IPCP Webinar Series: POPs in plastic and monitoring approaches

Part II: Sampling of plastics from major sectors to monitor POPs in plastics; 19.5.2023

Introduction to the Stockholm Convention "Draft guidance on sampling, screening and analysis of persistent organic pollutants in products and recycling" PART 1

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https://scholar.google.com/citations?user=-Cexto4AAAAJ&hl=en

34 POPs listed in the Stockholm Convention (05/2023)

Chemical	Pesticides	Industrial chemicals	Unintentional production	Annex
DDT	+			B
Aldrin, Dieldrin, Endrin, Chlordane, Chlordecone, Toxaphene	+			A
Alpha-, Beta-, Gamma-HCH	+		By-product of lindane	A
Endosulfan, Heptachlor, Mirex	+			A
Pentachlorophenol (PCP), *Dicofol*	+	+		A
Commercial PentaBDE		+		A
Commercial OctaBDE (Hexa/HeptaBDE)		+		A
Commercial DecaBDE		+		A
Hexabromobiphenyl (HBB)		+		A
Hexabromocyclododecane (HBCD)		+		A
PFOS, its salts and PFOSF	+	+		B
PFOA and related compounds		+		A
PFHxS and related compounds		+		A
Short chain chlorinated paraffins		+		A
PCB, PeCBz, HCB, PCN, *HCBD*	+	+	+	A/C
PCDD, PCDF			+	C

The original 12 POPs were mainly pesticides and unintentional POPs plus PCBs.

In 2009 the first plastic additives were listed. Meanwhile many of the new listed POPs are additives in plastic and just early the month two more plastic additives largely used in electrical & electronic equipment, vehicles & buildings.

Therefore control & management of plastics in sectors containing POPs – often in plastic/polymers - becomes a major task in implementing the Convention. This requires screening, monitoring and separation strategies for POPs containing products and recycling flows.

POP Review Committee: Chlorpyrífos, MCCP, LC-PFAA. **COP11 listed:** Methoxychlor; **UV328, Dechlorane Plus**

Guidance documents for the Stockholm Convention National Implementation Plan - development, update and implementation

General guidance

- Guidance for **developing** a NIP
- Guidance for **action plan costing**
- Guidance for **socio-economic assessments**

Inventory Guidances

- **POP Pesticide materials**
- **PCB guidance materials**
- **PFOS inventory** guidance
- **PBDE inventory** guidance
- **HBCD inventory** guidance
- **PCN inventory** guidance
- **PCP inventory** guidance
- **HCBD inventory** guidance
- **SCCP inventory** guidance
- **Dioxin/U-POP Toolkit**

Action plan development

BAT/BEP

- Guidelines for **BAT /BEP Unintentional POPs**
- Guidance for **BAT /BEP** for production & use **PFOS**
- Guidance for BAT /BEP for **recycling & disposal of articles** containing **PBDEs**
- Draft Guidance for **BAT/ BEP for the production and use of HBCD**
- Draft Guidance for **BAT/ BEP for production and use of PCP**

Alternatives

- **General guidance on alternatives to POPs**
- **Guidance Alternatives to HBCD**
- Consolidated **Guidance Alternatives to PFOS**
- Prelim. **Draft Guidance Alternatives to SCCPs**
- Prelim. **Draft Guidance Alternatives decaBDE**

Others

- Guidance for the **control of the import and export** of POPs
- **Monitoring of POPs in products & recycling**
- **Guidance on Labelling** of products and articles

http://www.pops.int/Implementation/NationalImplementationPlans/Guidance/tabid/7730/Default.aspx

Background of “Guidance on Sampling, Screening and Analysis of POPs in Products and Articles”

Background of guidance development on POPs in products:

When in 2009 several POPs used as plastic additives or used otherwise in consumer products were listed - in particular c-PentaBDE and homologues of c-OctaBDE used in electronics, in vehicles, in building insulation or certain textiles **with exemption for recycling - the Secretariat of the Basel, Rotterdam Stockholm Convention (BRS Secretariat) saw that:**

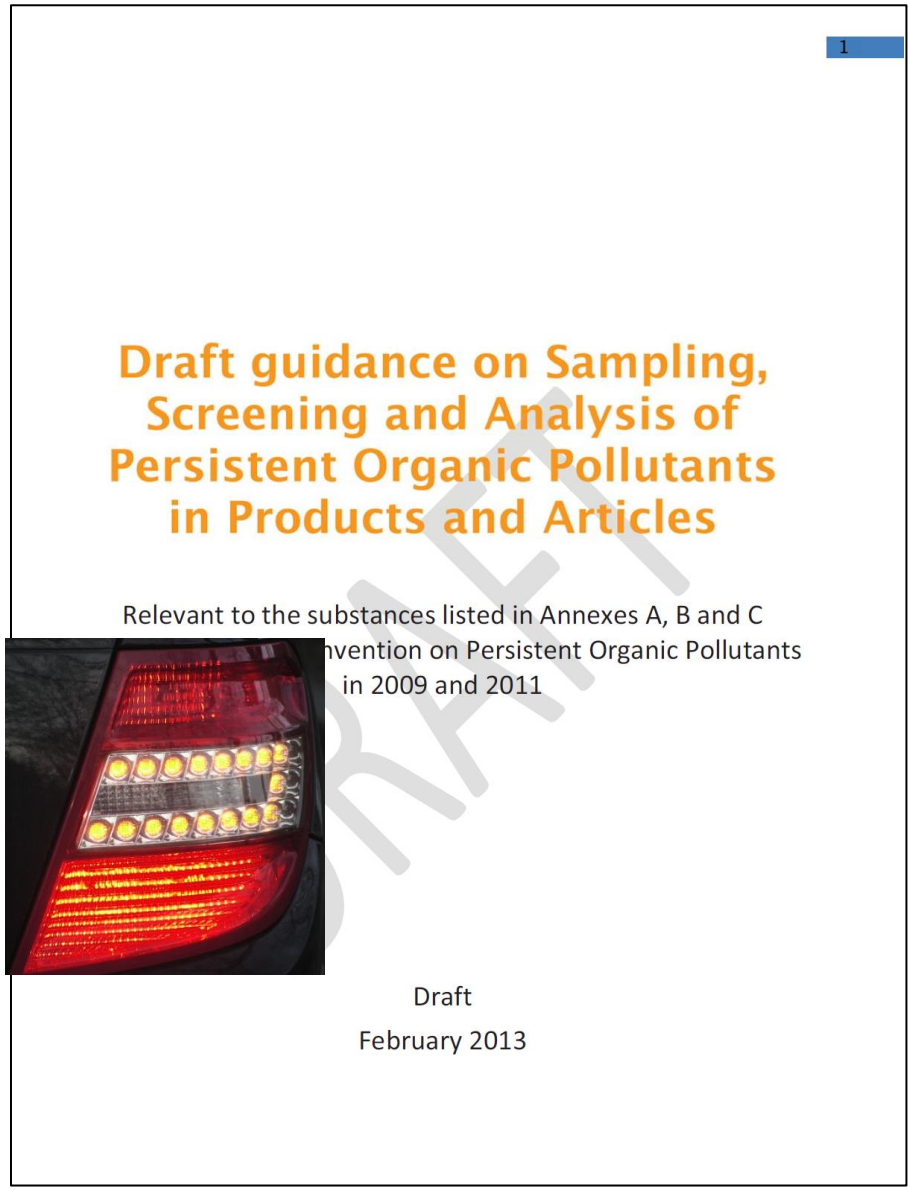
1) Some monitoring in plastic of EEE/WEEE in developing countries is needed to better understand the extent of contamination of plastic in end-of-life and risk for recycling
2) A guidance document should be developed that supports parties in the monitoring of PBDEs in products and gives information on PBDEs in products.

- Therefore the BRS Secretariat initiated in 2010 a monitoring activity for PBDEs in cathode ray tube casings in Nigeria financed by a small grant project of the Norwegian government.
- Professor Osibanjo from Basel Convention Regional Center in Nigeria and I were tasked to guide and conduct/support the monitoring study. Aditionally I was tasked to **develop a guidance document on monitoring PBDEs in WEEE plastic**.

Background of “Guidance on Sampling, Screening and Analysis of POPs in Products and Articles”

Background of guidance development on POPs in products:

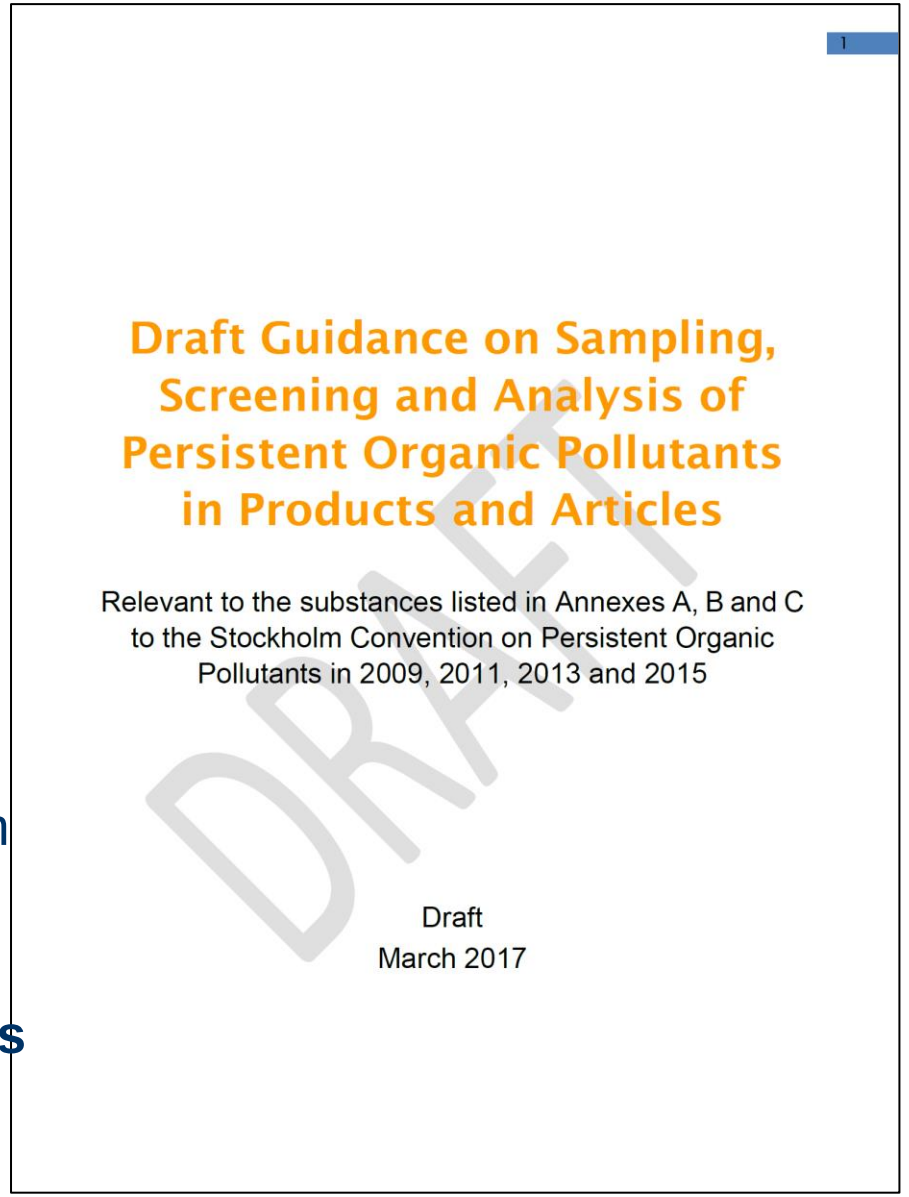
- After developing a PBDE monitoring guidance draft, the BRS Secretariat was satisfied with the outcome and asked if it would be possible to add two more chapters on POPs listed in SC in 2009 which were also present in consumer products:
  - A chapter on PFOS and precursor chemicals which had exemptions for polymers (carpets, textiles, paper) and others
  - A chapter on PeCBz where in a POPRC document the relevance of PeCB in some products has been documented. Furthermore the Government of Japan had submitted documents on the presence of HCB in pigments (e.g. Solvent Red 135 in car taillights) & high volume pigment precursor (tetrachlorophthalic acid) with up to 3000 mg/kg HCB.
- Therefore I developed a guidance for screening PBDEs, PFOS & precursor compounds and PeCBz/HCB. This contained a basis to monitor the three major halogen groups – brominated, fluorinated and chlorinated POPs – in consumer products.



Guidance on Sampling, Screening and Analysis of POPs in Products and Articles (2017)

Update and extension of the monitoring guidance 2016/17:

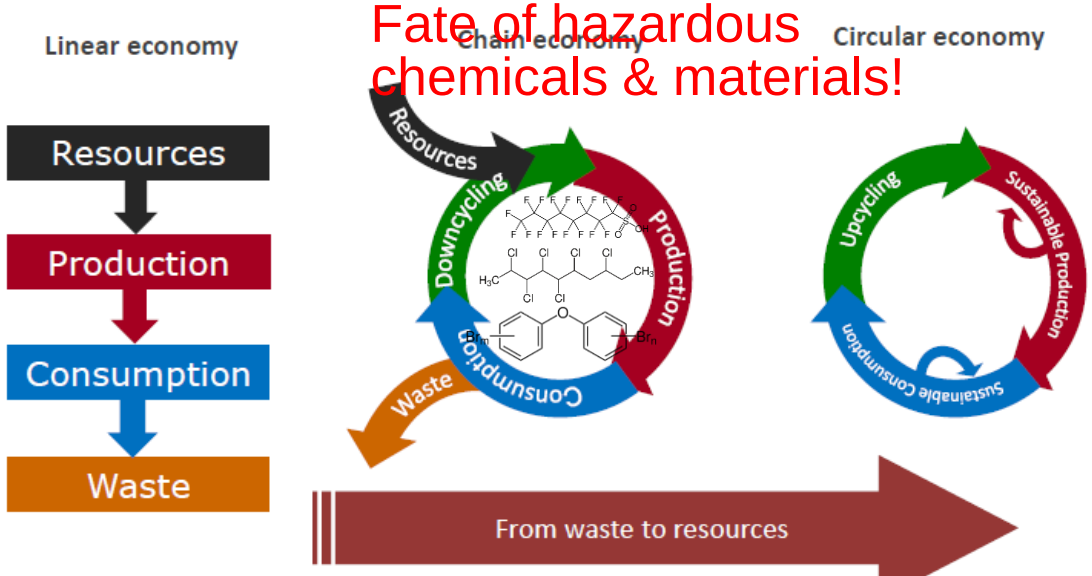
- **The guidance was updated in 2016/17 to include POPs listed 2013 and 2015 (HBCD, PCNs, PCP, HCBD).**
- The main use of HBCD was in plastic (EPS, XPS, HIPS) and synthetic textiles (unsaturated polyester).
- PCNs were used as additives in cables and rubber. Additionally PCNs are unintentionally POPs in SCCPs used as plastic additive
- The major use of PCP was also **for treating polymers: but not synthetic polymers but the natural polymers wood** (cellulose which is a linear polysaccharide polymer and lignin which is an aromatic complex polymer hydroxyphenylpropanes, and different hemicelluloses) **and leather** (protein based polymer collagen which is a polyamide).
- **Therefore also for these new listed POPs major use sectors were plastics and other polymers including consumer products**



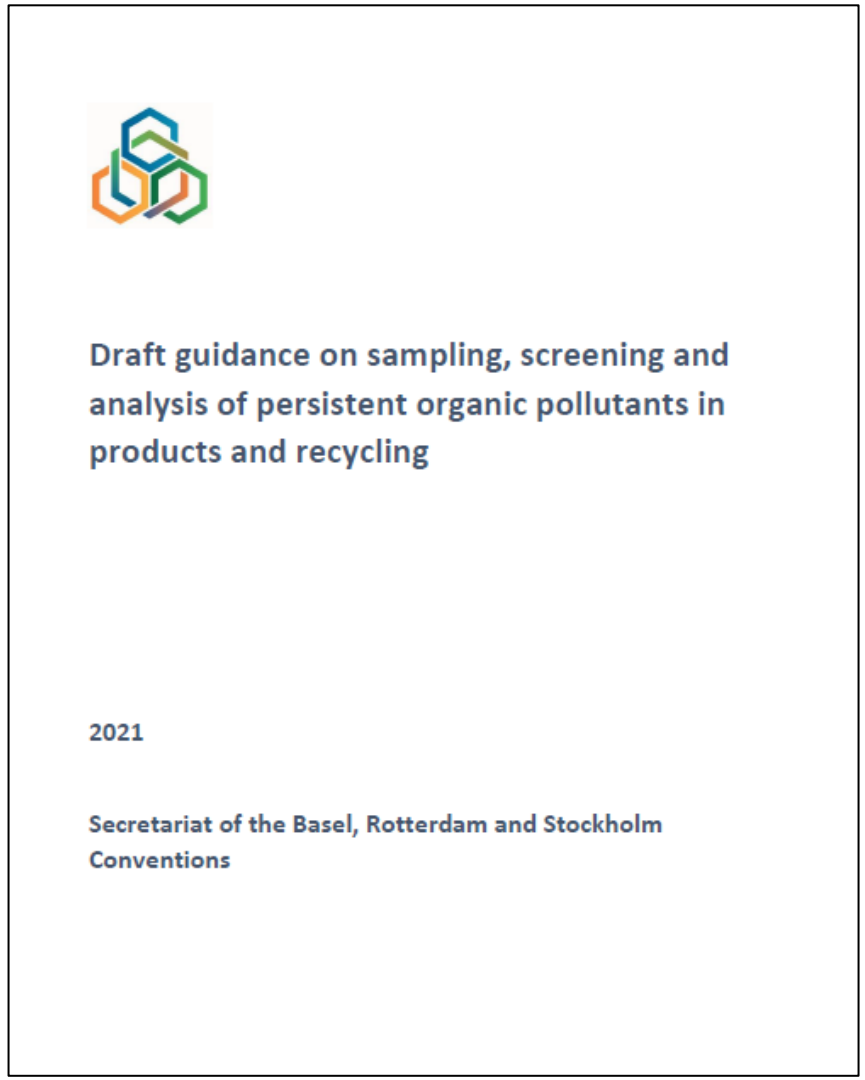
Guidance on Sampling, Screening and Analysis of POPs in Products and Recycling (2021)

Update and extension of the guidance in 2021:

- **The guidance was updated in 2021 to include POPs listed 2017 and 2019 (DecaBDE, SCCP, PFOA).**
- The main use of DecaBDE was/is plastic (wide range of plastics).
- For SCCP the major use is in PVC, rubber and PUR spray foam.
- In the update the circular economy & recycling aspect was included in the guidance and in the title considering the need and the global push for circular economy and associated need to control POPs.



Fate of hazardous chemicals & materials!



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

2021

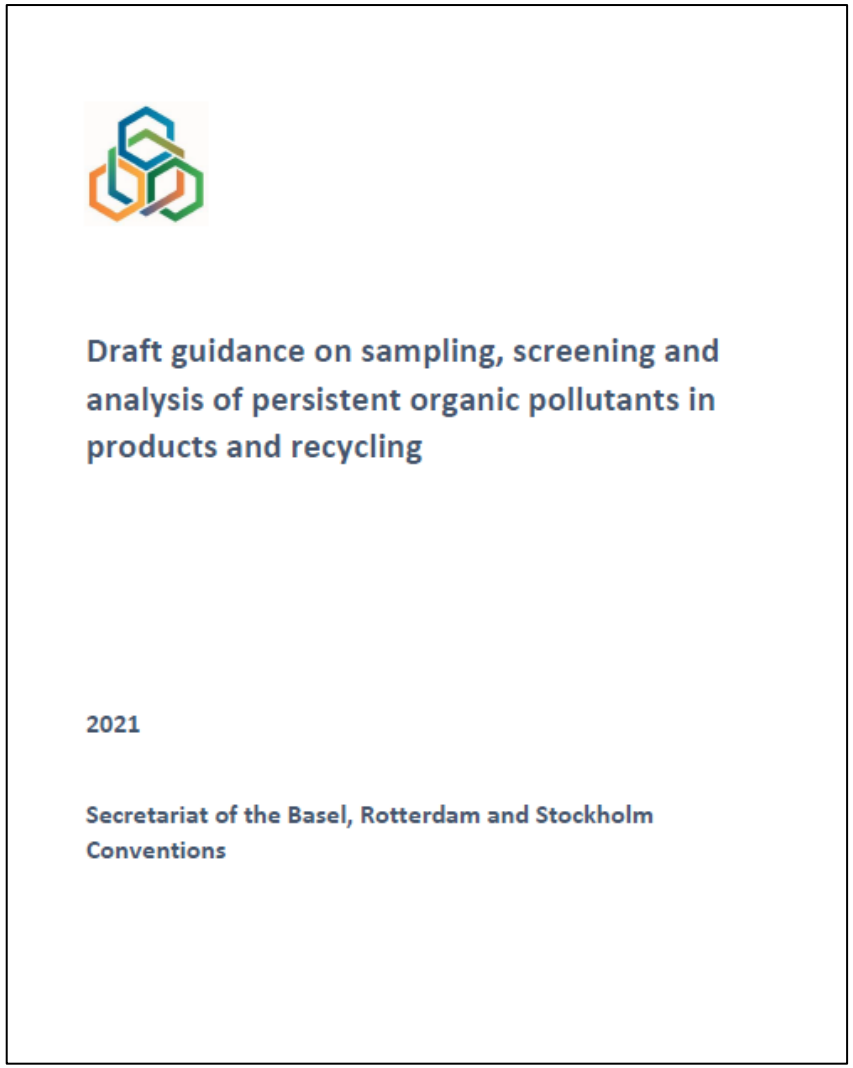
Secretariat of the Basel, Rotterdam and Stockholm Conventions

Guidance provided by the monitoring document

Therefore the document provides guidance on monitoring (sampling, screening and analysis) of the POPs content in articles and products in use and in the recycling streams for industrial POPs listed from 2009 to 2022 and unintentional POPs.

Guidance is provided:

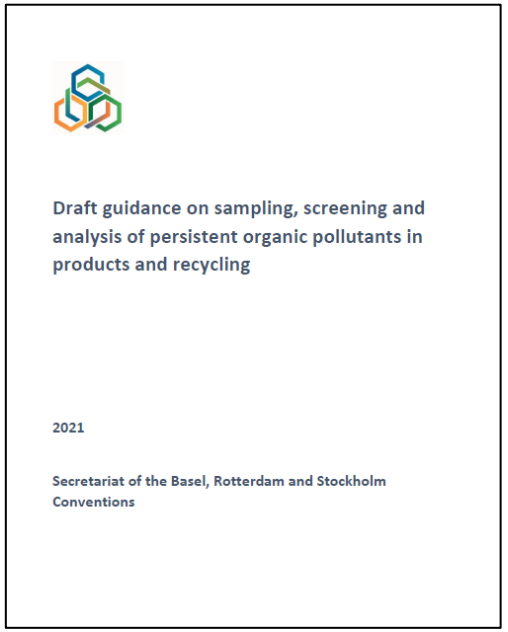
- On articles and products possibly containing POPs listed
- To develop strategies for monitoring of **POPs in products & recycling streams (important for circular economy!!)**;
- On inventory development aspects such as determining emission/impact factors;



POPs and related products considered in the guidance

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

- 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),
- PCNs and PCBs in products and recycling (Chapter 5)
- Short-chain chlorinated paraffins (SCCPs) (Chapter 6),
- Pentachlorophenol (PCP), its salts and esters (Chapter 7).
- Furthermore, all unintentional POPs in products listed in Annex C (PCDD/PCDF, PCB, HCBD, PeCB, and PCNs), are addressed in Chapter 8.

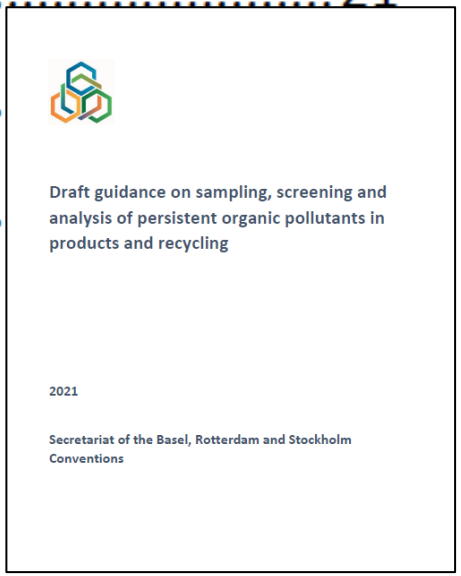


General considerations on monitoring POPs in products

The monitoring guidance has Chapter 2 on general consideration and cross-cutting issues for monitor POPs in products and recycling

Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

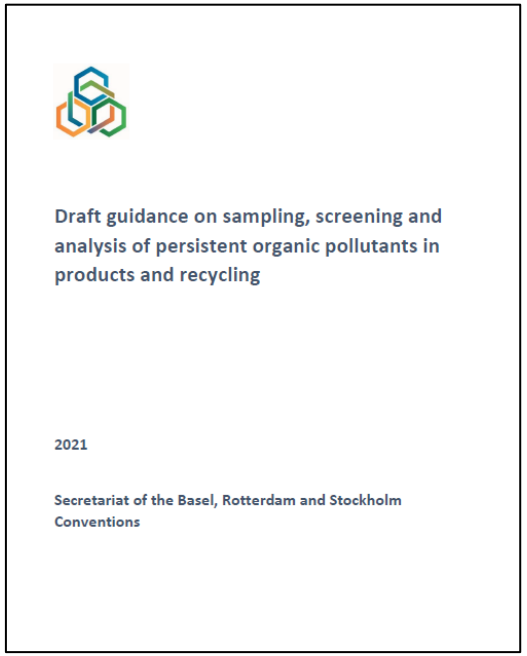
The monitoring guidance has a step by step approach to monitor POPs in articles and products and these steps are elaborated for the major POPs groups.



Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

Step 1: Survey of products and recycling flows possibly containing POPs

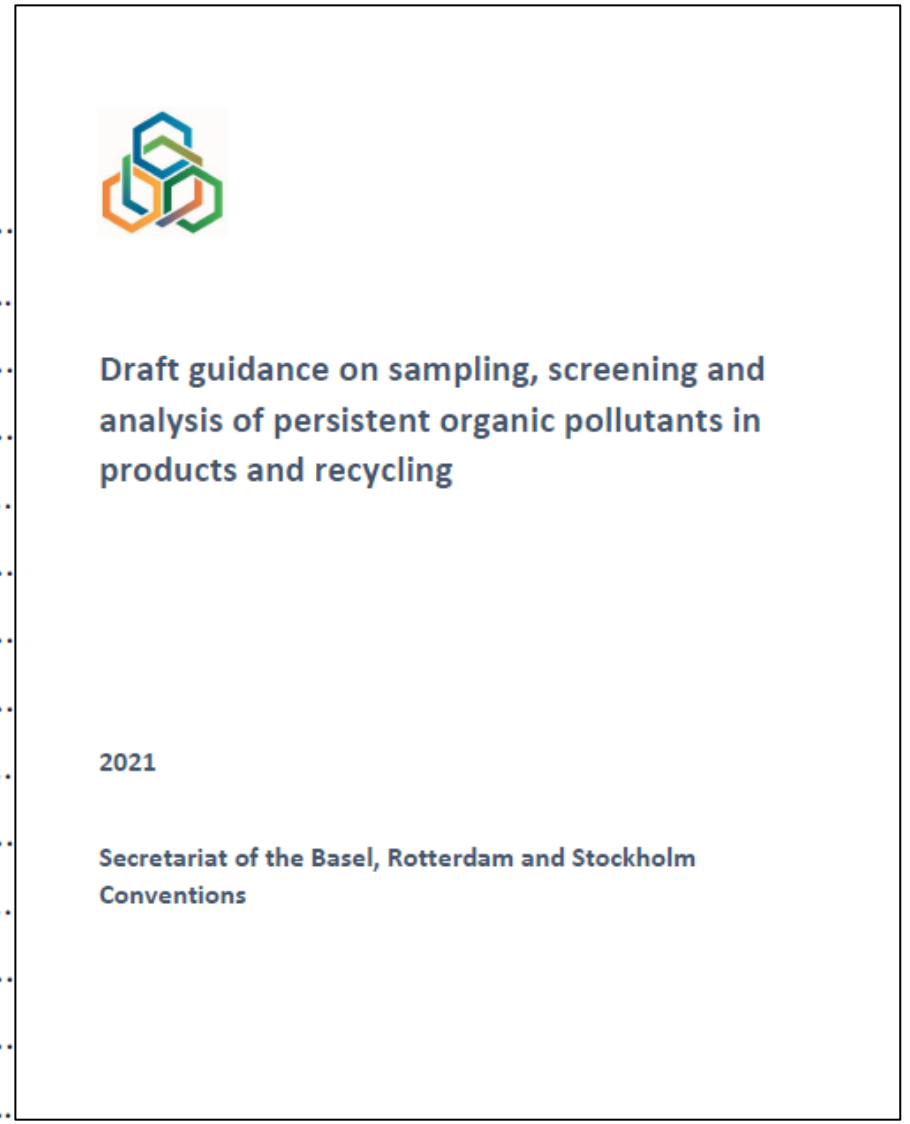
- Before collecting samples, a survey would be conducted to preliminarily determine major consumer products in use and re-use in the country that might contain POPs.
- Also material flows known to possibly contain POPs and further used in recycling (e.g. plastic from WEEE recycling, polyurethane (PUR) foam from different end-of-life products; carpets or textiles) would be targeted.



Guidance on sampling, screening and analysis of POPs in products and recycling – overview on products & recycling

Compiling lists of products which might contain POPs:

- In Annex 1 Products and major recycling streams are compiled which can contain POPs with short description to support screening and sampling. For example for PBDEs:



Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

Step 2: Sample collection

- Relevant stakeholders for the different consumer product categories might be contacted for input, support, and possibly for providing samples. Relevant stakeholders to be contacted for the different POPs use sectors are compiled in the POPs inventory guidance documents.
- Sampling campaigns might be conducted by research institutions possibly in collaboration with the ministry or other competent authorities or directly with the industry or waste management facilities.
- Samples can also be collected e.g. by the customs at the import or by competent authorities such as factory control or consumer protection authorities and related institutions.

- Reference is also made to documents with a detailed sampling methodology e.g. for “WEEE plastic” developed and described in Wäger et al. (2010).

Step by step approach of Stockholm Convention guidance on monitoring POPs in products and recycling

Step 3: Screening in the field or laboratory

- Only a (minor) share of target products contain POPs. E.g. less then 20% of CRT casings contained PBDEs. Also only a share of carpets or textiles contain PFOS/PFOA or PFAS.
- Sample articles can be screened for the presence of bromine or fluorine in the field or in the laboratory to minimize the effort of extraction, clean-up and analysis for samples.
- Such screening enables relatively cheap and simple pre-selection of some article groups with regards to their possible POPs content (e.g. WEEE plastic or PUR foams for bromine as indication of PBDE content, or carpets for fluorine as indication for PFOS or other PFAS).
- Screening helps to minimise the time and expenses (by pre-selection of samples) for confirmation analysis, which requires extraction and appropriate clean-up steps.

Step by step approach of Stockholm Convention guidance on monitoring POPs in products and recycling

Step 3: Screening in the field or laboratory:

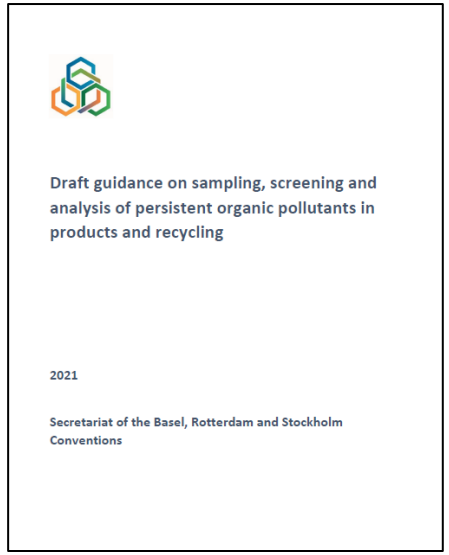
- The Stockholm Convention guidance for monitoring POPs in products and recycling gives an introduction to screening approaches in the sampling step.
- The guidance compiles information on screening methods for bromine, chlorine and fluorine in products and recycling which can be used for sample selection.
- Also some instrumental screening methods for the individual POPs are described which do not need extraction and clean-up.

- When screening methods are applied it has to be ensured that the detection limit of the screening method is more sensitive than the limit required for the sampling (e.g. required by a legislation limit). For example if the Basel Convention low POPs limit is 50 mg/kg then the screening method needs to have a lower detection limit (can be met e.g. by handheld x-ray fluorescence (XRF) spectroscopy).

Example: Screening methods for bromine as indicator

Step 3: Screening in the field or laboratory for sample selection

A range of technologies for bromine in plastics are currently applied as screening tools. These technologies can also be used for screening bromine in materials like PUR foams, textile or rubber and suspected consumer products.



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

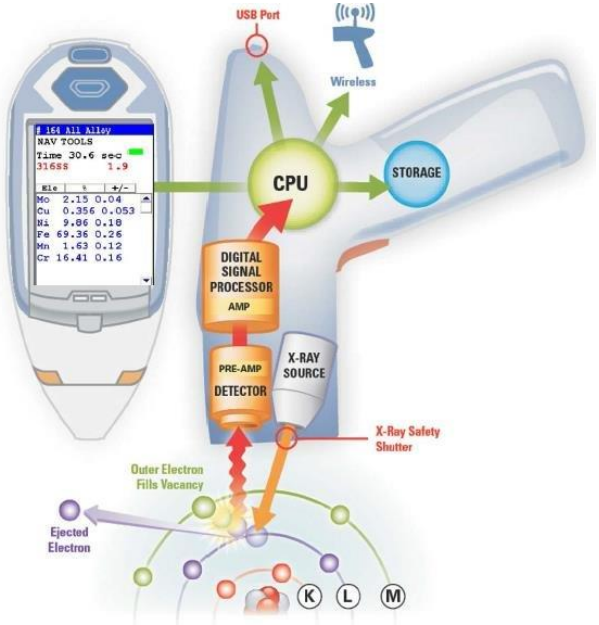
2021

Secretariat of the Basel, Rotterdam and Stockholm Conventions

Screening methods for bromine as indicator

Step 3: Screening in the field or laboratory for sample selection – XRF spectrometer

- The X-ray fluorescence (XRF) technology can be used for detection of bromine in polymers or other materials with a low detection limit (10-50 ppm).
- XRF analysis is limited to the detection of bromine (or other elements) in the material, without any capacity to identify the type of brominated flame retardant (listed POP or allowed BFR).
- Using handheld instruments the time requirement for a measurement is less then a minute. Precision of XRF screening measurements is limited and thus relative standard deviations of up to 30% may be obtained. Only problematic if the detected level is close to regulatory limit.



Screening methods for bromine as indicator for BFRs in plastic

Step 3: Screening in field or laboratory for sample selection – Sliding spark spectroscopy

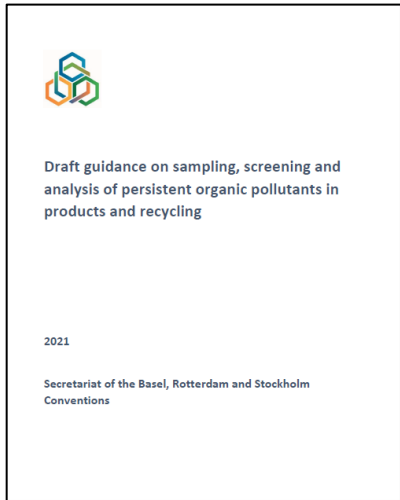
- Sliding spark spectroscopy is a surface screening method by thermal vaporization, ionization and excitation of surface substrate using a train of high-current sliding sparks. The components in the spark plasma are activated to emit radiation. From the atomic spectrum, information on the composition and the element concentration in the sample can be obtained.
- With a comparatively simple hand-held system, sliding spark spectroscopy allows direct in-situ analysis of plastic and other compact non-conductive material to detect bromine, chlorine, fluorine and inorganic additives within a few seconds without sample preparation.
- The method is capable to detect at concentration down to ~0.1%. Therefore primary brominated flame retarded WEEE plastic (containing >2% bromine) can be detected and e.g. separated in recycling facilities. However this method cannot be used to screen waste or recyclates to meet RoHS standards of 1000 mg/kg or updated EU POP regulatory standard of 500 mg/kg or even the Basel provisional low POP content.

Seidel et al. (1993) Fresenius' Journal of Analytical Chemistry 347, 92-102.

Guidance on sampling, screening and analysis of POPs in products and recycling – best practice case studies (Annex 2)

Compilation of best practice case studies:

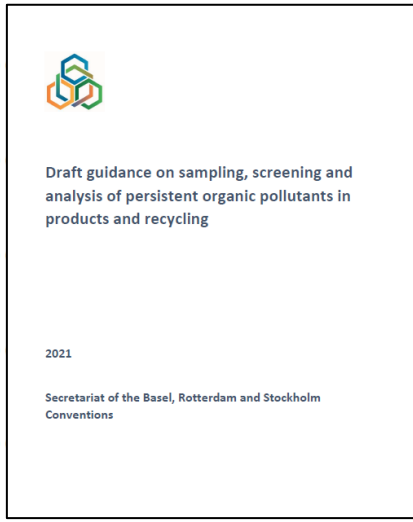
- Where available, best practice case studies for monitoring of key products categories possibly containing POPs are referenced in the respective chapters and described in Annex 2. Where possible, case studies or publications were selected with reports available in the public domain and the links to the studies are provided.
- By inclusion of case studies, the guidance endeavours to provide information on already performed studies, and the approaches used.
- These case studies can be assessed with the view of selecting the most appropriate approaches and methodologies (for screening, sampling and analysis) – and to add a good case study (but not to repeat!).
- Some of the case studies reveal that many former applications of PFOS and PBDE are not relevant anymore e.g. in recent surveys PFOS and related substances in Europe were no more detected in coated paper (but other PFCs).



Guidance on sampling, screening and analysis of POPs in products and recycling – best practice case studies (Annex 2)

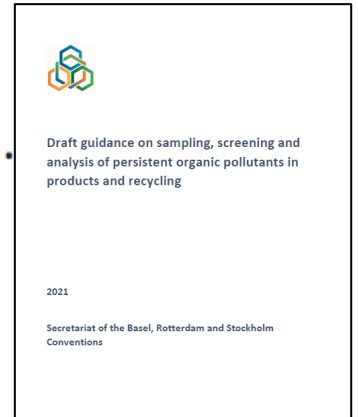
Compilation of best practice case studies:

The Guidance compiled useful case studies for the individual POPs in products and recycling (Annex 2) which gives an overview on how key monitoring studies on POPs in products and recycling were conducted including studies using pre-screening methods,



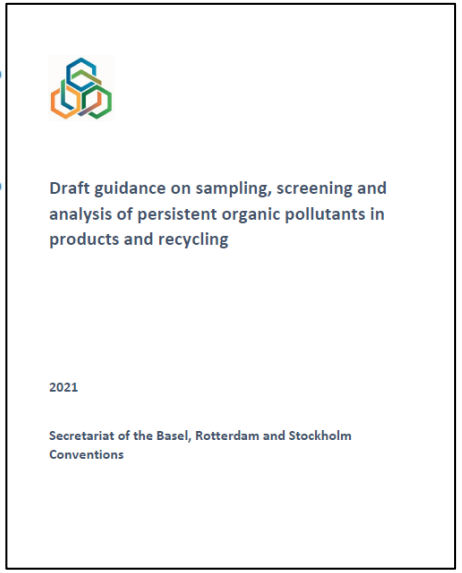
Guidance on sampling, screening and analysis of POPs in products and recycling – best practice case studies (Annex 2)

Best practice case studies for PBDEs (Annex 2-B):



PART I: Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

Today in Part 1 I only introduced to the features of the first 3 steps of the guidance.
On 23 May a short Part II on the quantification part mean instrumental analysis



Thank you for your attention !

More Information

UNEP Chemical in Plastics: www.unep.org/resources/report/chemicals-plastics-technical-report

UNEP Plastics Treaty: https://www.unep.org/about-un-environment/inc-plastic-pollution

Basel Convention: www.basel.int

Stockholm Convention: http://chm.pops.int/

Rotterdam Convention: www.pic.int

SAICM: http://www.saicm.org/

OECD/IOMC: http://www.oecd.org/chemicalsafety/

Industry: https://endplasticwaste.org/; http://www.suschem.org/

Science: www.ipcp.ch; https://www.plasticstreaty.org/scientists-declaration/

NGO: www.ban.org; www.ipen.org; https://www.ciel.org/; www.chemsec.org

Better-world-links: http://www.betterworldlinks.org/

IPCP International Panel on Chemical Pollution

UN environment programme

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