IPCP Webinar Series: POPs in plastic and monitoring approaches

Part III: Sampling of plastics from major sectors to monitor POPs in plastics; 23.5.2023

Introduction to the Stockholm Convention "Draft guidance on sampling, screening and analysis of persistent organic pollutants in products and recycling" PART 2

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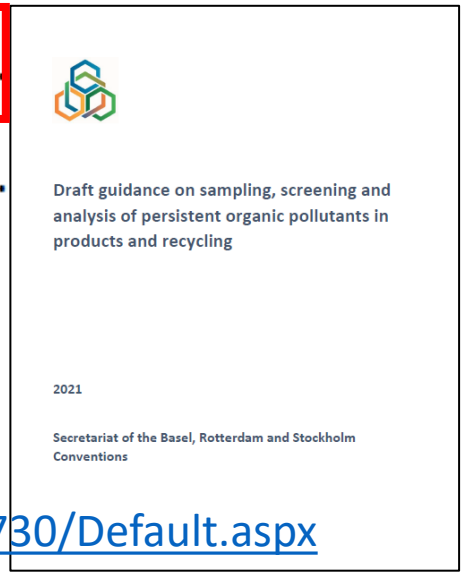
Step by step approach of Stockholm Convention Guidance for monitoring POP in products and recycling

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



Under „Inventory“ http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/tabid/7730/Default.aspx

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

Step 4: Quantification of POPs in products and recycling.

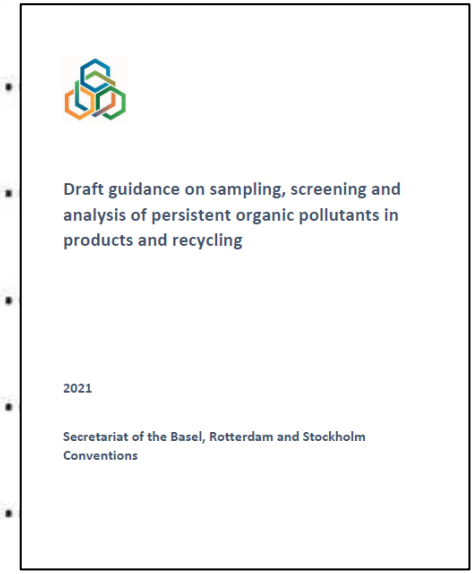
- The guidance include for main matrices technical information on extraction and clean-up of samples and information of sample preparation.

- Sample preparation need to be adjusted & optimized to the complex materials like plastic.
- Care has to be taken that the polymers do not contaminated the instruments (MS) and GC-columns. Optimized clean-up!!!

Step by step approach for monitoring PBDE in articles and products

Step 4: Quantification of POPs in products and recycling

- For the individual POPs the guidance contain sections on quantitative (and sometimes semiquantitative) methods.

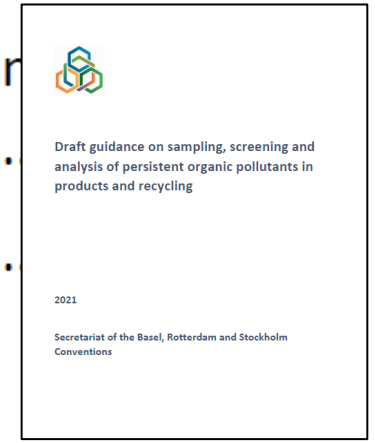


Guidance on monitoring of POPs in products and recycling – Referencing to available international standards

Step 4: Quantification of POPs in products and recycling

The approach of this guidance is to:

- Refer to international standards where they are available and sufficient for the analysis of the respective POPs in products (also mention limitations for products)


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

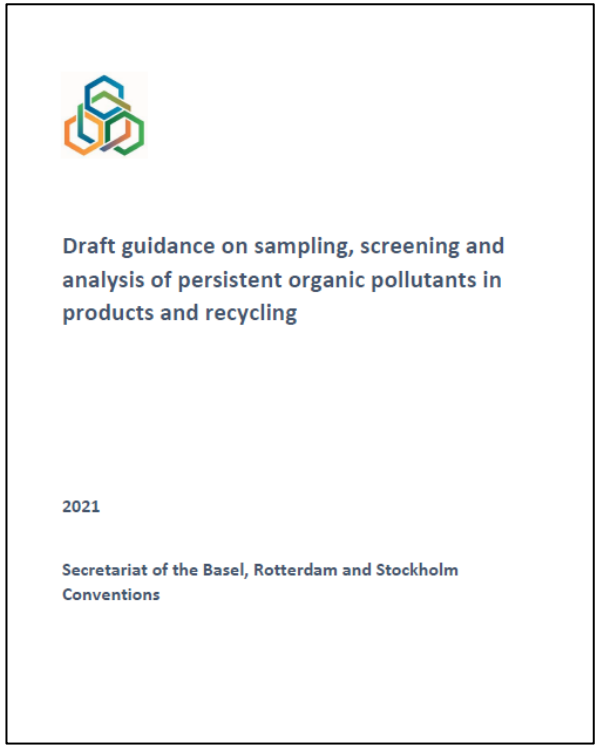
2021

Secretariat of the Basel, Rotterdam and Stockholm Conventions

Guidance on monitoring of POPs in products and recycling – Referencing to available international standards

Step 4: Quantification of POPs in products and recycling

- For a number of product matrices no international standards are available for sampling, extraction & clean-up.
- For those, where available, some inhouse methodologies used by laboratories experienced in the analysis of POPs in products and recycling are described.
- The guidance further describe case studies (Annex 2) with reference to some reports where monitoring or analytical procedures for a POP in certain product matrix is described.



Examples for instrumental setting for individual POPs

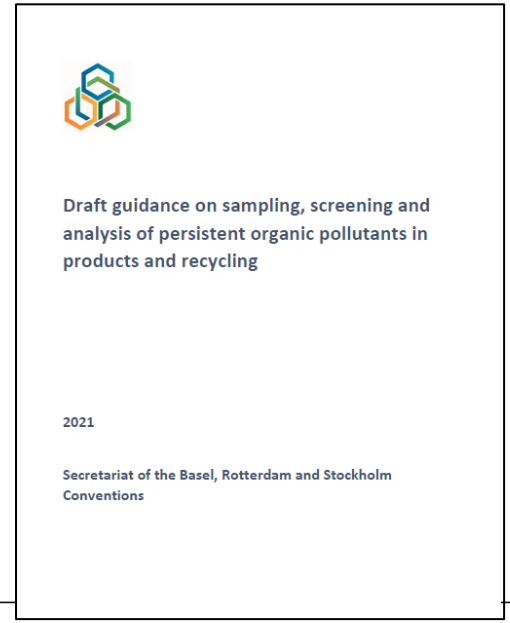
Annex 3 contain for each of the POPs a full analytical method for instrumental analysis

Examples for instrumental setting for individual POPs

- One example of a full instrumental setting is given for each of relevant POP in products/plastic.
- Example here for PBDE analysis
- With a suggested temperature program
- And options of GC columns including column length
- The method options are from experienced commercial or national laboratories.

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



Examples for instrumental setting for individual POPs

- Full masses for the individual POPs are provided for high resolution mass spectroscopy setting which can be used with reduced digits also for low resolution mass spectrometry.
- For chlorinated and brominated POPs having isomer clusters two masses for each homologue are given (for quantification and confirmation)
- This includes also the masses of the respective ^{13}C standards

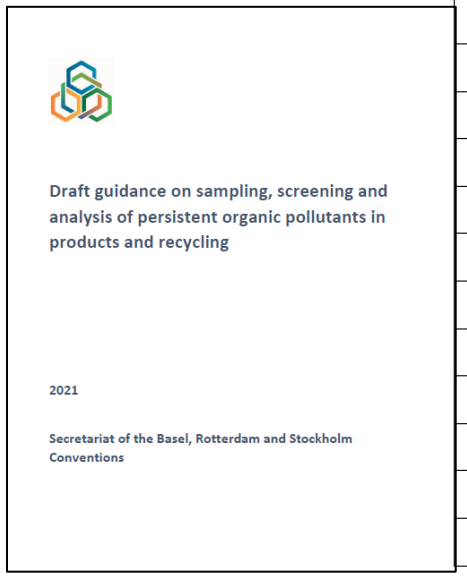
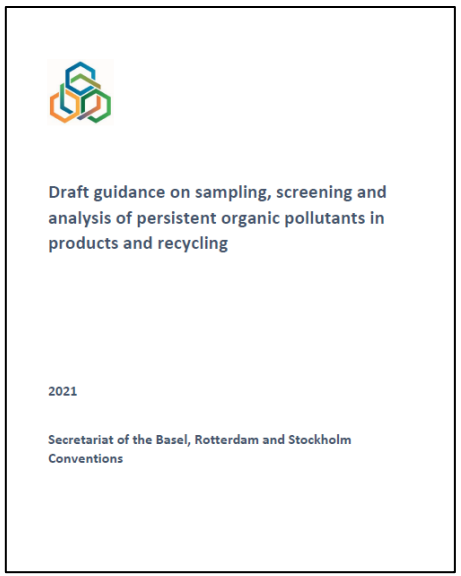


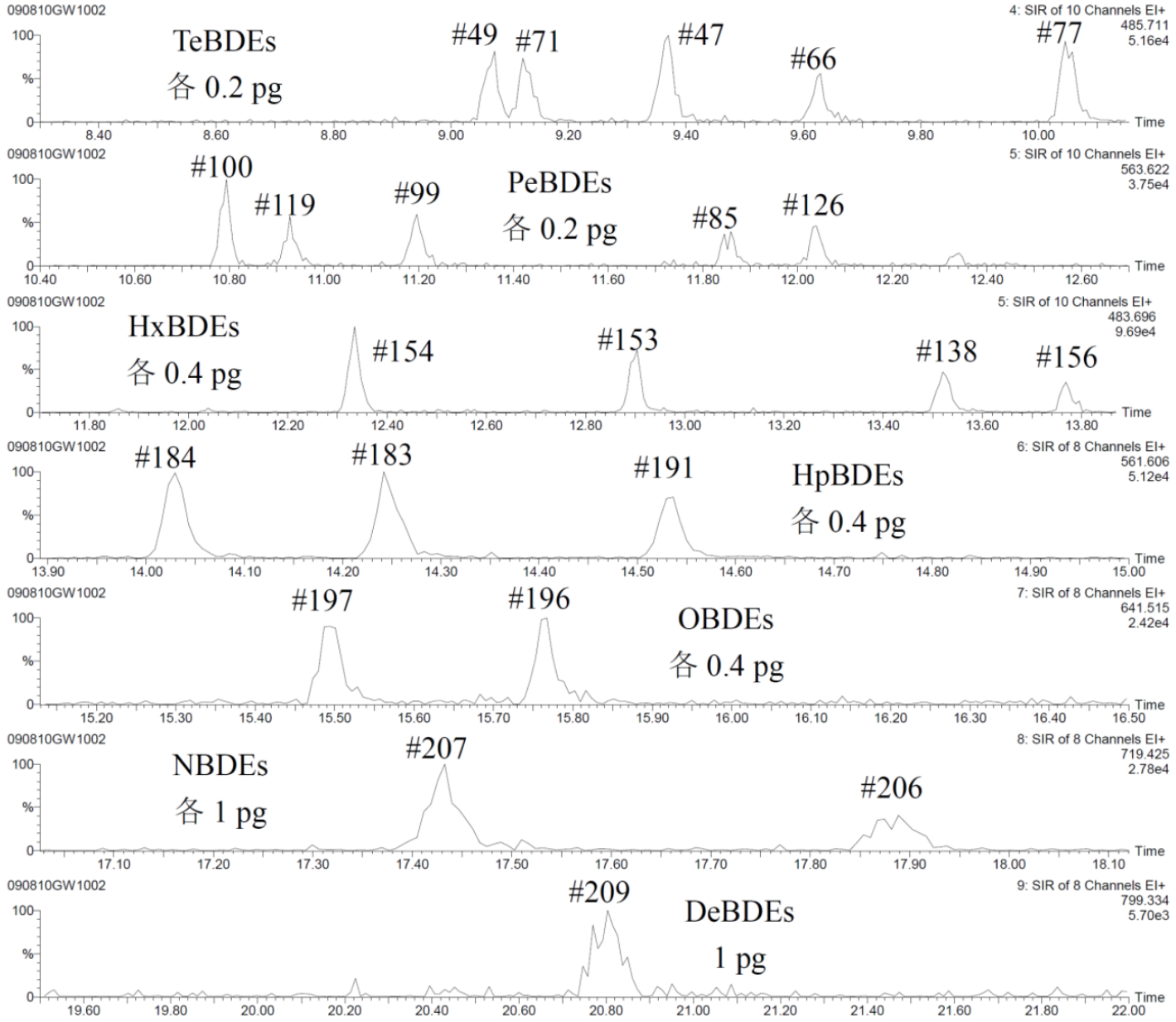
Table A3-A2: Masses of detected ions (*m/z*'s) for PBDE (HRMS masses; for LRMS reduc

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	

GC Chromatograms for individual POPs

- GC Chromatograms are provided for the individual POPs: Example PBDEs
- With assignment of individual congeners.

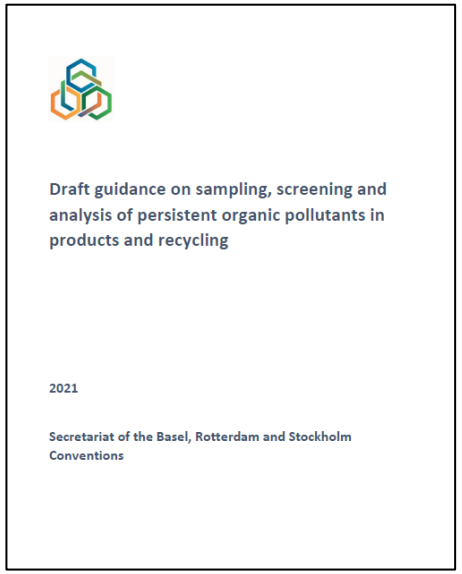


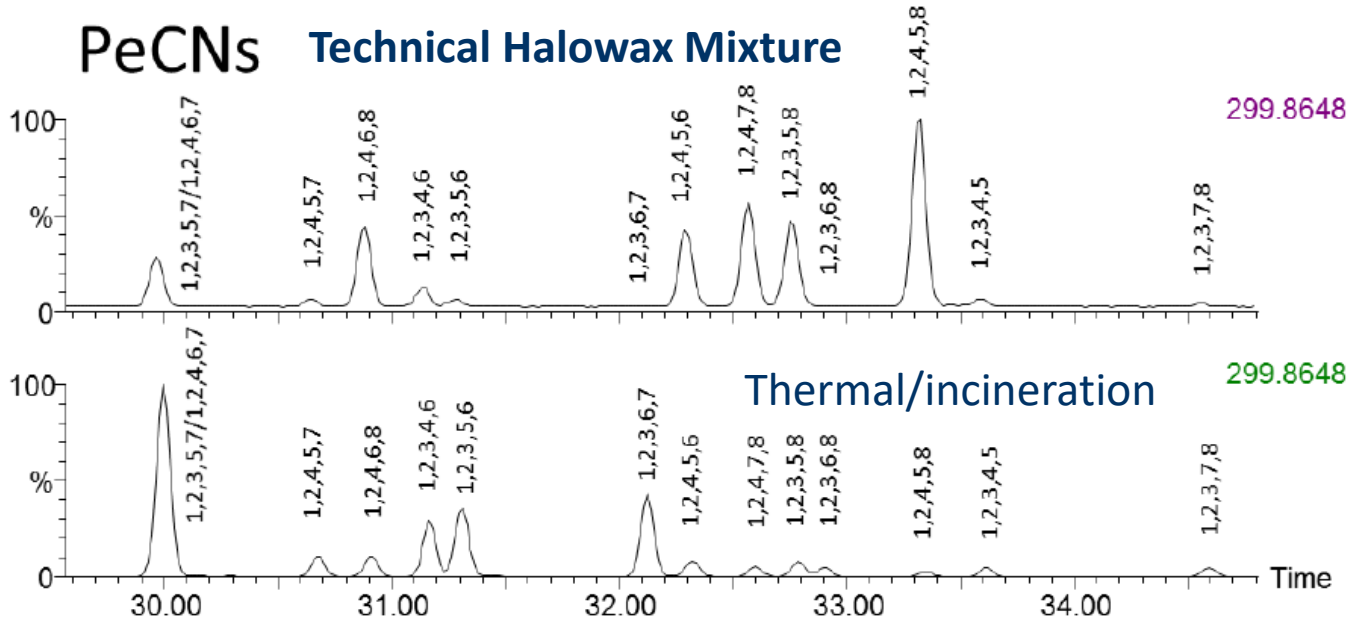


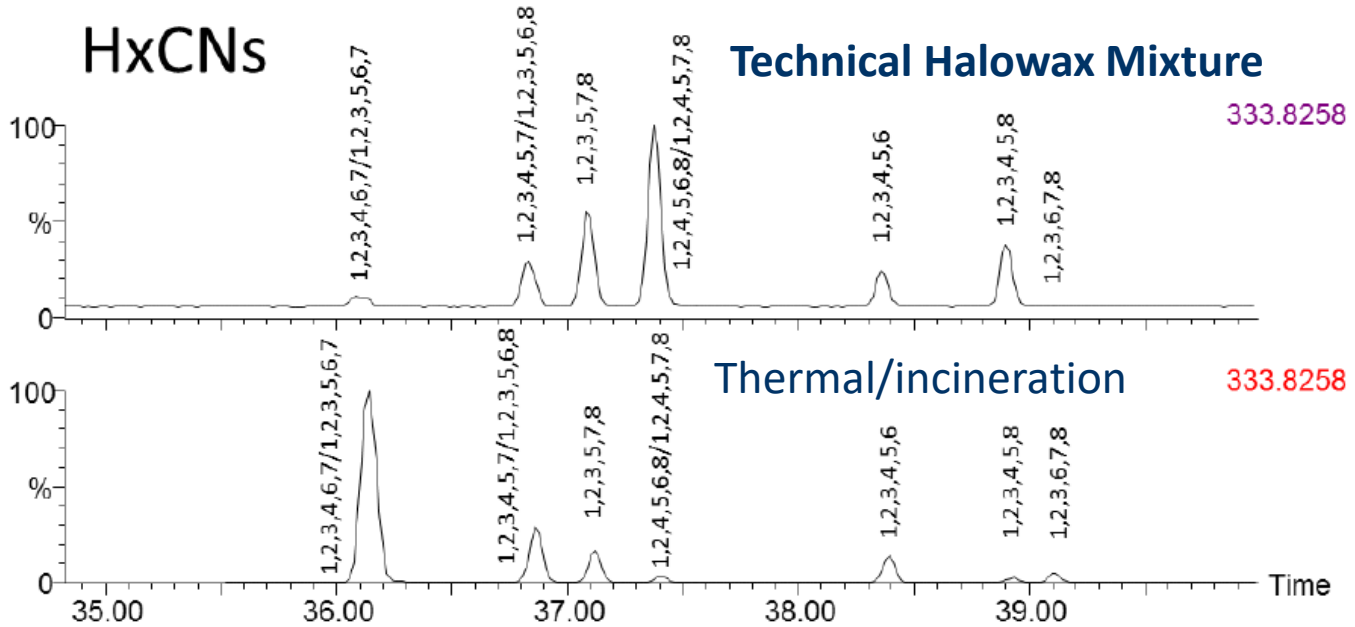
GC Chromatograms for individual POPs

GC Chromatograms are provided for the individual POPs: Example PCNs

- For PCNs the chromatograms of technical PCN mixtures are provided which might be found in plastic cables (1930 to 1970) or neoprene rubber (until 2000) and related recycling.
- Also the thermal pattern of unintentional PCN from incineration samples including open burning or fires is provided for comparison.





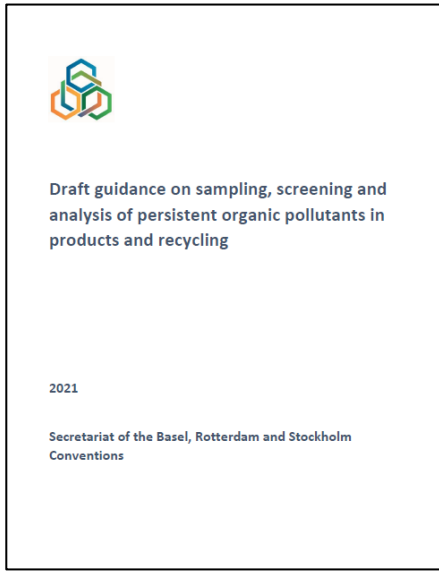


Examples for instrumental setting for individual POPs

Annex 3 contain for each of the POPs a full analytical method for instrumental analysis

For chlorinated paraffins three analytical methods are described in the guidance:

- A low resolution GC/ECNI-LRMS (electron-capture negative ionization) method which would also be suitable for developing countries
- A high resolution GC/HRMS method with „Orbitrap“
- The LC-MS/MS method of the National Institute for Environmental Studies (Tsukuba, Japan) which allows the monitoring of SCCP, MCCP and LCCP.



Examples for instrumental setting for individual POPs

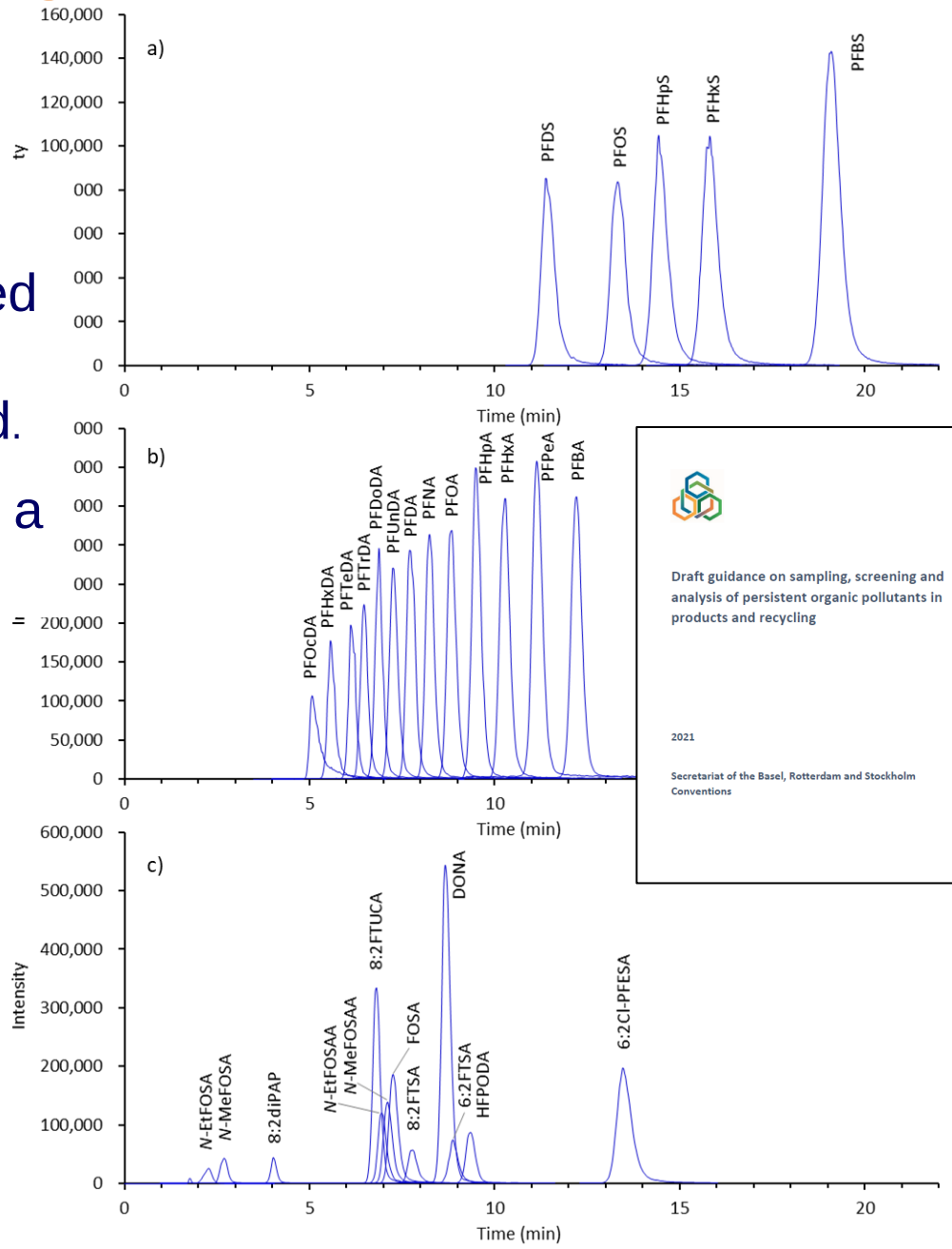
Annex 3 contain for each of the POPs a full analytical method for instrumental analysis

For POP PFAS three analytical methods are described:

- Two LC-MS methods are described. One method provided by National Institute of Advanced Industrial Science and Technology (AIST) is acoording the to ISO 21675 method.
- A GC/MS method which has been developed in a PhD of a Kenyan researcher (Professor Francis Orata).
- One challenge is that for most of PFOA/PFAS related substances (several 100!) no analytical standard is available for the quantification of e.g. PFOA related compounds.
- Currently the TOP-Assay is the most comprehensive approaoch for quantification of the complex precursor

Annex 3-I-1: LC-MS/MS analysis of PFOS, PFOA, PFHxS (inst

Annex 3-I-2: GC-MS/MS analysis of PFOS, PFOA and PFHxS

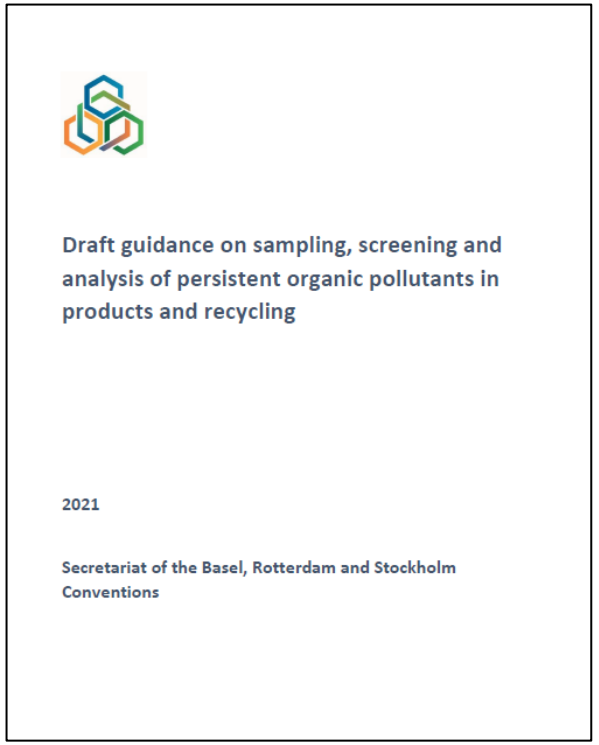


Need of further update of the guidance for monitoring POPs in products and recycling

The guidance on POPs in products and recycling is updated when needed:

What information to be added in the next update?

- Inclusion of monitoring methods for the new listed POPs 2023: UV-328 and Dechlorane Plus
- Inclusion of useful case studies published 2022/2023
- New international (and national standards) on analysis of POPs in products and recycling (e.g. ISO is developing monitoring standards for textiles)



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/

IOMC/OECD: https://iomctoolbox.org/; http://www.oecd.org/chemicalsafety/

Science: www.ipcp.ch; www.foodpackagingforum.org/; www.isde.org/; https://ikhapp.org/scientistscoalition/

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

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

Better-world-links: http://www.betterworldlinks.org/; https://www.plasticstreaty.org/scientists-declaration/

IPCP International Panel on Chemical Pollution

UN environment programme

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