/min to 300 °C (11 min). Total time 17.8 min.
Detection	Electron capture negative ion (ECNI), reaction gas: methane
Data acquisition	Full scan mode (*m/z* 250-810), R=120,000 (FWHM), extraction of three most abundant isotopologues of $[M\text{-}Cl]^-$ and $[M\text{-}HCl]^-$ adduct ions for each homologue via TraceFinder software (Thermo Fisher Scientific, Waltham, MA, USA)

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[511] Yuan, Bo; Bogdal, Christian; Berger, Urs; MacLeod, Matthew; Gebbink, Wouter A.; Alsberg, Tomas; Wit, Cynthia A. de (2017): Quantifying Short-Chain Chlorinated Paraffin Congener Groups. In: Environ. Sci. Technol. 51 (18), S. 10633-10641. DOI: 10.1021/acs.est.7b02269.

[512] Schinkel, Lena; Bogdal, Christian; Canonica, Elia; Cariou, Ronan; Bleiner, Davide; McNeill, Kristopher; Heeb, Norbert V. (2018): Analysis of Medium-Chain and Long-Chain Chlorinated Paraffins. The Urgent Need for More Specific Analytical Standards. In: Environ. Sci. Technol. Lett. 5 (12), S. 708-717. DOI: 10.1021/acs.estlett.8b00537.

[513] K. Krätschmer, A. Schächtele, R. Malisch, W. Vetter, Chlorinated paraffins (CPs) in salmon sold in southern Germany: Concentrations, homologue patterns and relation to other persistent organic pollutants, Chemosphere 227 (2019) 630–637. https://doi.org/10.1016/j.chemosphere.2019.04.016.

Table A3-H2-2: *m/z* values monitored for target ion and confirmation ions (CFI) in full scan mode

SCCPs	target ion	CFI 1	CFI 2	MCCPs	target ion	CFI 1	CFI 2	LCCPs	target ion	CFI 1	CFI 2
C10Cl5	277.99821	276.00116	279.99526	**C14Cl5**	334.06081	332.06376	336.05786	**C18Cl5**	390.1231	388.12636	392.12046
C10Cl6	312.96706	314.96411	310.97001	**C14Cl6**	368.02184	370.01889	366.02479	**C18Cl6**	424.08444	426.08149	422.08739
C10Cl7	346.92809	348.92514	344.93104	**C14Cl7**	402.99069	404.98774	400.99364	**C18Cl7**	459.05329	461.05034	457.05624
C10Cl8	380.88912	382.88617	384.88322	**C14Cl8**	436.95172	438.94877	440.94582	**C18Cl8**	493.01432	495.01137	497.00842
C10Cl9	416.84720	414.85015	418.84425	**C14Cl9**	472.90980	470.91275	474.90685	**C18Cl9**	528.97239	526.97535	530.96945
C10Cl10	450.80822	448.81117	452.80527	**C14Cl10**	506.87082	504.87377	508.86787	**C18Cl10**	562.93342	560.93637	564.93047
C11Cl5	292.01386	290.01681	294.01091	**C14Cl11**	540.83185	542.82890	538.83480	**C18Cl11**	596.89445	598.89150	594.89740
C11Cl6	325.97489	327.97194	323.97784	**C14Cl12**	574.79288	576.78993	572.79583	**C18Cl12**	630.85545	632.85253	628.85843
C11Cl7	360.94374	362.94079	358.94669	**C14Cl13**	610.75096	608.75391	604.75981	**C18Cl13**	666.81356	664.81651	668.81061
C11Cl8	394.90477	396.90182	398.89887	**C14Cl14**	644.71198	642.71493	646.70903	**C18Cl14**	700.77458	698.77753	702.77163
C11Cl9	430.86285	428.86580	432.85990	**C15Cl5**	348.07646	346.07941	350.07351	**C18Cl15**	734.73561	736.73266	732.73856
C11Cl10	464.82387	462.82682	466.82092	**C15Cl6**	382.03749	384.03454	380.04044	**C18Cl16**	768.69664	770.69369	766.69959
C11Cl11	498.78490	500.78195	496.78785	**C15Cl7**	417.00634	419.00339	415.00929	**C19Cl5**	404.13906	402.14201	406.13611
C12Cl5	306.02951	304.03246	308.02656	**C15Cl8**	450.96737	452.96442	454.96147	**C19Cl6**	438.10009	440.09714	436.10304
C12Cl6	339.99054	341.98759	337.99349	**C15Cl9**	486.92545	484.92840	488.92250	**C19Cl7**	473.06894	475.06599	471.07189
C12Cl7	374.95939	376.95644	372.96234	**C15Cl10**	520.88647	518.88942	522.88352	**C19Cl8**	507.02997	509.02702	511.02407
C12Cl8	408.92042	410.91747	412.91452	**C15Cl11**	554.84750	556.84455	552.85045	**C19Cl9**	542.98804	540.99099	544.98509
C12Cl9	444.87850	442.88145	446.87555	**C15Cl12**	588.80853	590.80558	586.81148	**C19Cl10**	576.94907	574.95202	578.94612
C12Cl10	478.83952	476.84247	480.83658	**C15Cl13**	624.76661	622.76956	626.76366	**C19Cl11**	610.91010	612.90715	608.91305
C12Cl11	512.80055	514.79761	510.80350	**C15Cl14**	658.72763	656.73058	660.72468	**C19Cl12**	644.87113	646.86818	642.87408
C12Cl12	546.76158	548.75863	544.76453	**C15Cl15**	692.68866	694.68571	690.69161	**C19Cl13**	680.82921	678.83216	682.82626
C13Cl5	320.04516	318.04811	322.04221	**C16Cl5**	362.09211	360.09506	364.08916	**C19Cl14**	714.79023	712.79318	716.78728
C13Cl6	354.00619	356.00324	352.00914	**C16Cl6**	396.05314	398.05019	394.05609	**C19Cl15**	748.75126	750.74831	746.75421
C13Cl7	388.97504	390.97209	386.97799	**C16Cl7**	431.02199	433.01904	429.02494	**C19Cl16**	782.71229	784.70934	780.71524
C13Cl8	422.93607	424.93312	426.93017	**C16Cl8**	464.98302	466.98007	468.97712	**C20Cl5**	418.15471	416.15766	420.15176
C13Cl9	458.89415	456.89710	460.89120	**C16Cl9**	500.94110	498.94405	502.93815	**C20Cl6**	452.11574	454.11279	450.11869
C13Cl10	492.85517	490.85812	494.85222	**C16Cl10**	534.90212	532.90507	536.89917	**C20Cl7**	487.08459	489.08164	485.08754
C13Cl11	526.81620	528.81325	524.81915	**C16Cl11**	568.86315	570.86020	566.86610	**C20Cl8**	521.04456	523.04267	525.03972
C13Cl12	560.77723	562.77428	558.78018	**C16Cl12**	602.82418	604.82123	600.82713	**C20Cl9**	557.00369	555.00665	559.00075
C13Cl13	596.73531	594.73826	598.73236	**C16Cl13**	638.78226	636.78521	640.77931	**C20Cl10**	590.96472	588.96767	592.96177
				C16Cl14	672.74328	670.74623	674.74033	**C20Cl11**	624.92575	626.92280	622.92870
				C16Cl15	706.70431	708.70136	704.70726	**C20Cl12**	658.88678	660.88383	656.88973
				C16Cl16	740.66534	742.66239	738.66829	**C20Cl13**	694.84486	692.84781	696.84191
				C17Cl5	376.10776	374.11071	378.10481	**C20Cl14**	728.80588	726.80883	730.80293
				C17Cl6	410.06879	408.07174	412.06584	**C20Cl15**	762.76691	764.76396	760.76986
				C17Cl7	445.03764	447.03469	443.04059	**C20Cl16**	796.72794	798.72499	794.73089
				C17Cl8	478.99867	480.99572	482.99277				
				C17Cl9	514.95675	512.95970	516.95380				
				C17Cl10	548.91777	546.92072	550.91482				
				C17Cl11	582.87880	584.87585	580.88175				
				C17Cl12	616.83983	618.83688	614.84278				
				C17Cl13	652.79791	650.80086	654.79496				
				C17Cl14	686.75893	684.76189	688.75599				
				C17Cl15	720.71996	722.71701	718.72291				
				C17Cl16	754.68099	756.67804	752.68394				
				C17Cl17	790.63907	788.64202	792.63613				

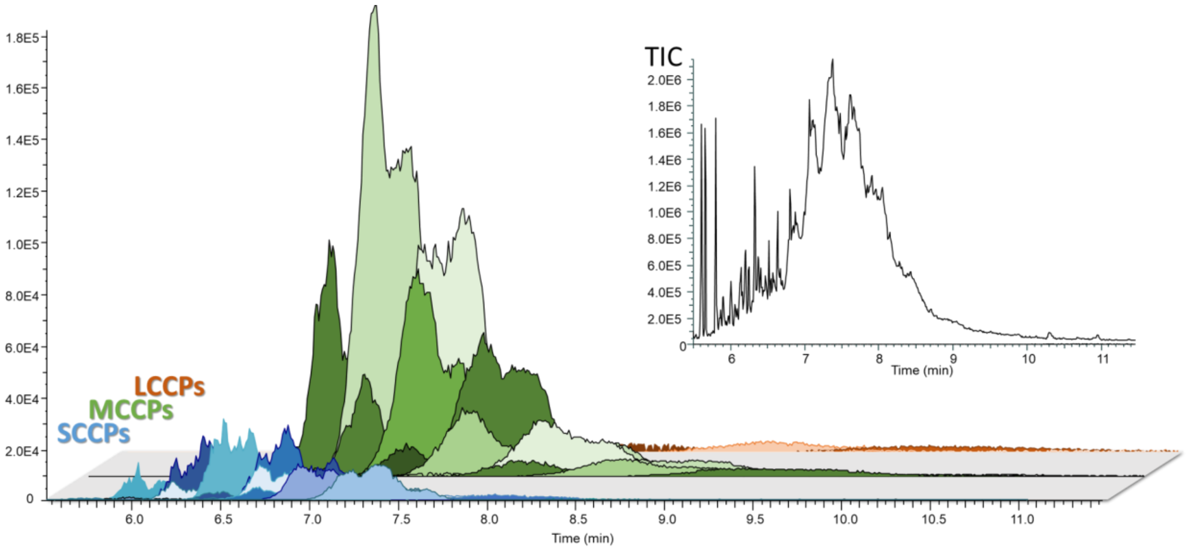

Figure A3-H2-1: Total ion count (TIC) and examples of S-, M- and LCCP mass traces found in extra virgin olive oil on the German market using GC-ECNI-Orbitrap-HRMS.

Please note: While HRMS is able to compensate for many interferences, NCI or ECNI ionisation can lead to a variety of ion fragments with very similar masses.[514] However, these potentially interfering masses of other CP homologues can easily be identified by retention time.[515]

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[514] Yuan, Bo; Alsberg, Tomas; Bogdal, Christian; MacLeod, Matthew; Berger, Urs; Gao, Wei et al. (2016): Deconvolution of Soft Ionization Mass Spectra of Chlorinated Paraffins To Resolve Congener Groups. In: Anal. Chem. 88 (18), S. 8980-8988. DOI: 10.1021/acs.analchem.6b01172.

[515] Krätschmer K; Cojocariu C; Schächtele A; Malisch R; Vetter W (2018): Chlorinated paraffin analysis by gas chromatography Orbitrap high-resolution mass spectrometry. Method performance, investigation of possible interferences and analysis of fish samples. In: J. Chromatogr. A 1539, S. 53-61. DOI: 10.1016/j.chroma.2018.01.034.

Annex 3-H3: LC-MS/MS analysis of SCCPs, MCCPs and LCCPs (instrumental setting; chromatogram)

LC-MS/MS conditions for SCCPs (example)

An example of instrumental setting for the LC-MS/MS analysis for SCCPs (Matsukami et al., 2020)[516] is given in Table A3-H3-1.

Chromatogram of SCCP homologues by LC-ESI-MS/MS analysis is shown in Figure A2-8.

Table A3-H3-1: SCCP LC-MS/MS conditions (example)

Instrument	LC-MS/MS	
Column	ZORBAX SB-CN RRHD column (100 mm × 2.1 mm, i.d. 1.8 µm) Agilent Technologies Inc.	
Desolvation and nebulizer gas	Nitrogen	
Desolvation temperature and gas flow	400 ° C and 1000 L h－1	
Collision gas	Argon	
phase A	Milli-Q water containing 5 mM ammonium acetate	
phase B	Methanol containing 5 mM ammonium acetate	
gradient	0-15 min B：60→99% 15-17 min B：99% 17-17.1 min B：99→60%	
Flow rate	0.4 mL/min	
Col. Temp.	40 ° C	
Inj. volume	5 μL	
Capillary voltage	0.75 kV	
Source temperature	110 ° C	
Cone gas flow	20 L h-1	
MS conditions		
Instrument	ACQUITY UPLC H-Class/Xevo TQ-S micro (Waters Corp.)	
Ionization	ESI negative	
Monitor ions (m/z)	C10Cl4	339→59
	C10Cl5	373→59
	C10Cl6	407→347
	C10Cl7	441→381
	C10Cl8	477→417
	C11Cl4	353→59
	C11Cl5	387→59
	C11Cl6	421→361
	C11Cl7	455→395
	C11Cl8	491→431
	C11Cl9	525→465
	C12Cl4	367→59
	C12Cl5	401→59
	C12Cl6	435→375
	C12Cl7	469→409
	C12Cl8	505→445
	C12Cl9	539→479
	C12Cl10	573→513
	C13Cl4	381→59
	C13Cl5	415→59
	C13Cl6	449→389
	C13Cl7	483→423
	C13Cl8	519→459
	C13Cl9	553→493
	C13Cl10	587→527

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[516] Matsukami et al. (2020) Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes. Chemosphere 244, 125531.

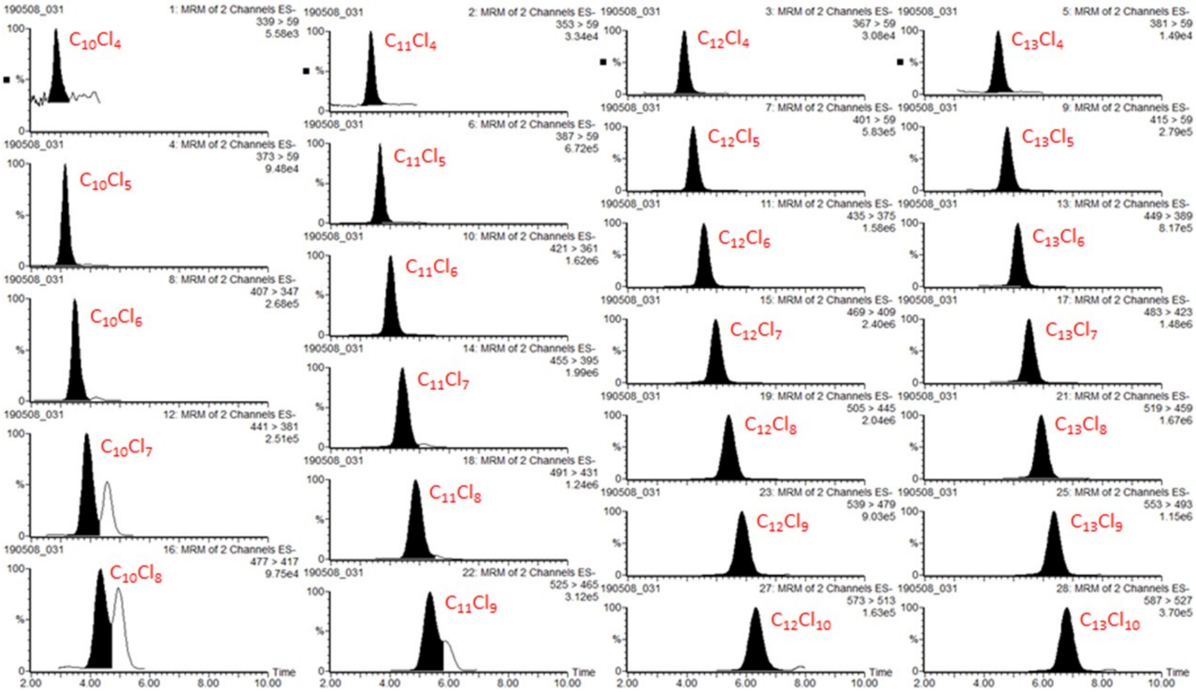

Figure A3-H3-1: Multiple-reaction-monitoring chromatograms of SCCP homologues detected in SCCP-CS by an LC–ESI-MSMS system equipped with a ZORBAX SB-CN RRHD column.

Annex 3-I-1: LC-MS/MS analysis of PFOS, PFOA, PFHxS (instrumental setting; chromatogram)

LC-MS/MS conditions for PFOS, PFOA, PFHxS and selected other PFAS analysis (example 1 and example 2)

An example of instrumental setting for the LC-MS/MS analysis of for PFOS, PFOA, PFHxS and selected PFASs separated using reversed-phase column is given in Table A3-I-1 and monitor ions of PFASs in Table A3-I-2 modified from Taniyasu et al.[517].

Chromatograms of 30 PFASs which are measured in ISO 21675[518] and 8:2 FTOH from LC-MS/MS analysis is shown in Figure A3-I-1.

Example 1 (Table A3-I-1) and example 2 (Table A3-I-3) provide reverse elution of target chemicals in HPLC and cross check using two stationary phases enable no co-elution problem, as described in Taniyasu et al.[519] and ISO 21675[520].

Table A3-I-1: Instrument settings for PFAS analysis by LC-MS/MS (example 1)

LC column:	Main column: Betasil®C18, 5 µm, 2.1 mm × 50 mm Guard column: XDB®C8, 5 µm, 2.1 mm × 12.5 mm
Injection volume:	5 µL
Flow rate:	0.22 mL/min
Mobile phase:	A: 9:1 2 mmol/L aqueous ammonium acetate solution in methanol B: Methanol
Gradient program (% of B):	10% at 0 min → 50 % at 2 min → 100 % at 10 min (4 min hold) → 10% at 15 min
Column temperature:	30 °C
Multiple draw injection program:	1. Draw 5 µL of sample 2. Draw 10 µL of 2 mM aqueous ammonium acetate solution 3. Inject
Type of equipment:	Triple quadrupole
Ionization:	ESI negative
Mode:	Multiple reaction monitoring (MRM)
Source temperature:	450 °C

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[517] Taniyasu S., Kannan K., Yung L.W.Y., Kwok K.Y., Lam P.K.S., Yamashita N. (2008) Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C5–C18), Analytica Chimica Acta 619, 221–230.

[518] ISO 21675:2019, Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)

[519] Taniyasu S., Kannan K., Yung L.W.Y., Kwok K.Y., Lam P.K.S., Yamashita N. (2008) Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C5–C18), Analytica Chimica Acta 619, 221–230.

[520] ISO 21675:2019, Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)

Table A3-I-2: Monitor ions for PFOS, PFOA, PFHxS some related compounds (precursors) and other standard PFASs by LC-MS/MS (example 1 and 2)

Abbreviation	**Compound name**	**CAS-RN**	**Monitor ion**	
			Quantifier	**Qualifier**
PFBS	Perfluoro-*n*-butanesulfonic acid	375-73-5	299>80	299>99
PFHxS	**Perfluoro-*n*-hexanesulfonic acid**	**355-46-4**	**399>80**	**399>99**
PFHpS	Perfluoro-*n*-heptanesulfonic acid	375-92-8	449>80	449>99
PFOS	**Perfluoro-*n*-octanesulfonic acid**	**1763-23-1**	**499>80**	**499>99**
PFDS	Perfluoro-*n*-decanesulfonic acid	335-77-3	599>80	599>99
FOSA	**Perfluorooctanesulfonamide**	**754-91-6**	**498>78**	**498>169**
***N*-MeFOSA**	***N*-methyl perfluorooctanesulfonamide**	**31506-32-8**	**512>169**	**512>219**
***N*-EtFOSA**	***N*-ethyl perfluorooctanesulfonamide**	**4151-50-2**	**526>169**	**526>219**
***N*-MeFOSAA**	***N*-methyl perfluorooctanesulfonamidoacetic acid**	**2355-31-9**	**570>419**	**570>512**
***N*-EtFOSAA**	***N*-ethyl perfluorooctanesulfonamidoacetic acid**	**2991-50-6**	**584>419**	**584>526**
6:2 FTSA	**6:2 Fluorotelomer sulfonic acid**	**27619-97-2**	**427>407**	**427>81**
8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	527>507	527>81
6:2 Cl-PFESA (9Cl-PF3ONS)	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	73606-19-6	531>351	531>83
PFBA	Perfluoro-*n*-butanoic acid	375-22-4	213>169	
PFPeA	Perfluoro-*n*-pentanoic acid	2706-90-3	263>219	263>69
PFHxA	Perfluoro-*n*-hexanoic acid	307-24-4	313>269	313>119
PFHpA	Perfluoro-*n*-heptanoic acid	375-85-9	363>319	363>169
PFOA	**Perfluoro-*n*-octanoic acid**	**335-67-1**	**413>369**	**413>169**
PFNA	Perfluoro-*n*-nonanoic acid	375-95-1	463>419	463>219
PFDA	Perfluoro-*n*-decanoic acid	335-76-2	513>469	513>219
PFUnDA	Perfluoro-*n*-undecanoic acid	2058-94-8	563>519	563>269
PFDoDA	Perfluoro-*n*-dodecanoic acid	307-55-1	613>569	613>269
PFTrDA	Perfluoro-*n*-tridecanoic acid	72629-94-8	663>619	663>269
PFTeDA	Perfluoro-*n*-tetradecanoic acid	376-06-7	713>669	713>369
PFHxDA	Perfluoro-*n*-hexadecanoic acid	67905-19-5	813>769	813>369
PFOcDA	Perfluoro-*n*-octadecanoic acid	16517-11-6	913>869	913>369
8:2 FTUCA	8:2 Fluorotelomer unsaturated carboxylic acid	70887-84-2	457>393	457>343
8:2 diPAP	**8:2 Polyfluoroalkyl phosphate diester**	**678-41-1**	**989>97**	**989>543**
HFPODA	Hexafluoropropylene oxide dimer acid	13252-13-6	329>169	329>285
DONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	377>251	377>85
8:2 FTOH	**8:2 Fluorotelomer alcohol**	**678-39-7**	**463>355**	**463>403**

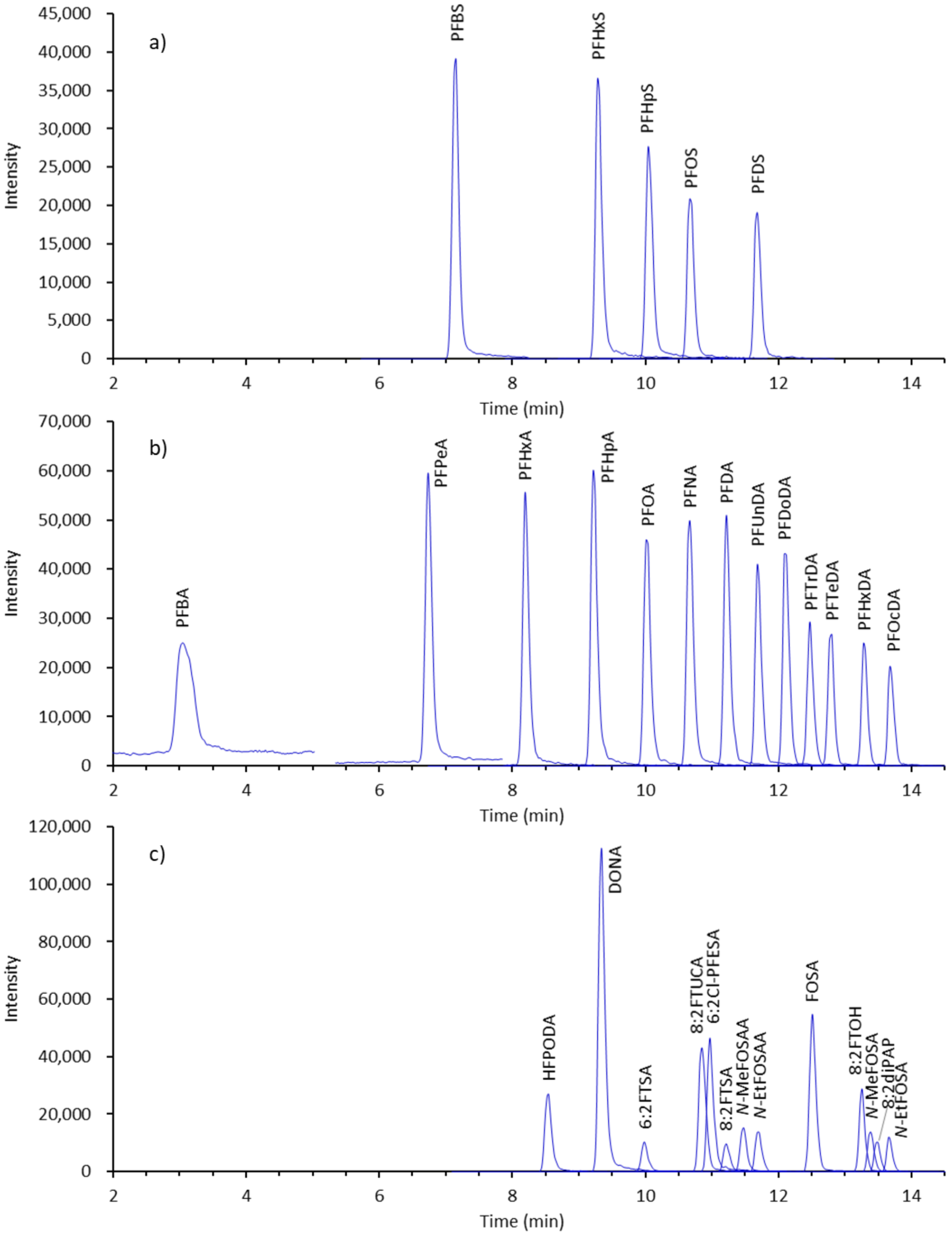

Figure A3-I-1: Chromatograms of a) perfluoroalkyl sulfonic acid (PFSA) b) perfluoroalkyl carbocyclic acid (PFCA) and c) other per- and polyfluoroalkyl substances (PFASs) using LC-MS/MS separated by reversed-phase column, example 1. (5 ng/mL of each compound except for 2 µg/mL of 8:2FTOH.)

LC-MS/MS conditions for PFAS analysis (example 2)

An example of instrumental setting for the LC-MS/MS analysis of for PFOS, PFOA, PFHxS and selected PFASs separated using reversed-phase column is given in Table A3-I-3 and monitor ions of PFASs in Table A3-I-2 modified from Taniyasu et al.[521].

Chromatograms of 30 PFASs which measured in ISO 21675 [522] from LC-MS/MS analysis is shown in Figure A3-I-2.

Table A3-I-3: Instrument settings for PFAS by LC-MS/MS (example 2)

Equipment:		Agilent® 1260 liquid chromatograph interfaced with a Sciex Triple Quad 4500
LC	**LC column:**	Main column: Shodex®RSpak JJ-50 2D, 2.0 mm × 150 mm Guard column: OPTI-GUARD®DVB, 1 mm × 15 mm
	Injection volume:	10 µl
	Flow rate:	0.22 ml/min
	Mobile phase:	A: 50 mmol/l aqueous ammonium acetate solution (pH 9 adjusted by aqueous ammonia)
		B: Methanol
	Gradient program (% of B):	80% at isocratic condition
	Column temperature:	40 °C
MS	**Ionization:**	ESI negative
	Mode:	Multiple reaction monitoring (MRM)
	Source temperature:	450 °C
	Curtain gas:	35 psi

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[521] Taniyasu S., Kannan K., Yung L.W.Y., Kwok K.Y., Lam P.K.S., Yamashita N. (2008) Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C5–C18), Analytica Chimica Acta 619, 221–230.

[522] ISO 21675:2019, Water quality — Determination of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in water — Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS)

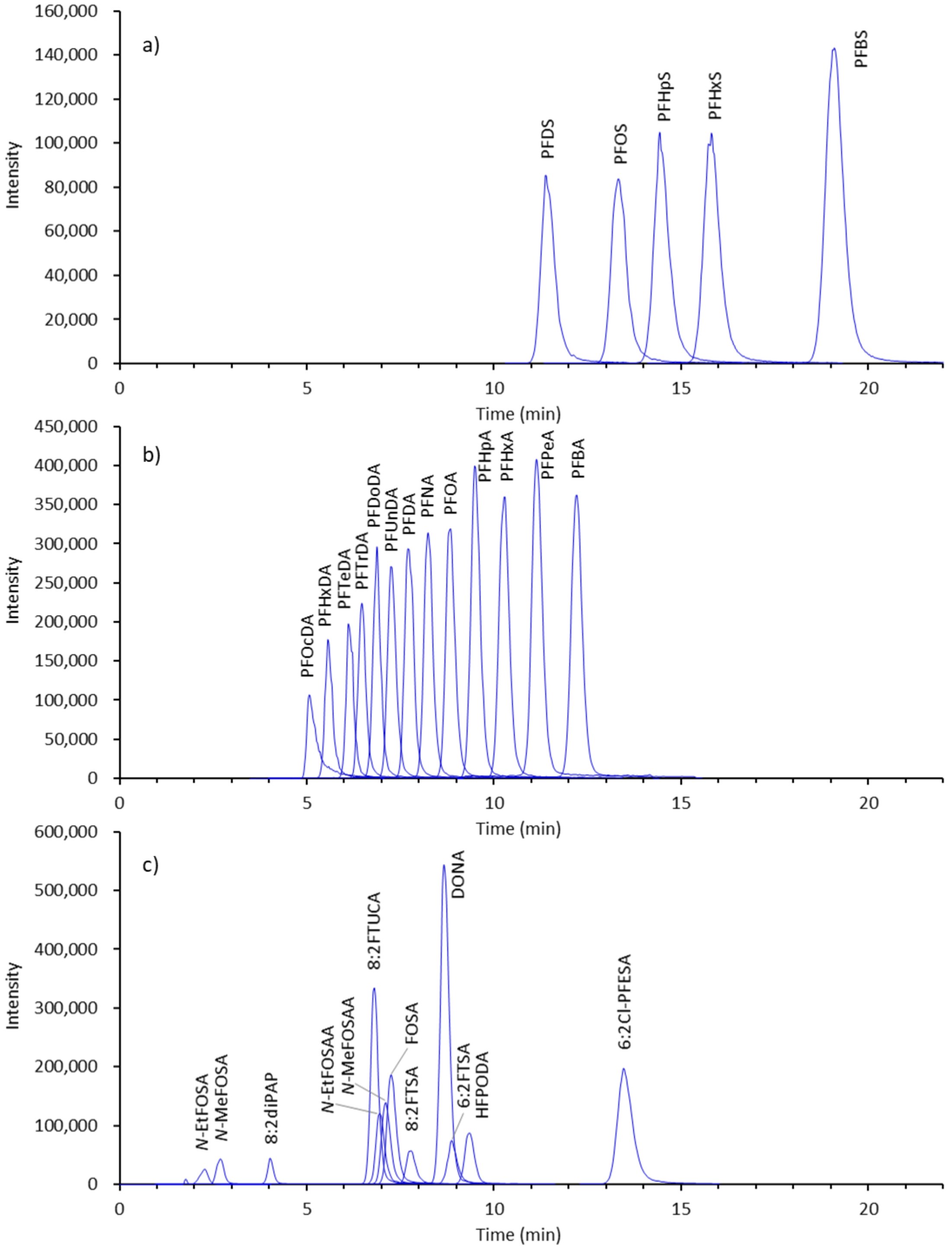

Figure A3-I-2: Chromatograms of a) perfluoroalkyl sulfonic acid (PFSA) b) perfluoroalkyl carbocyclic acid (PFCA) and c) other per and polyfluoroalkyl substances (PFASs) using LC-MS/MS separated by mixed-mode column, example 2. (5 ng/mL of each compound.)

Annex 3-I-2: GC-MS/MS analysis of PFOS, PFOA and PFHxS (instrumental setting; chromatogram)

An example of instrumental setting for the GC-MS/MS analysis of for selected PFASs is given in Table A3-I2-1 and monitor ions of PFASs in Table A3-I2-2 modified from Yamazaki et al.[523].

A chromatogram of PFASs from GC-MS/MS analysis is shown in Figure A3-I2-1.

Table A3-I2-1: Instrument settings for PFAS analysis by GC-MS/MS (PFAS example 3)

GC column:	Main column: DB-WAX 30 m×0.25 mm, 0.25 µm (Agilent Technologies) Retention gap column: 5 m×0.25 mm (Hewlett Packard Enterprise)
Injection volume:	2 µL
Injection method:	Splitless
Injector temperature:	200 °C
Carrier gas:	He (1.9 mL/min)
Oven temperature:	40 °C (2 min) - (5 °C/min) - 70 °C - (3 °C/min) - 100 °C - (8 °C/min) - 170 °C - (20 °C/min) - 250 °C (5 min)
Ion source temperature:	200 °C
Interface temperature:	200 °C
Ionization:	Electron ionization (EI)
Ionization energy:	70 eV

Table A3-I2-2: Monitor ions for PFASs by GC-MS/MS (PFAS example 3)

Abbreviation	**Compound name**	**CAS-RN**	**Monitor ion**		
			Quantifier	**Qualifier 1**	**Quantifier 2**
_N_-MeFOSA	**_N_-methyl perfluorooctanesulfonamide**	**31506-32-8**	**430>111**	**448>119**	**448>69**
_N_-EtFOSA	**_N_-ethyl perfluorooctanesulfonamide**	**4151-50-2**	**448>69**	**512>69**	**448>78**
_N_-MeFOSE	**_N_-methylperfluorooctanesulfonamidoethanol**	**24448-09-7**	**526>169**	**462>93**	**526>69**
N-EtFOSE	*N*-ethylperfluorooctanesulfonamidoethanol	1691-99-2	540>57	540>169	540>69
4:2 FTOH	4:2 Fluorotelomer alcohol	2043-47-2	244>196	244>127	244>95
4:3 FTOH	4:3 Fluorotelomer alcohol	83310-97-8	277>189	257>189	277>95
6:2 FTOH	6:2 Fluorotelomer alcohol	647-42-7	296>127	344>127	344>95
6:3 FTOH	6:3 Fluorotelomer alcohol	80806-68-4	295>95	295>69	295>225
8:2 FTOH	**8:2 Fluorotelomer alcohol**	**678-39-7**	**396>127**	**444>127**	**396>77**
8:3 FTOH	**8:3 Fluorotelomer alcohol**	**1651-41-8**	**395>95**	**395>69**	**395>145**
10:2 FTOH	10:2 Fluorotelomer alcohol	865-86-1	496>127	544>127	496>77
6:2 FTI	6:2 Fluorotelomer iodide	2043-57-4	474>326	474>277	474>263
8:2 FTI	**8:2 Fluorotelomer iodide**	**2043-53-0**	**574>427**	**574>65**	**574>181**
10:2 FTI	10:2 Fluorotelomer iodide	2043-54-1	674>69	527>69	674>131
PFDeI	1-Iodoperfluorodecane	423-62-1	269>69	519>69	519>219
PFDoI	1-Iodoperfluorododecane	307-60-8	619>69	619>131	619>230
PFBuDiI	Octafluoro-1,4-diiodobutane	375-50-8	327>181	327>127	453>327
PFHxDiI	Dodecafluoro-1,6-diiodohexane	375-80-4	427>127	281>181	554>127
PFODiI	Hexadecafluoro-1,8-diiodooctane	355-70-6	527>127	527>177	527>69
C8H3BrF6	1-Bromo-3,5-bis(trifluoromethyl)benzene	328-70-1	292>213	292>163	
C6BrF5	Bromopentafluorobenzene	344-04-7	167>117	246>117	246>167

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[523] Yamazaki E., Taniyasu S., Wang X. Yamashita N (2021) Per- and polyfluoroalkyl substances in surface water, gas and particle in open ocean and coastal environment, Chemosphere 272, 129869.

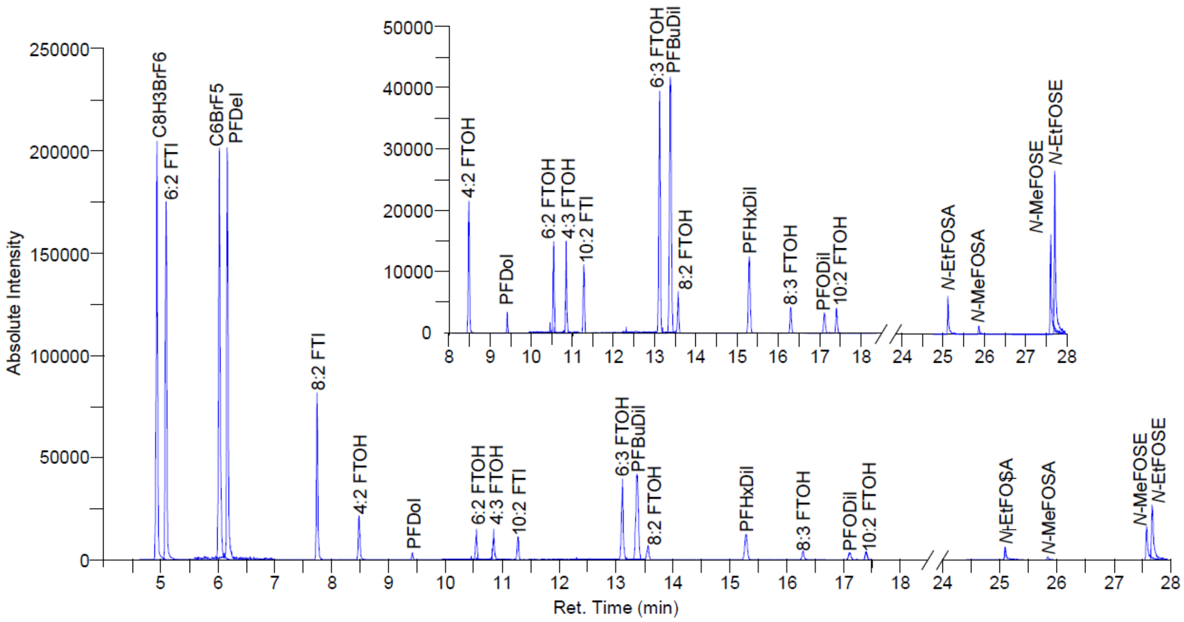

Figure A3-I2-1: Chromatogram of PFASs using GC-MS/MS, example 3. (50 ng/mL of each compound.)

Annex 3-J: 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}C-labeled masses is given in Table A3-J-1.

A chromatogram of HBCD from HPLC-MS/MS analysis is shown in Figure A3-J-1.

Table A3-J-1: HPLC-APCI-MS/MS conditions for HBCD analysis (example)[524]

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	
MS conditions		
Instrument	: LC MS/MS	
Ionization	: APCI negative ion mode	
Monitor ions (*m/z*)	: HBCD	639.8 → 78.8 (Quant.)
	HBCD	639.8 → 80.8 (confirm)
	$^{13}C_{12}$-HBCD	652.1→ 78.8

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[524] 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.

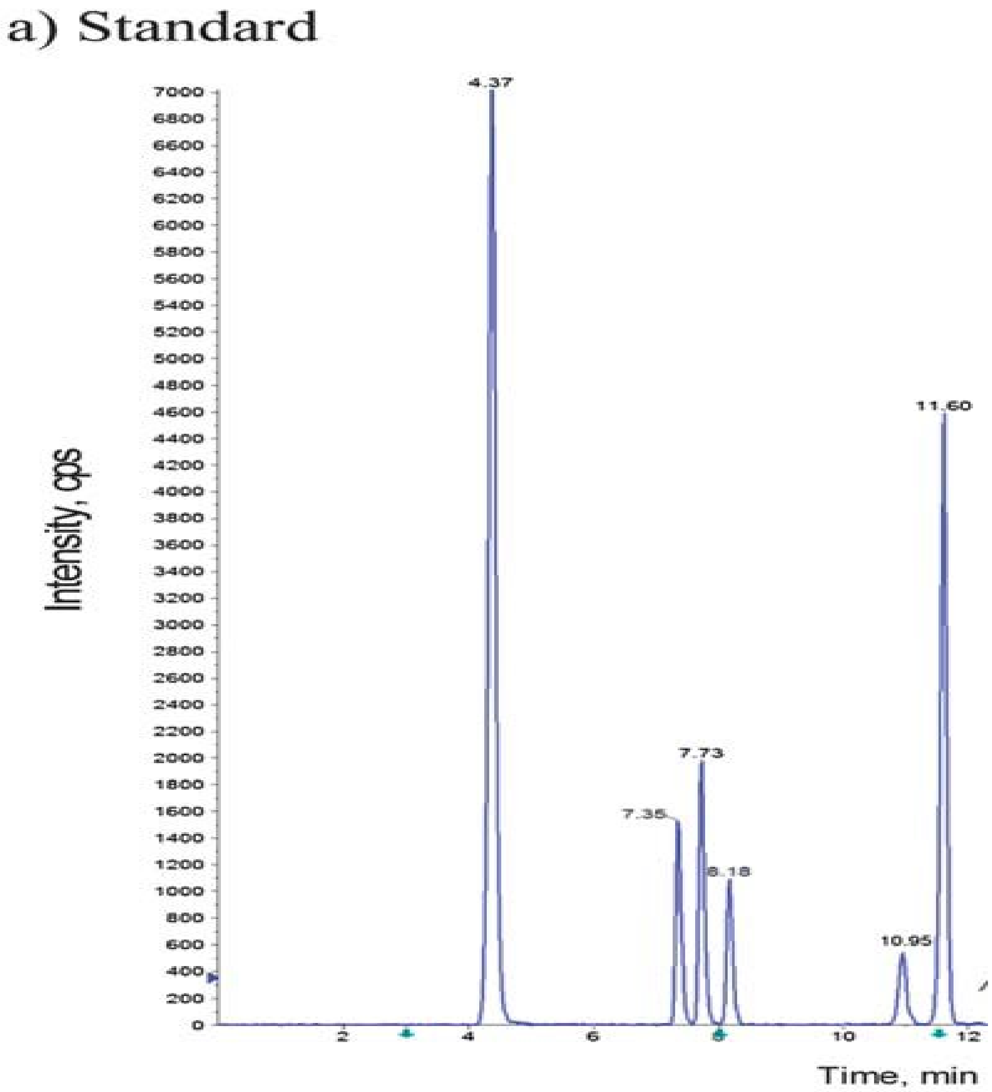

Figure A3-J-1:
Chromatogram of HBCD of the total multiple reaction monitoring (MRM) of standards, with the 3 HBCD isomers eluting at 7.35, 7.73 and 8.18 min.