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

Sampling of POPs in plastic in major POPs use sectors

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

IPCP International Panel on Chemical Pollution

UN environment programme

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Content of Presentation

- Sampling of plastics in the environment and in biota
- Monitoring POPs in plastics along the life cycle in the technosphere
- Sampling of plastics in electrical and electronic equipment (EEE) and waste (WEEE)
- Sampling & monitoring POPs in plastics in the transport sector
- Sampling & monitoring POPs in plastics in the building and construction sector
- Some other priority plastic use sectors for monitoring POPs
- More chemicals of concern ahead for monitoring in plastics

Sampling of plastic in the environment and in biota

This presentation addresses sampling of plastics in use sectors and related end-of-life of major sectors of POPs-use in plastic. Therefore the presentations of todays Webinar:

- Do not address sampling of plastic in the environment. **Major sampling in marine environment is described in UN document of GESAMP.** The global plastic pellet sampling of Prof. Takada was presented in the first IPCP webinar in this series and can be found in the recordings and his “Pellet Watch” activities and publications (http://pelletwatch.org/).
- Do not address sampling of plastics in biota including humans. The sampling of plastic in marine related biota was addressed by Prof. Takada in the first IPCP webinar in this series including monitoring of POP in individual plastic pieces and related contamination of biota. Also I made a presentation on POPs in plastic and human exposure. Both presentations can be found in the recording of the Webinars. IPCP Webinar Series: Part I, Day 1: Understanding POPs in plastics: https://www.youtube.com/watch?v=fc6BzT8rU_Y&t=9s

http://www.gesamp.org/publications/guidelines-for-the-monitoring-and-assessment-of-plastic-litter-in-the-ocean

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	+			A
Endosulfan, Heptachlor, Mirex	+		By-product of lindane	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 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 two more plastic additives have been listed in the convention at COP11 (05/2023).

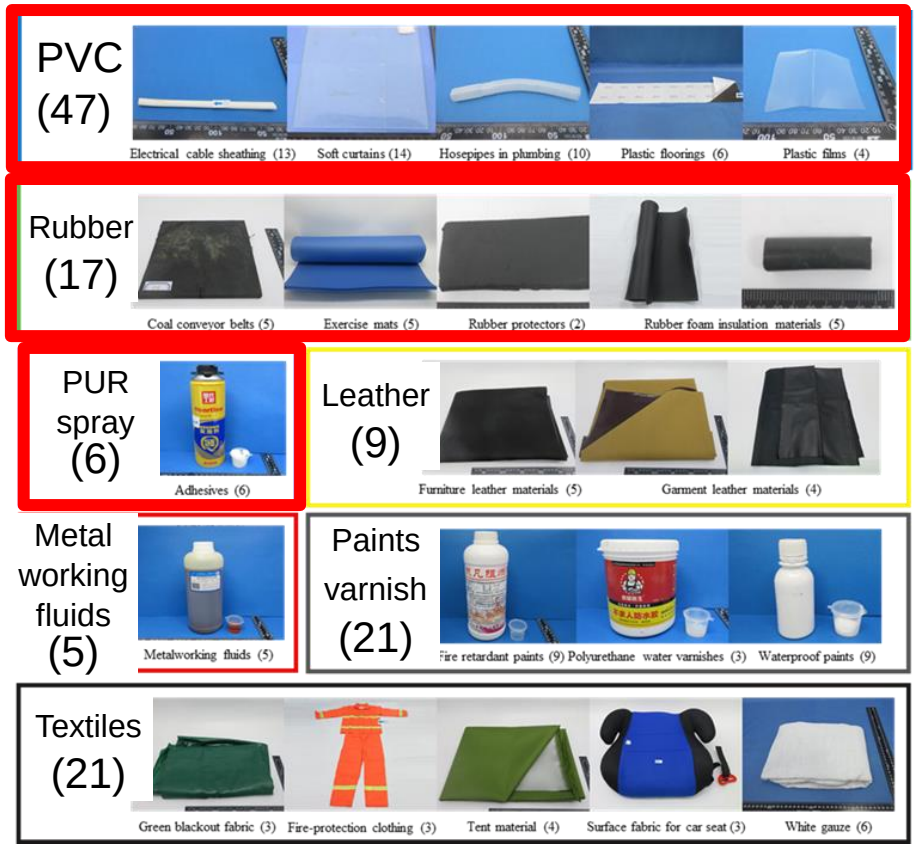
Therefore the control and management of plastic containing POPs becomes a major task in implementing the Stockholm Convention and can become an impulse or a role model for the management of chemicals of concern in plastic.

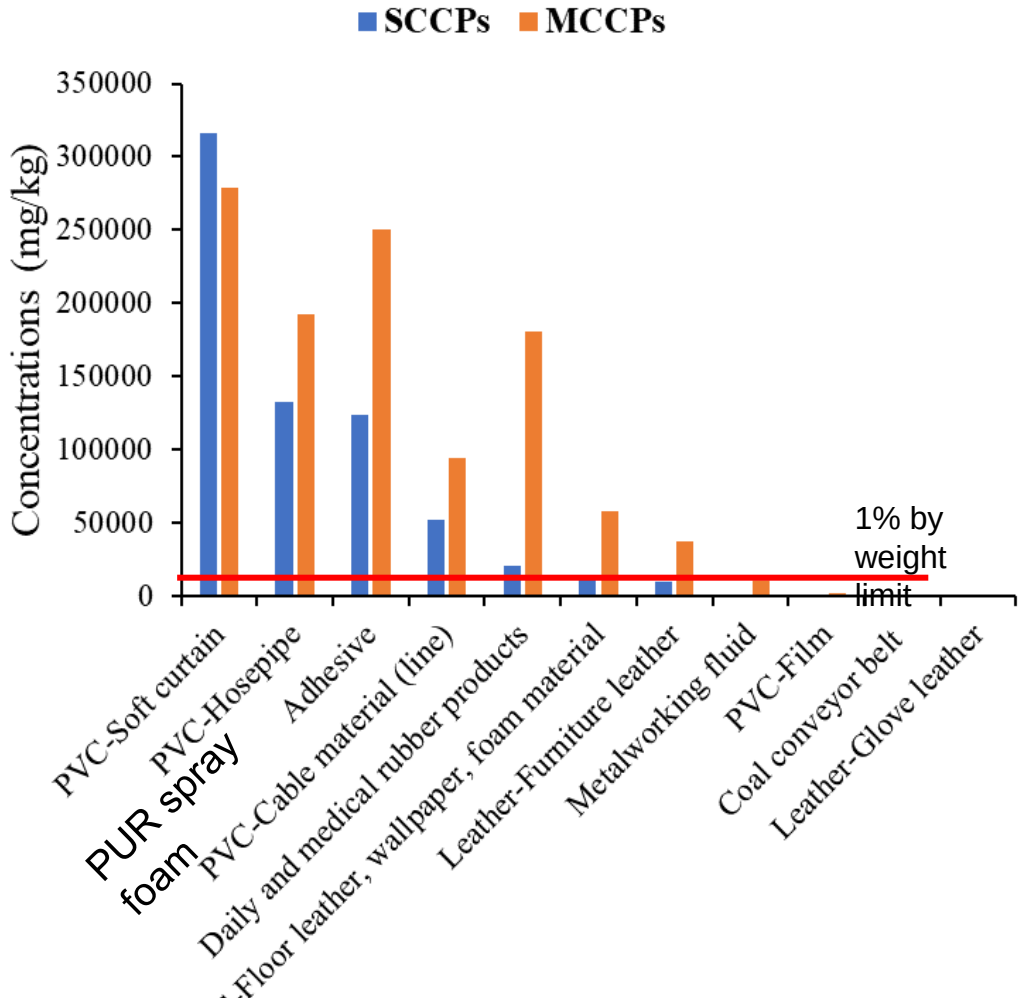
POP Review Committee: Chlorpyrífos, MCCP, LC-PFAA. **COP11 listed:** Methoxychlor; **UV328, Dechlorane Plus**

Market survey of POPs in the major uses of individual POP: S/MCCP

One approach for assessing POPs in use is sampling and monitoring of products of the (assumed) major uses of the respective POPs

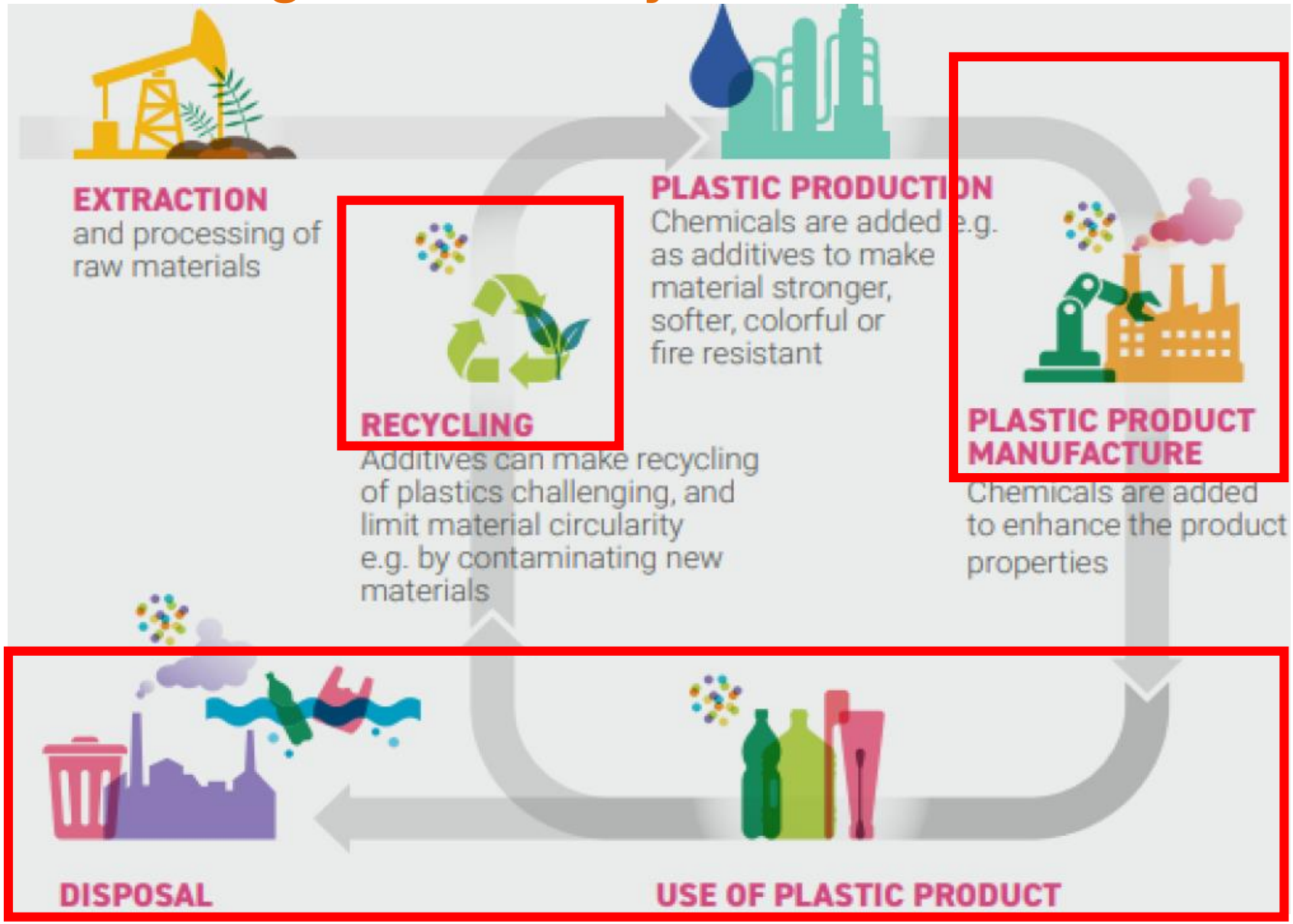
- Good example is screening of 124 product samples from Chinese markets for SCCP/MCCP.
- High share in soft PVC, rubber & PUR spay foam; Low in metal working fluids; conveyor belt.





Chen et al. (2021) Environ. Sci. Technol. 55, 7335–7343.
https://doi.org/10.1021/acs.est.0c07058

Monitoring POPs in major POPs-use sectors in the life cycle



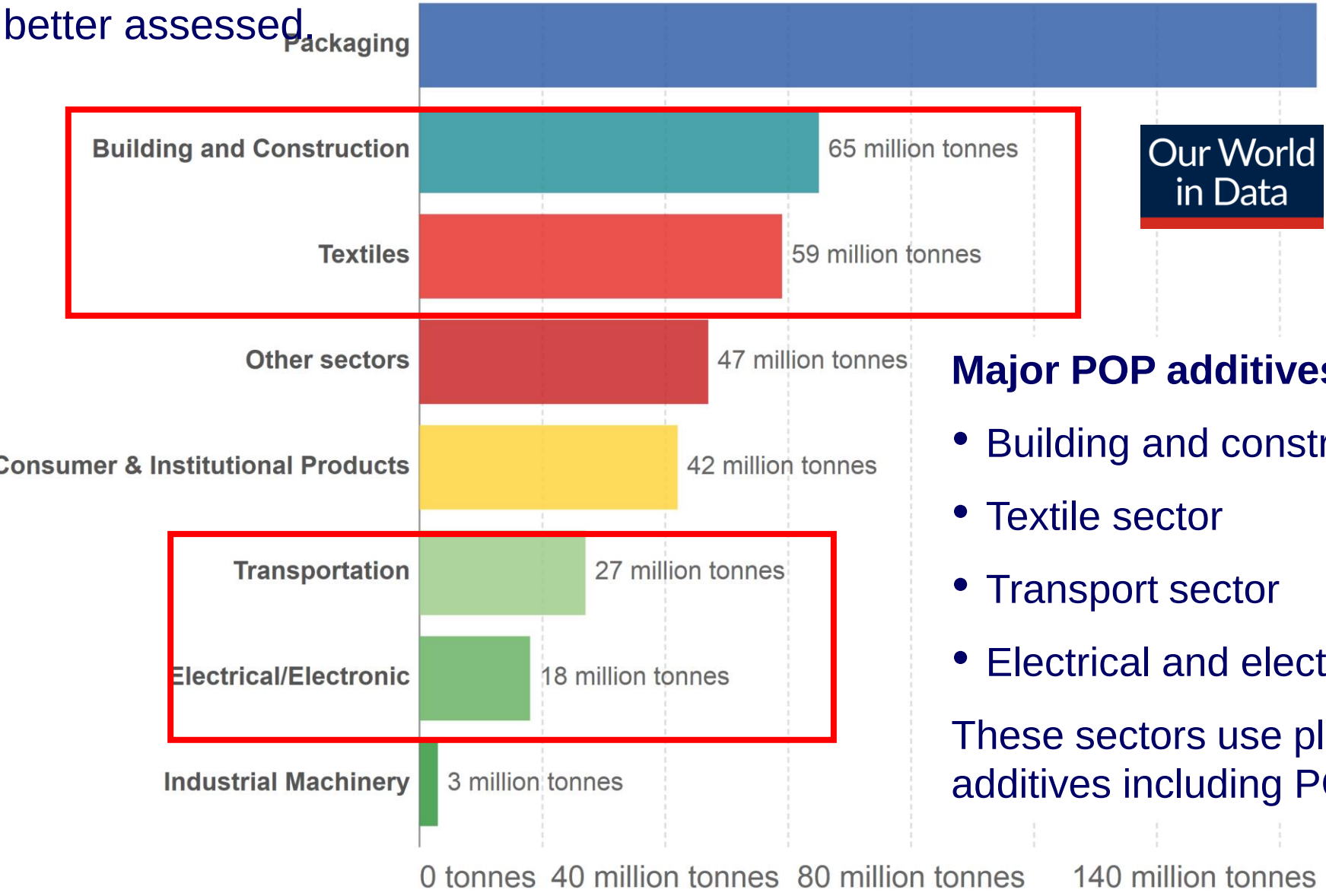
For POPs plastic additives with exemptions and current production also market surveys can be conducted (DecaBDE, SCCP, PFOA, UV-328, Dechlorane Plus).

For all POPs plastic additives relevant waste streams and recycling flows can be monitored as well as products in current use.

UNEP and BRS Secretariat (2023). Chemicals in plastics: a technical report. https://www.unep.org/resources/report/chemicals-plastics-technical-report

Alternatively: Monitoring of POPs according to industrial sector of use

The advantage of monitoring POPs in major plastic uses is that the life-cycle of POPs in plastic can be better assessed.



Major POP additives in plastic are used in the:

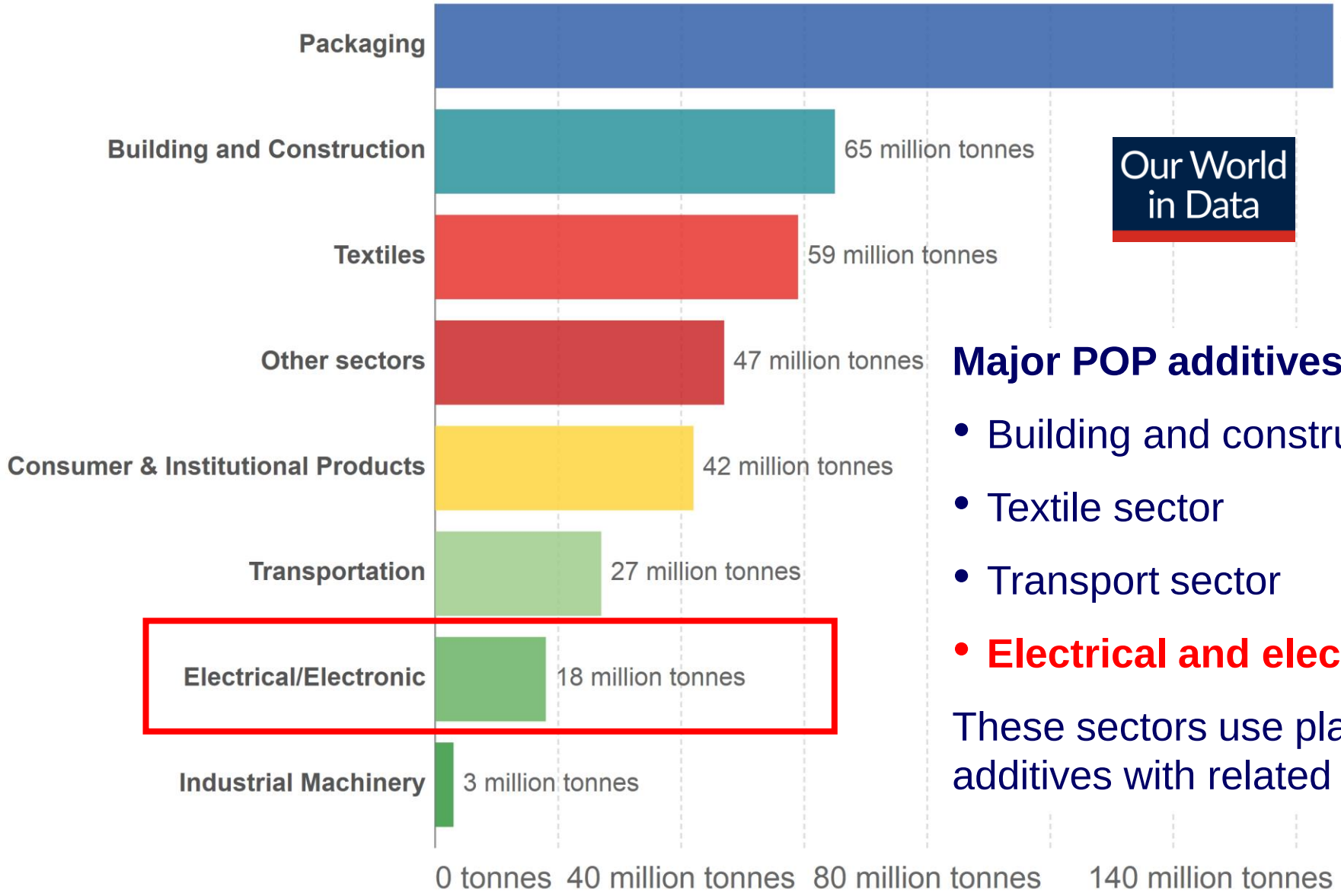
- Building and construction sector,
- Textile sector
- Transport sector
- Electrical and electronic sector.

These sectors use plastics with large amount of additives including POPs with related exposure risk.

Major Plastic use Sectors 2015; Based on Geyer et al (2017) Sci. Adv. 2017;3: e1700782

Monitoring of POPs according to industrial sector of use: EEE/WEEE

A large share of POPs plastic additives have been used in electrical and electronic equipment (EEE)



Major POP additives in plastic are used in the:

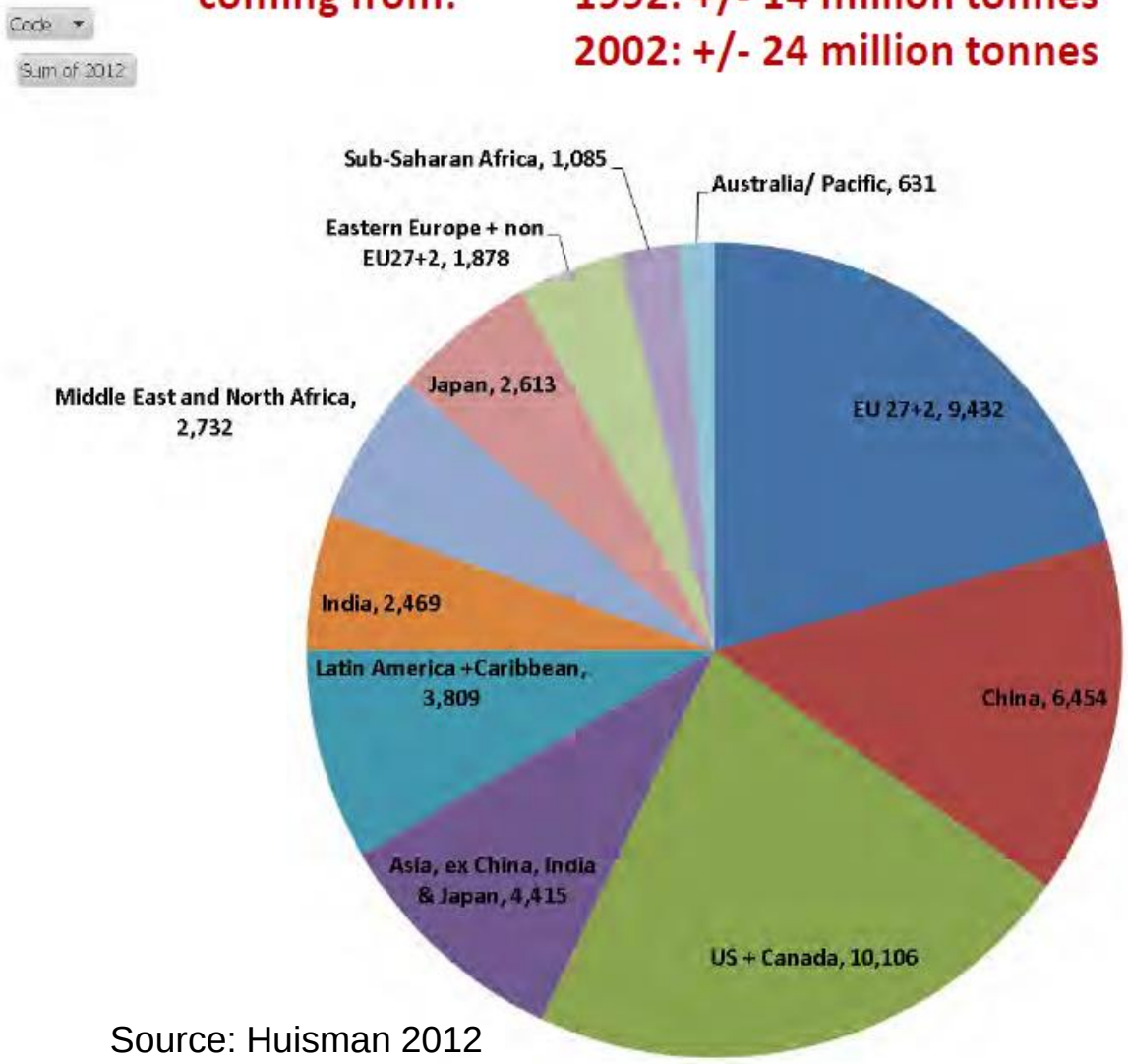
- Building and construction sector,
- Textile sector
- Transport sector
- **Electrical and electronic sector.**

These sectors use plastics with large amount of additives with related exposure risk.

Major Plastic use Sectors 2015; Based on Geyer et al (2017) Sci. Adv. 2017;3: e1700782

E-waste: fast growing waste stream containing plastics & POP

coming from: 1992: +/- 14 million tonnes
2002: +/- 24 million tonnes



Source: Huisman 2012

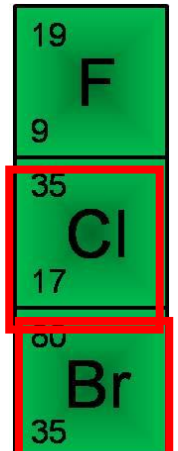
2019 total: ~53.6 million tonnes

2030 estimate: ~74 million tonnes

Average plastic in EEE: 20%. Therefore 10.7 and 15 million t WEEE plastic in 2019 and 2030

E-waste: fast growing waste stream containing plastics & POP

- **Only a fraction of the WEEE plastic contains POPs.**
- But these parts are mixed with other equipment and therefore contaminate the entire WEEE
- Detailed information on contamination of EEE/WEEE categories to be generated by monitoring
- And this information must reach then the people who are managing & recycling WEEE plastic.



Some key hazardous chemicals in EEE/WEEE and relation to chemical conventions (Synergy)

Substance	Function/occurence in EEE
PBDEs, PBBs, Dechlorane Plus	Flame retardants in plastic parts with ignition risk
SCCP/MCCP	Cables, other PVC parts; rubber parts
Polychlorinated biphenyls (PCBs)	Cables, condensers, transformers (older than 1990)
Polychlorinated naphtalenes (PCNs)	Cables, Condensers, transformers (older than 1980)
UV-328	UV-stabilizer in plastic
PBDD/PBDF	Unintentional byproducts from PBDE and other BFRs in plastics
Chlorofluorocarbons (CFCs; HCFCs)	Cooling units, insulation foam
Hydrofluorocarbons (HFCs)	Cooling units, insulation foam
Americium (Am)	Smoke detectors
Antimony	Flame retardants in plastics
Arsenic	gallium arsenide in light emitting diodes
Barium	Getters in CRT
Cadmium	NiCd-batteries, fluorescent layer (CRTs), printer inks toners
Chromium VI	Data tapes, floppy-disks
Lead	Some plastic; CRT screens, batteries, printed wiring boards
Mercury	Fluorescent lamps, some alkaline batteries, switches

Swiss market survey of BFRs in EEE and other products

The Swiss authorities monitored 2000 consumer products for the presence of BFRs, including EEE, building materials and lighting equipment. The aim of the survey was to evaluate the compliance of commercial products with the provisions of the Swiss restrictions on BFRs.

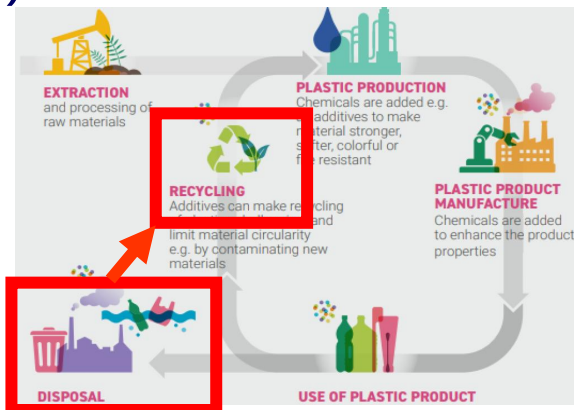
Monitoring approach taken:

- Screening of bromine in products to indicate BFRs (bromine screening in laboratory)
- GC-MS analysis of Br-positive samples for prohibited PBDEs and commonly used flame retardants
- In bromine positive samples, where commonly used BFRs were not detected, non-target screening for new brominated flame retardants was carried out.
- The study showed that the PBDE content in current products on the Swiss (and likely European) market is small.

17 samples contained decaBDE above the RoHS threshold of 0.1%.
And only 2 from the approximately 2000 samples contained c-OctaBDE above the 0.1% RoHS threshold.

Monitoring of individual WEEE: CRT casings of TVs & computers

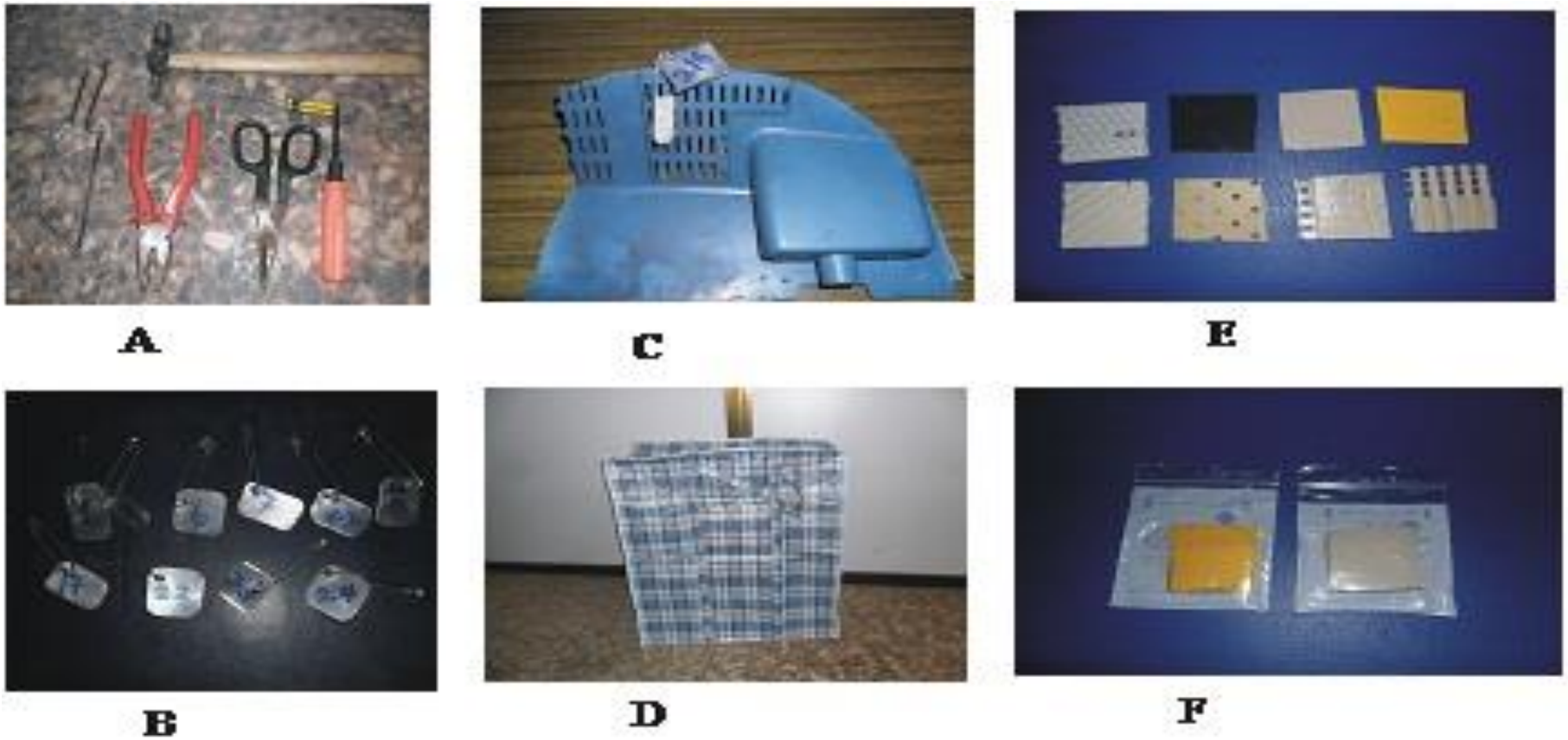
- Casings of Cathode Ray Tubes (CRTs) of TVs and computers were screened in Nigeria.
- This WEEE category contains the largest average content of PBDEs within EEE/WEEE.
- 382 single CRT casings were sampled at WEEE storage sites in Nigeria.
- Information on the manufacturer, brand, model, serial number, year and origin of production. The aim was to understand the former use of PBDEs (c-OctaBDE and DecaBDE) as well as use of other BFRs.
- Approach was
  - Prescreening with XRF
  - Confirmation analysis with GC/ECD
  - South-North cooperation (Nigeria-Germany; presentation Dr. Sindiku)
- The approx. 400 individual CRTs were the minimum number to roughly get a statistical insight into the distribution of c-DecaBDE (30 treated) and c-OctaBDE (5 treated) of CRT casings.



Sindiku et al. (2015) Environ Sci Pollut Res Int. 22, 14489-14501.

Monitoring of individual WEEE: CRT casings of TVs & computers

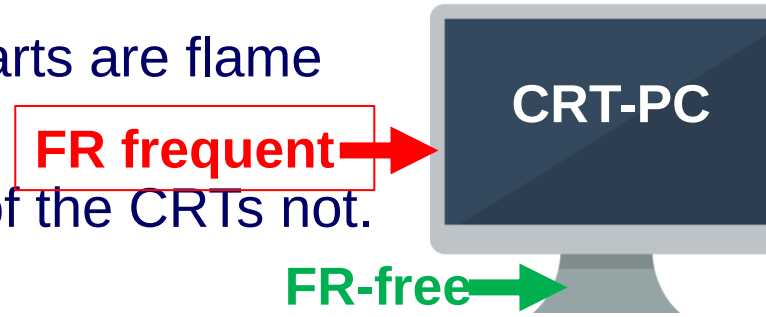
CRT casing sample preparation and labelling for XRF screening (desk XRF 4x4 cm samples)



Sindiku et al. (2015) Environ Sci Pollut Res Int. 22, 14489-14501.

Monitoring of individual EEE: Screening if individual plastic parts

- Most EEE consist of several plastic parts. Often only a few of these parts are flame retarded. Therefore some screening of plastic parts might be needed
- E.g. computer CRTs casings are often flame retarded but the stands of the CRTs not.



Best practice study for monitoring PBDEs in large & small EEE individual plastic parts in UK/Wales:

- Screening of plastic parts in fridges showed that only a few pieces in some fridges contained high levels of POP-BFRs (electrical & compressor casings, electrical junction box, cable boxes) but the outer major plastic parts (door, side panel, back, trays, shelves) do not contain BFRs/POPs.
- Also in other large household appliances (washing machine/dish washer) only a few controller boxes contained POP-BFRs while all outer/major plastic components did not contain BFRs.

ICER and WRC (2020) An assessment of the levels of persistent organic pollutants (POPs) in waste electronic and electrical equipment in England and Wales. Report Reference: UC14161.3 https://icer.org.uk/wp-content/uploads/2020/03/UC14161.3-An-assessment-of-the-levels-of-persistent-organic-pollutants-POPs-in-waste-electronic-and-electrical-equipment-in-England-and-Wales-FINAL-REPORT.pdf

- More studies on monitoring individual plastic parts of EEE for POPs additives are needed including also the new listed UV-328 and Dechlorane Plus; best with assigning all FRs included.

WEEE categories and plastic volumes – determining impact factors

The major amount of plastic is in a few EEE categories: large household appliances (freezers, refrigerators, air conditioners, washing machines etc.), small household appliances (e.g. microwave ovens, toasters, coffee-makers). ICT equipment (computers & screens, copy/fax machines, scanner and printers). A last large category is consumer equipment including e.g. TVs (CRTs and flat screens), radio, video & camera.

WEEE Category/Product Category	Plastic share [in % by weight]	Annual plastic flow in the EU [in t/year]
Large household appliances w/o cooling appl.	19%	**500'500**
Cooling and freezing appliances	28%	**473'100**
Small household appliances	37%	**369'400**
ICT equipment w/o screens	42%	**317'600**
Computer screens (CRT and flat)	20%	**156'100**
Consumer equipment w/o screens	24%	**180'900**
TV screens (CRT and flat)	20%	**200'100**
Lighting equipment – Lamps	3%	**7'300**
Electrical and electronic tools	11%	**37'800**
Toys, leisure and sports equipment	73%	**7'600**
Medical devices	3%	**400**
Monitoring and control instruments	60%	**11'900**
Automatic dispensers	20%	**3'500**
Total amount	**Average of ca. 20%**	**2'266'100**

Estimation of the total plastic quantities in European WEEE for the year 2008. Printed wiring boards and cables are not included. (Source: Wäger et al. 2010)

The use of flame retardants depends on the equipment category and the flammability standards in regions.

In particular equipment which can get hot like heating appliances, or TVs in particular CRTs frequently contain flame retardants.

On the other hand, cooling appliances contain considerable less flame retardants.

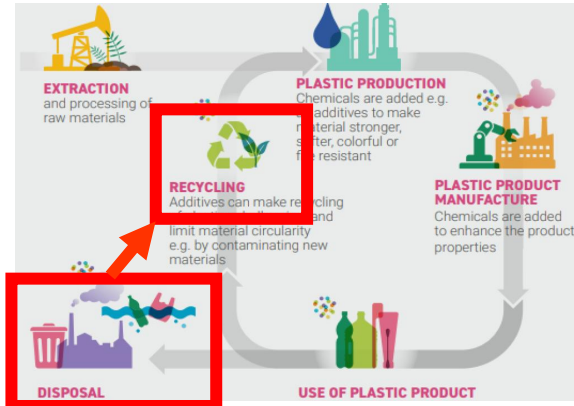
For managing plastic of the respective categories POPs **impact factors** are needed.

Monitoring of shredded WEEE plastic for POP inventory & management

- In WEEE recycling, the e-waste is frequently shredded and the metal fraction separated with a remaining plastic fraction with impurities. Also, if WEEE is manually dismantled, the plastic needs finally to be shredded for economic shipment & further processing.
- Therefore, the major samples from WEEE plastic to be gathered and analysed is often from such shredded WEEE plastic which can give average contamination levels (impact factors).
- The understanding of the POP (PBDE, dechlorane plus) contamination in such plastic fraction decides if the plastic shred can be used in recycling or needs further separation considering Basel Convention low POPs limits or national regulation.

The correct sampling of WEEE plastic for POPs needs to take into account the interrelated issues:

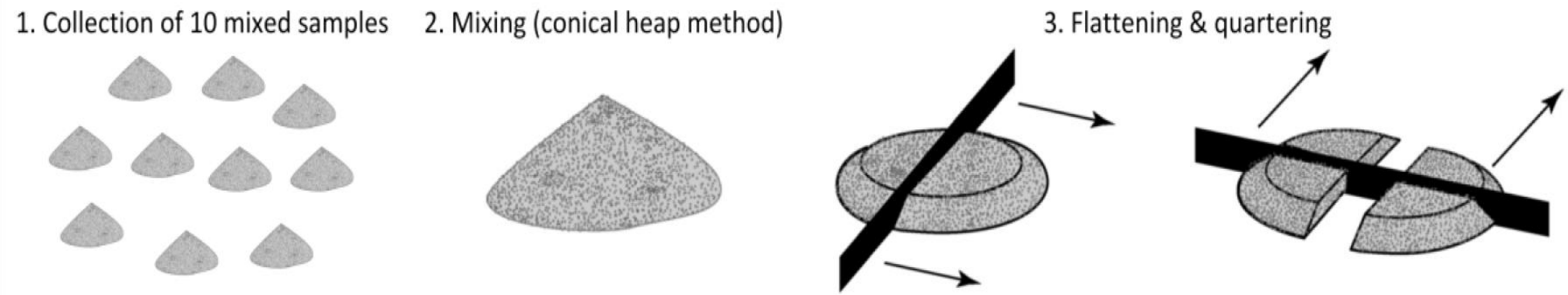
- the distribution of the concentrations of POPs in the waste products and waste fractions;
- the statistical questions of the determination of the size of a representative sample;
- the chemical characterization of particles and samples.



Sampling of shredded WEEE plastic for POP monitoring

Best practice: EMPA methodology for monitoring POPs in shredded WEEE plastic

- The Swiss national material testing institute EMPA developed a standardized methodology for sampling of WEEE plastic for a survey of POP-BFRs and other RoHS regulated substances in WEEE plastic.
- 3–7 tonnes of plastic shreds are sampled with 20 single samples. Ten single samples each are mixed to a mixed sample with the “heap method”. The resulting two mixed samples are, if necessary, reduced to the size of laboratory samples.



- Technical Specification TS 50625-3-1:2015 standard (CENELEC 2015) defines minimum size of single, composite and laboratory samples
- .

Max. grain size (95% of plastic particles) [mm]	Min. single sample [litre]	Min. volume of mixed sample [litre]	Amount of Lab.-sample [litre]
> 2 to < 20	3	30	4
> 20 to < 50	5	50	12
> 50 to < 120	10	100	25

[1] CENELEC, 2015. CLC/TS 50625-3-1 Collection, logistics & treatment requirements for WEEE - Part 3 - 1: Specification for de-pollution - General. CENELEC, Brussels, Belgium.

Commercial PBDE mixtures in shredded WEEE plastics (EU 2010)

Flame retardant use depends on WEEE category and flame risk for plastic parts		**Penta BDE**	**Octa BDE**	Deca BDE	Deca BB
	Cooling and freezing appliances (all plastics, except foams)			ABS HIPS,PP	
	Vacuum cleaners w/o hoses			ABS HIPS	
	Small appliances for high temperature applications			ABS HIPS,PP	
	CRT monitors		ABS	ABS HIPS	
	Printers			ABS HIPS	
	CRT TVs		ABS	ABS HIPS	

not detected or at average concentrations clearly below RoHS limit of 0.1%

average concentrations below (yellow cells) or in the vicinity (orange cells) of the RoHS MCV

average concentrations above the RoHS MCV of 0.1% (Source: Wäger et al. 2010; and 2012)

Plastic & POP-PBDE content in EEE/WEEE plastic

Two best practice case studies (Switzerland; France) were used to determine impact factors for PBDEs for different WEEE plastic fractions for the Stockholm Convention PBDE inventory guidance.

Table: Total polymer fractions and c-octaBDE and decaBDE concentrations in relevant EEE categories (data from Europe; Waeger et al., 2010; Hennebert & Filella 2018)

Relevant EEE	Total polymer fraction (mean)	Hexa/heptaBDE content (mean) in plastics	DecaBDE content (mean) in plastics
	$f_{Polymer}$ [in % by weight]	$C_{\sum hexa/heptaBDE;Polymer}$ in [kg/tonne]*]	$C_{decaBDE;Polymer}$ in [kg/tonne]*]
Cooling/freezing appliances; washing machines	25%	<0.05	<0.05
Heating appliances	30%	<0.05	**0.8**
Small household appliances	37%	<0.05	0.17
ICT equipment. w/o monitors	42%	0.12	**0.8**
CRT comp. monitor casings	30%	**1.37**	**3.2**
Consumer equipment w/o monitors (1 composite sample)	24%	0.08	0.8
TV CRT monitor casings	30%	**0.47**	**4.4**
Flat screens TVs (LCD)	37%	0.009	**2.75**

Provisional Basel Convention low POP content: 1 kg/t (0.1%) or 500 g/t (0.05%) or 50 g/t (0.005%)

UNEP (2019) Stockholm Convention PBDE inventory guidance.

Plastic recyclates produced or imported

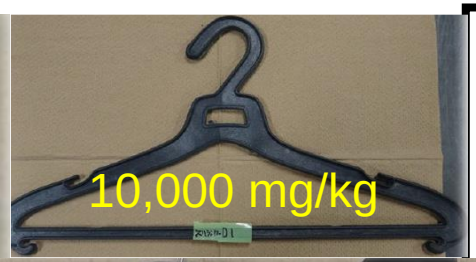
- Relevant plastic samples for analysis, are imported plastic recyclates and granulates which are used for manufacturing of new plastic products in a country.
- Lack of screening with only a few data from developing countries (IPEN study of HDPE 2021)
- Samples can be pre-screened with XRF and samples containing a certain amount of bromine (or chlorine) should be analysed in laboratory for POP-BFRs/CFRs and possibly other POPs.

Screening and analysis of **consumer products** imported or on the market

- Plastic containing PBDEs is recycled into products including sensitive consumer products such as toys, food contact materials, and other goods documented by a wide range of studies.
- Frequently, plastic containing PBDEs from recycling is black. Therefore, a starting point for monitoring of PBDEs/POPs in plastic products is the screening of black plastic in e.g., food contact materials, toys.

PBDE children toys China (Chen, ES&T 43, 4200, 2009)

Toys in Africa (IPEN , 2021)



PBDE in consumer goods in 18 countries (Kajiwara Chemosphere 289, 133179 2022)

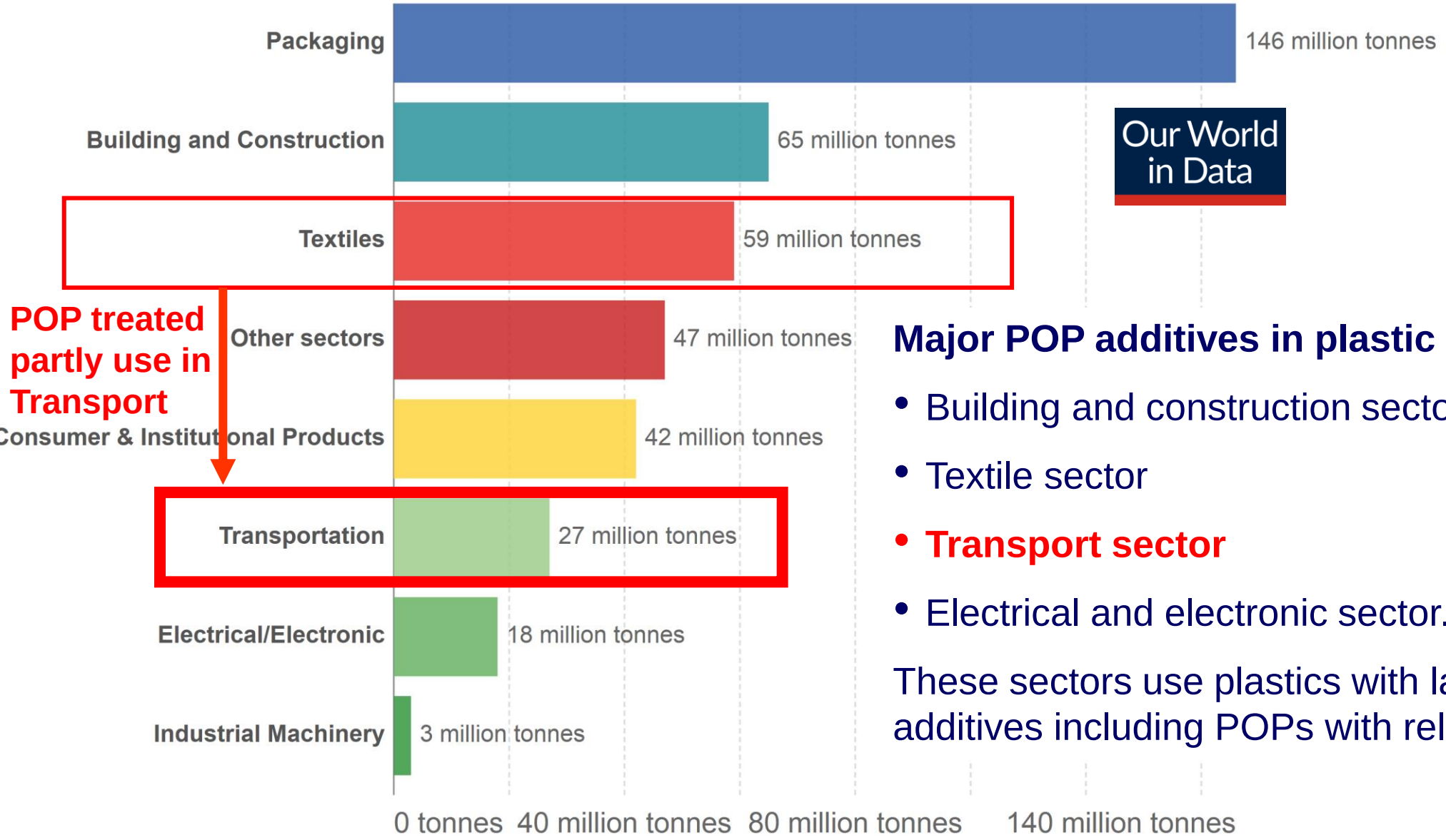
PBDE in thermo-cup (Samsonek & Puype Food Add. & Contam. 2013

⇒ Study from NIES on monitoring >1100 consumer goods from 18 countries were presented in the last IPCP Webinar and recording (https://www.ipcp.ch/activities/ipcp-webinar-series-pops-in-plastic-and-monitoring-approaches)

⇒ Further studies needed including e.g. new listed POPs UV-328 and Dechlorane Plus.

Monitoring of POPs according to industrial sector of use: Transport

A large share of POPs plastic additives have been used in the transport sector including textiles used there.



Major POP additives in plastic are used in the:

- Building and construction sector,
- Textile sector
- **Transport sector**
- Electrical and electronic sector.

These sectors use plastics with large amount of additives including POPs with related exposure risk.

Major Plastic use Sectors 2015; Based on Geyer et al (2017) Sci. Adv. 2017;3: e1700782

POP-BFRs are contained in large waste flows – plastic in vehicles

End-of Life Vehicle and related POPs containing plastic/polymer waste

- The global light-duty vehicle fleet is **1.31 billion vehicles** (2020) expected @2.2 billion by 2050.
- With a service live of approx. 20 years approx. ~65 million ELVs/year. Considering that an **average vehicle contains approx. 200 kg of plastic/polymers, every year ~13 Mt of plastics** and other polymer **waste partly containing POPs are generated.**

Some key hazardous chemicals in vehicles and relation to chemical conventions (Synergy)

Substance	Function/occurence in vehicles
PBDEs, PBBs, Dechlorane Plus	Flame retardants in plastic parts with ignition risk
SCCP/MCCP	Cables, other PVC parts; rubber parts (not tires)
Polychlorinated biphenyls (PCBs)	Cables, condensers, transformers (older than 1990)
Polychlorinated naphtalenes (PCNs)	Cables, Condensers, transformers (older than 1980)
UV-328	UV-stabilizer in plastic, paints coatings
PBDD/PBDF	Unintentional byproducts from PBDE and other BFRs in plastics
Chlorofluorocarbons (CFCs; HCFCs)	Air conditioning, insulation foam in refrigerator trucks
Hydrofluorocarbons (HFCs)	Air conditioning, insulation foam in refrigerator trucks
Antimony	Flame retardants in plastics
Lead	Lead acid batteries, solders, finishings, connectors, printed circuit boards
Mercury	Anti-lock braking systems (ABSy), high intensity discharge (HID), active ride control systems, head and tail lights

Monitoring POPs/automotive parts in new vehicles on the market

There are no monitoring studies of POPs in new vehicles. A starting point for monitoring could be the exempted uses listed in the Stockholm Convention.

Exempted uses of DecaBDE in vehicles (SC § 2 of Part IX of Annex) give an indication what parts in vehicles might contain POP-FRs:

(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), speed sensors, hoses, fan modules and knock sensors;

(ii) **Fuel system applications**; fuel hoses, fuel tanks & 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.

(V) Reinforced plastics (instrument panels and interior trim);

(VI) Under the hood or dash (**terminal/fuse blocks**, higher-amperage **wires and cable jacketing** (spark plug wires));

(VII) **EEE** (battery cases/trays, engine control electrical connectors, components of radio disks, navigation satellite system, computer systems);

(VIII) **Fabric/textiles** such as for **automobile seats,** rear decks, upholstery, headliners, head rests, sun visors, trim panels, **carpets.**

Monitoring POPs/automotive parts in new vehicles on the market

For **Dechlorane Plus** some **compilation of uses** have been conducted for recent **POPs listing**

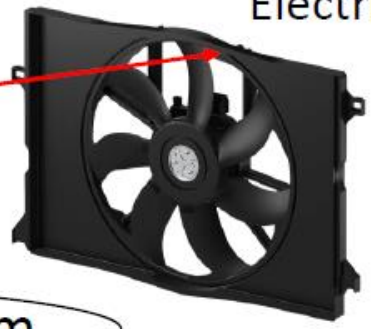
Battery

Li Battery pack

Dechlorane plus is contained in mass wire and interconnection wire and tapes

Fan modules

Electric fan



Dechlorane plus is contained in wire harness and tapes

Dechlorane Plus is contained in wire harness, mass wire, and tapes in many parts of underhood and power train applications in vehicles.

Mobile Air-conditioning (MAC) system

Radiator

Dechlorane plus is contained in wire harness and tapes

Electric fan

Cooling water flow control valve

Reserve tank

Water intercooler

Water temperature meter

*:Product photographs are taken from the websites of DENSO CORPORATION and TOKAI RIKA CO., LTD.

Monitoring POPs/automotive parts in new vehicles on the market

For **Dechlorane Plus** some **compilation of uses** have been conducted for recent **POPs listing**

DC-DC Converter

DC-DC Converter

Stater Unit

Stater

Heater Unit

Heater core

Dechlorane plus is contained in wire harness and tapes

Dechlorane Plus is contained in wire harness, mass wire, and tapes in many parts of underhood and power train applications in vehicles.

Motor

Dechlorane plus is contained in tapes

Motor generator stator

Blower motor

Variable nozzle turbo motor

Servomotor

*:Product photographs are taken from the websites of DENSO CORPORATION and TOKAI RIKA CO., LTD.

Monitoring POPs in new vehicles on the market

There are no published POPs monitoring studies of POPs in new vehicles. A starting point for a monitoring could be the exemptions listed in the Stockholm Convention.

Exempted uses of Dechlorane Plus For replacement parts for, and repair of, articles in the following applications until the end of the service life of the articles or 2044:

- **Motor vehicles** (all land-based vehicles, such as cars, motorcycles, agricultural & construction vehicles and industrial trucks; applications include **cables**, **wire harnesses**, **connectors** and **insulation tapes**);
- Stationary industrial machines (such as tower cranes, concrete plants and hydraulic crushers; applications include cables, wire harnesses, connectors and insulation tapes) for use in agriculture, forestry and construction;

Aerospace (such as aircraft engine fan case rub strip products and void-filling and edge-sealing products, aircraft engine manufacturing repairs, electrical items, structural panels and aircraft cabin interiors);

Space (such as satellites, probes and other exploration equipment, manned cabins and laboratories, heat-insulating materials for rocket motors and ground support equipment);

Defence (such as naval vessels, missiles, launch platforms, ordnance, communication equipment, radar and lidar systems and support equipment);

Monitoring POPs/automotive parts in new vehicles on the market

Also for **UV-328 some compilation of uses** have been conducted for the recent POPs listing

Paint and Resin

Uses UV328 for weather and sunlight resistance

The application of UV328 is mainly on outer parts such as bumpers, grill, sur roof, spoiler, or wheel cap.

Inside cars: e.g. displays.

Also the list of exemptions can be used as a start.

< Applications >

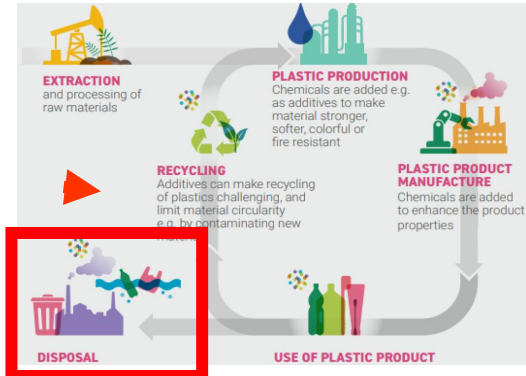
Source: APIA

Sampling and screening of POPs in plastics in vehicles in use and end-of life vehicles

- Monitoring of individual vehicles is useful to get an overview of the former use of POPs in the transport sector:
  - The age distribution of the use of POPs in vehicles
  - The regional distribution of the use of POPs in vehicles
  - If POPs use is associated with certain companies or series
- Therefore for such studies the following information is useful:
  - Year of production
  - Producer and model name
  - Country of origin (several producers were/are producing in different regions/countries with different flammability standards and therefore flame retardant use).

Sampling and screening of plastic parts in individual ELVs

- **One best practice case study** monitoring POPs (PBDEs, HBCD) in end-of-life vehicles (ELV)
- The study screened PBDEs and HBCD in 515 parts in 45 vehicles produced between 1993 and 2012 with XRF approach and then analysis in the laboratory (Kajiwara et al. 2014).



Kajiwara et al. (2014) Organohalogen Compounds 76, 1022-1025

Monitoring of PBDEs and HBCD in cars (Japan)

Components	*n*	ID	Br	PBDEs	HBCDs	PBDD/Fs
Seat fabric	16	*ELV-03*	50,000	78,000	<LOD	32
		ELV-39	45,000	62,000	<LOD	22
		ELV-24	41,000	52,000	11	23
		ELV-07	34,000	46,000	50	31
		ELV-27	34,000	49,000	0.46	32
		ELV-11	34,000	43,000	<LOD	28
		ELV-31	34,000	48,000	<LOD	41
		ELV-04	32,000	45,000	<LOD	34
		ELV-42	23,000	26,000	0.21	14
		ELV-10	5,600	5,500	<LOD	5.2
		ELV-46	5,400	<LOD	<LOD	<LOD
		ELV-01	5,200	<LOD	<LOD	<LOD
		ELV-43	4,500	7.0	1.8	<LOD
		ELV-32	3,700	110	0.15	0.044
		ELV-47	3,000	0.040	<LOD	<LOD
		ELV-29	2,600	100	<LOD	0.078
Floor covering	4	*ELV-43*	14,000	2.2	13,000	<LOD
		ELV-32	5,500	6,700	<LOD	2.2
		ELV-25	4,500	16	3,000	<LOD
		ELV-11	<LOD	16	<LOD	<LOD
Soundproof material	3	*ELV-11*	6,000	6,600	<LOD	2.4
		ELV-40	2,100	820	<LOD	0.32
		ELV-40	1,200	11	<LOD	<LOD
Seat PUF	2	*ELV-10*	38,000	52,000	0.17	3.4
		ELV-15	2,000	3.4	<LOD	<LOD
Headliner	1	*ELV-30*	5,600	8,200	<LOD	2.0
Door trim fabric	1	*ELV-44*	4,200	0.025	450	<LOD

- The XRF survey showed that 32 out of 515 materials/components investigated (6.2% of total) contained ≥0.1% bromine. 16 of these products contained PBDEs or HBCD ≥0.1%.
- Major components that contained PBDEs (or other BFR) ≥0.1% by weight were seat fabric, floor covering, and soundproof materials
- Furthermore, PUR foam in seats and in headliner from one car (US) contained PentaBDE. Plastic parts of car seats or dashboards did not contain BFRs above 1000 mg/kg in all 45 vehicles.

DecaBDE *n*=12 ➔ **Mainly seat fabrics**

C-PentaBDE *n*=2 ➔ **Only from US car (High toxicological relevance!)**

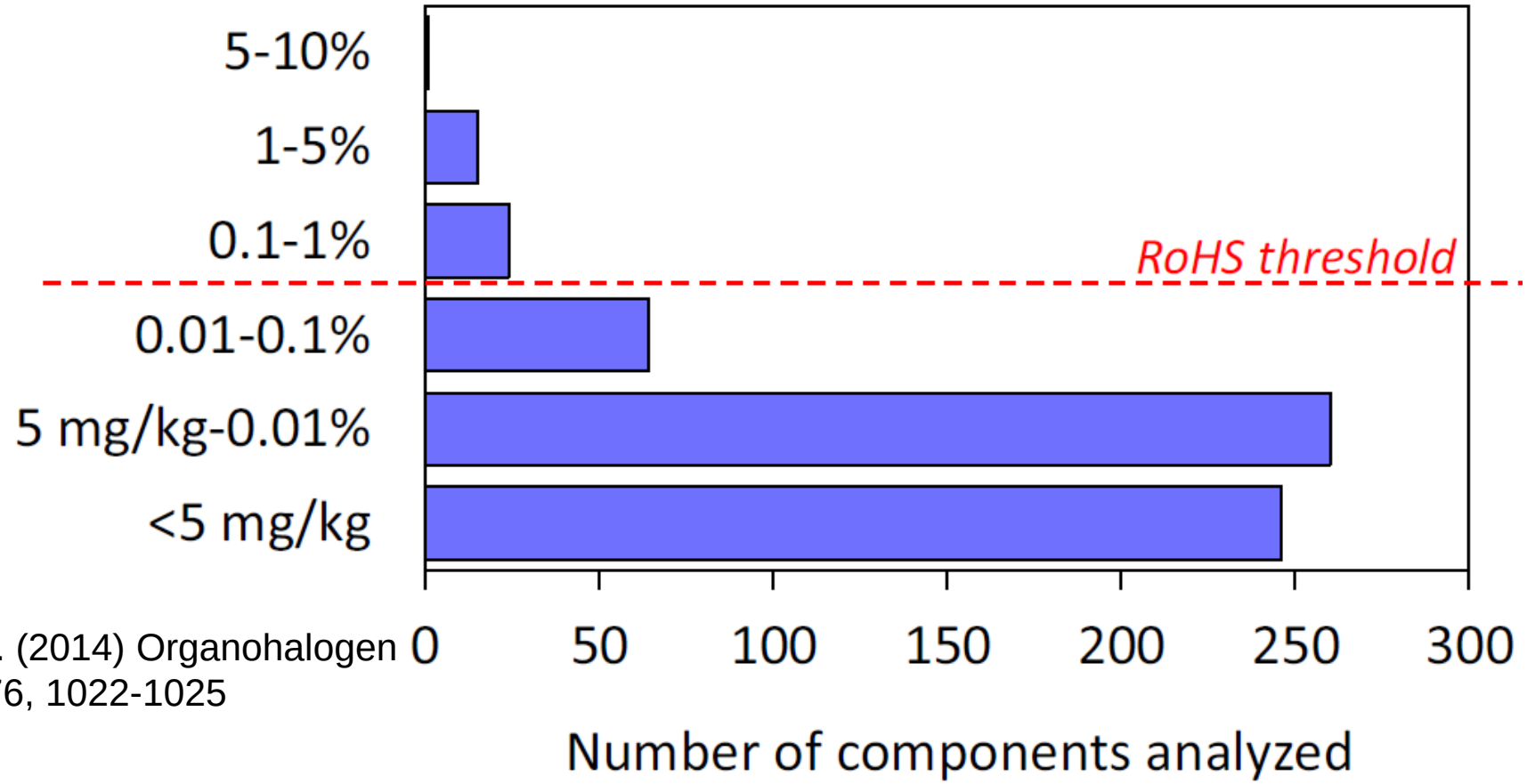
HBCD *n*=2 ➔ Only in floor coverings

Other BFRs? *n*=10

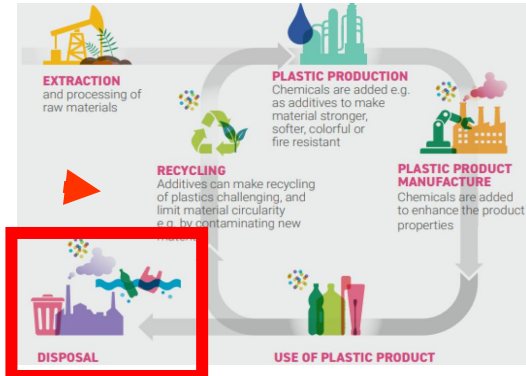
Kajiwara et al. (2014) Organohalogen Compounds 76, 1022-1025

Monitoring of PBDEs and HBCD in cars (Japan)

- 11/515 (2.1%) contained PBDE >1%; additionally 21/515 (4.1%) contained PBDE 1%>X>0.1%
- 60/515 parts had bromine content 0.01 to 0.1% and **260/515 parts** had bromine levels 5 to 100 mg/kg. This indicates that **>50% of interior plastic had a secondary BFR contamination**.



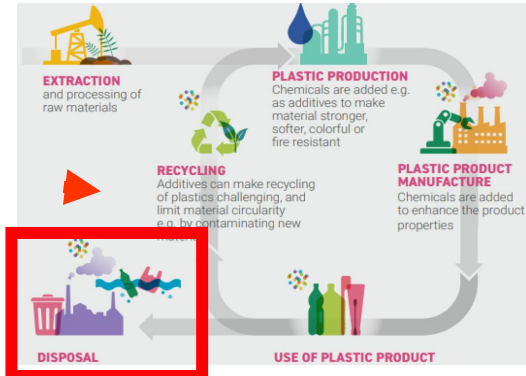
Kajiwara et al. (2014) Organohalogen Compounds 76, 1022-1025



- Similar screening of **cars from other regions is missing/is needed**
- **Including other POPs and chemicals of concern.**

Sampling of plastics from light shredder fractions of ELVs

- In industrial countries, the shredding of vehicles is the main treatment of ELV. After shredding, the shred is separated in a heavy and light shredder fraction(s).
- The light shredder fraction(s) (15 to 25% of the shredder) contains plastic, polymers, textiles and rubber including POPs in plastic. These light shredder fractions can be sampled and analysed for PBDEs, HBCD and other pollutants (e.g. SCCPs or heavy metals) relevant for further management.
- There is no standardized method developed to generate a representative ELV light shredder sample
- The European “Guidance document on how to perform a shredder campaign” suggests to use 100 vehicles for a campaign which is resulting in approx. 20 to 35 tonnes of light shredder residues.
- The selection of cars could include only specific cars e.g. produced before a certain year (where the PBDEs levels started decreasing) or cars from a specific region or producer.
- A standard sampling protocol as for WEEE plastic should be developed. The grain sizes from shredder samples from ELVs are however large and taking a “representative sample” is challenging.



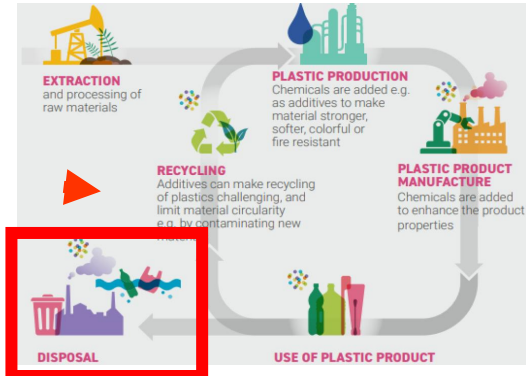
PBDEs in car shredder residues

PBDE content in light automotive shedder residues and recalculated to the PBDE content of a vehicle (depend on age of car fleet), considering a share of light ASR of 20% per weight.

	DecaBDE (mg/kg)	∑PBDEs 2009 (tetra-heptaBDE	POP-PBDE in average car* (g)	Reference
Car shredder residues (Cars produced before 1996 (Japan)	**406**	N.D	**81.2 g**	JAMA 2016
Car shredder residues (Cars) older than 1999 (Japan)	**335**	N.D	**77 g**	JAMA 2016
Car shredder residues (Cars) younger than 2000 (Japan)	**120**	N.D.	**24 g**	JAMA 2016
Car shredder residues (United States)	43	7	**10 g**	Petreas et al. 2009
Car shredder residues (Europe, Netherlands)	10 **(0.2-70)**	N.D.	**2 g**	IVM, IVAM 2013
Car shredder residues (Europe, UK)	450**	N.D.	**90 g**	Peacock et al. 2012
Car shredder residues (Europe, Ireland)	3.5	N.D.	**0.7 g**	Oekoinstitute 2018

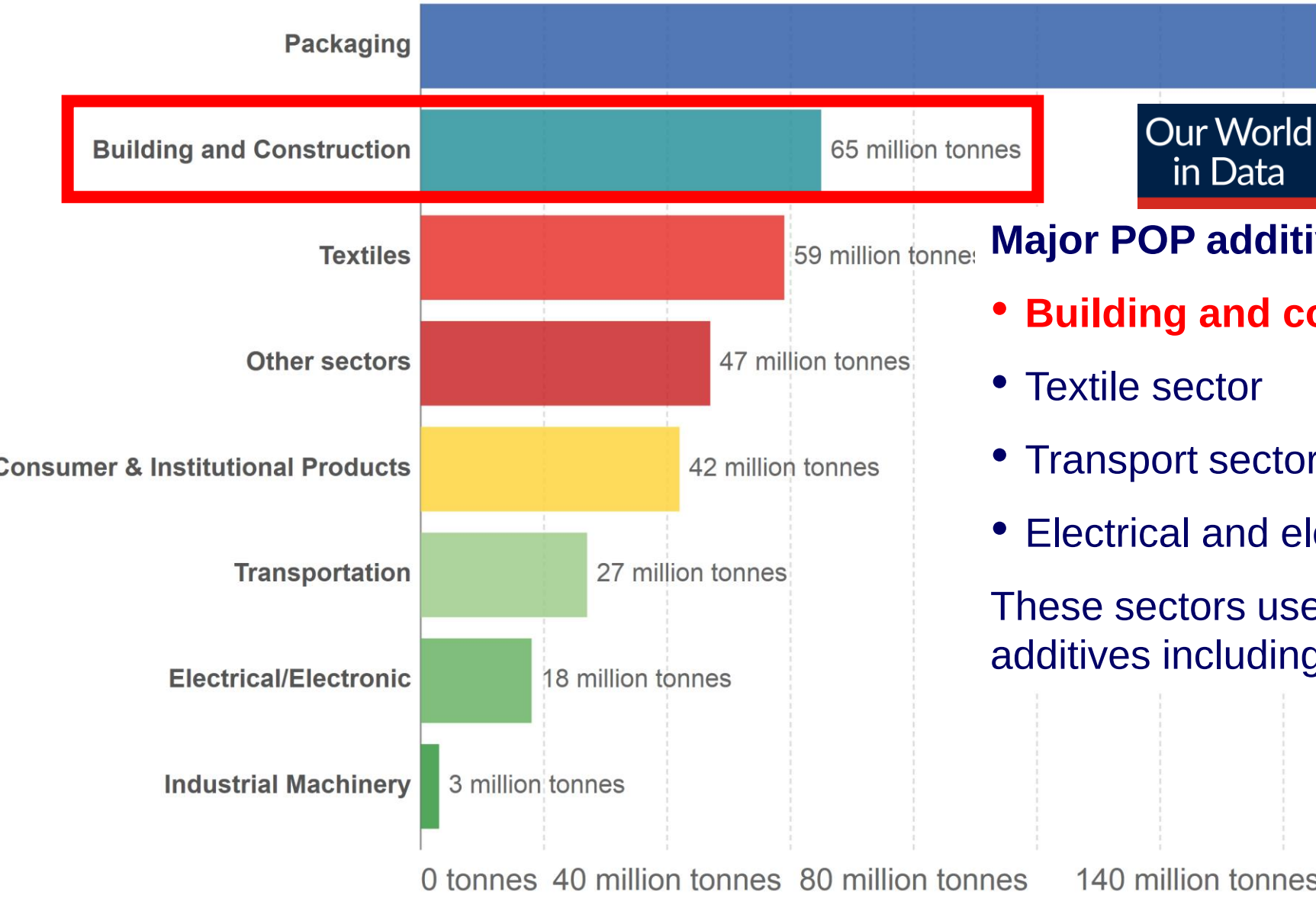
* Calculated based on approx. 200 kg light shredder residues per vehicle

**Average concentration of fluff (138 mg/kg), light plastic (118 mg/kg); heavy plastic (2163 mg/kg).



Monitoring of POPs according to industrial sector of use: Construction

A large share of POPs plastic additives have been used in the building & construction sectors.



Major POP additives in plastic are used in the:

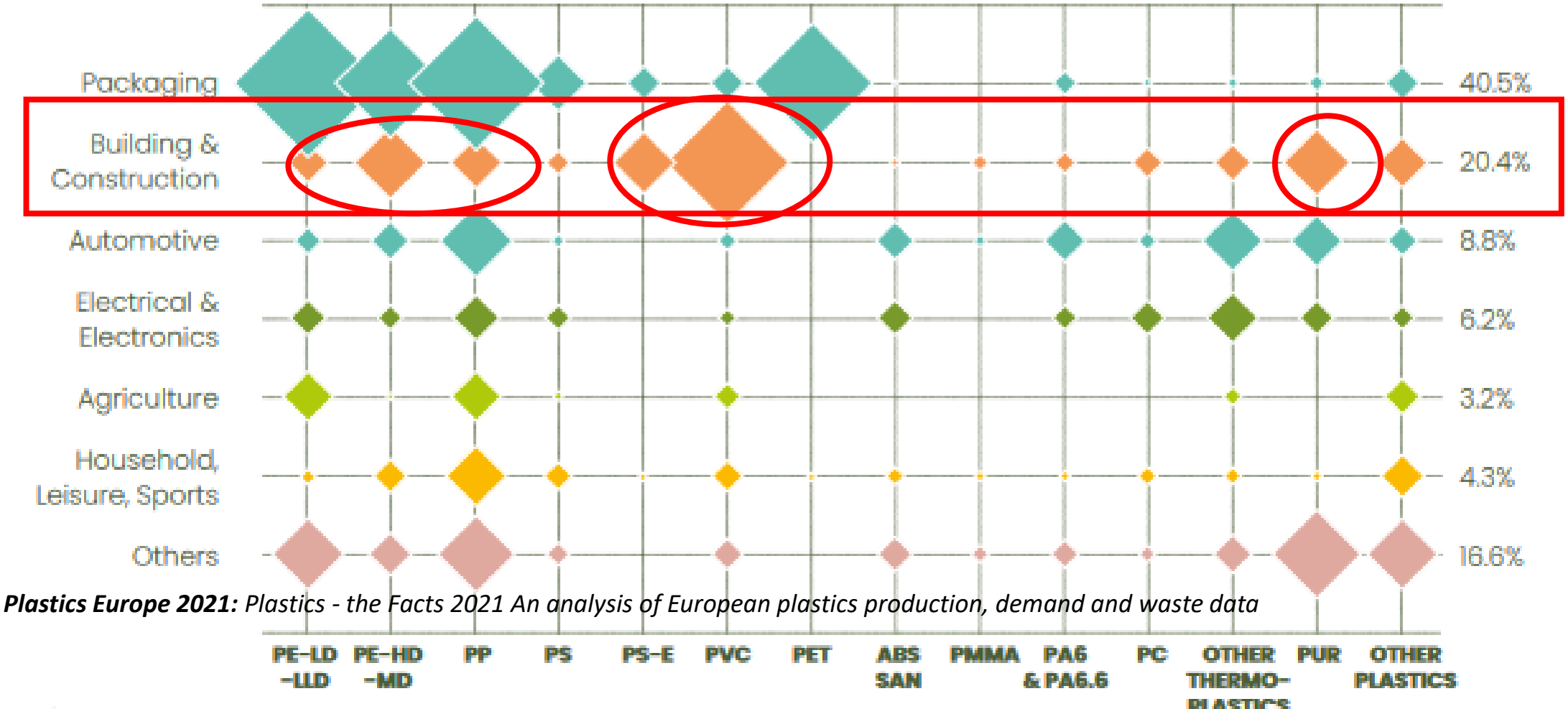
- **Building and construction sector,**
- Textile sector
- Transport sector
- Electrical and electronic sector.

These sectors use plastics with large amount of additives including POPs with related exposure risk.

Major Plastic use Sectors 2015; Based on Geyer et al (2017) Sci. Adv. 2017;3: e1700782

POPs in polymers in buildings

- Major plastics in buildings are PVC, expanded and extruded polystyrene (EPS/XPS), polyethylene and PUR.
- EPS/XPS and PUR in buildings were frequently flame retarded with POPs (PBDEs, HBCD) or other hazardous substances like halogenated phosphorous flame retardants (PFRs).
- PVC often contains large amounts of additives (up to 60%) including POPs (SCCP, MCCPs) EDCs (e.g. DEHP; DBP).



Plastics Europe 2021: *Plastics - the Facts 2021 An analysis of European plastics production, demand and waste data*

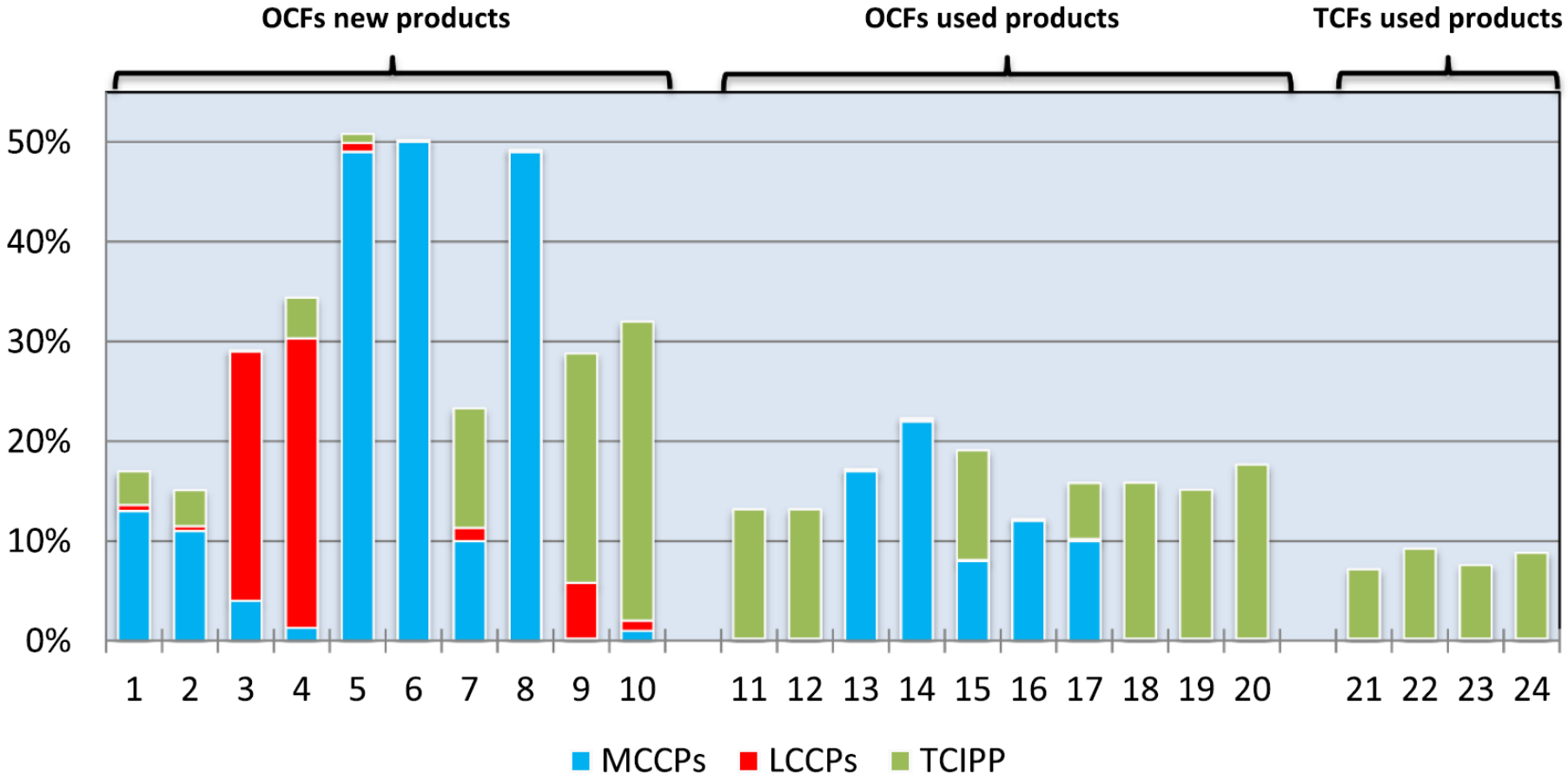
POPs in plastic in buildings and monitoring needs

- While we know which POPs were used and know their concentration in treated materials – the overall amount of most POPs in buildings is unclear (data for HBCD available to some extent).
- There are some studies of individual POPs in plastic in building but no systematic studies covering a range.
- Some studies focus on a few particular POP (e.g. HBCD or PCBs).
- Since there was no monitoring study of PBDEs in plastics in buildings we have initiated a master thesis Technical University Vienna on monitoring brominated POPs in buildings. The approach is to sample at a recycling center for construction & demolition waste using XRF screening.

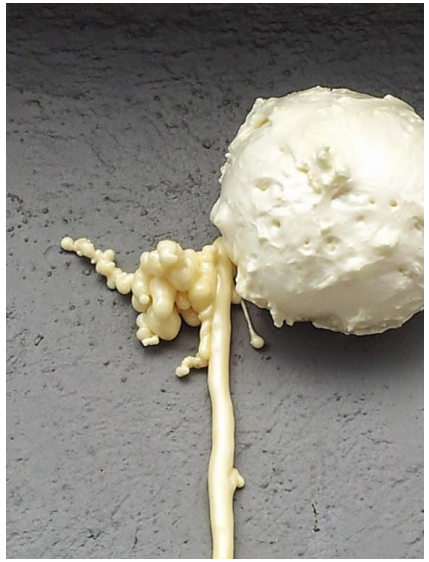
POP	Uses	Content (% wt)
HBCD	Expanded polystyrene (EPS)	0.5–1%
HBCD, DecaBDE	Extruded polystyrene (XPS)	1–3%
DecaBDE, PentaBDE	PUR foam in insulation	4–13%
DecaBDE, PentaBDE	PUR foam fillers	22%
DecaBDE	PE insulating foam	20%
DecaBDE	PE and PP plastic sheeting	10%
DecaBDE, PentaBDE, HBCD	Roller blind and curtain	4%
DecaBDE	Adhesive layer of reflective tapes	1–5%
DecaBDE, PentaBDE	Intumescent paint	2.5–10%
SCCP/MCCP, (DecaBDE)	PVC plastic sheeting	5–20% (5%)
SCCP/MCCP	PVC hosepipes for plumbing	0.5%–10%
SCCP/MCCP	PVC flooring, roofing, wall paper	0.5%–10%
SCCP/MCCP, PCB, PCNs	Cables	0.5%–10%

Screening polymers in market/use possibly containing POPs: PUR foam

- **A study in Netherlands screened SCCPs, MCCPs, LCCPs in one- and two-component spray polyurethane foams** (OCF; TCF) in 2020/21.
- **While SCCPs were not detected, MCCP & LCCP contents were up to 50% and 29%,** respectively **The organophosphorus flame retardant TCIPP was detected in 18/24 foams (up to 30%).**



Brandsma et al. (2021) Journal of Hazardous Materials 416, 125758



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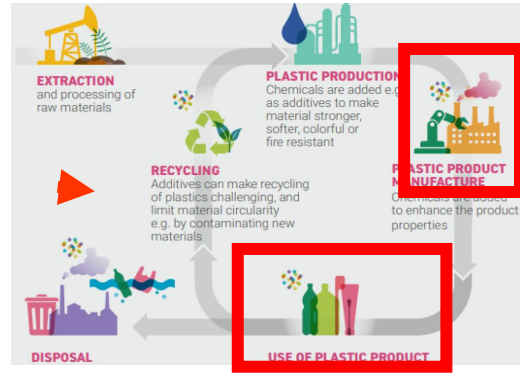
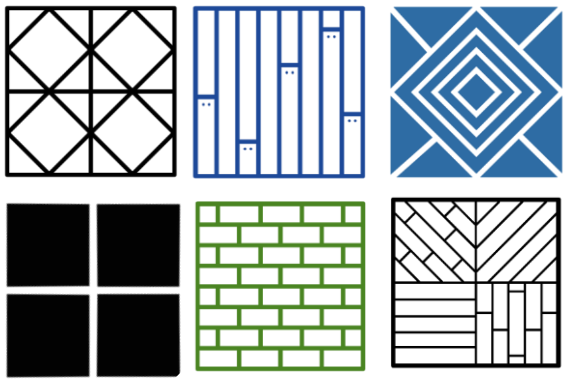


Various methods were used to characterize Swiss PVC building materials

Sampling information

- ***Polymer: polyvinyl chloride (PVC)***
- **Product: flooring**
- Year: 2021
- Country: Switzerland
- Age: new products
- **Sample size: 151**

flooring samples*
(n=151)



* varying sample properties
(e.g. color, hardness, layers)

Analysis targets

Method

Polymer type → confirm PVC → ATR-FTIR

orhto-Phthalates → Target GC-MS

Alternative plasticizers & others → Suspect GC-MS

Elements — Toxic: Cr, Pb, Ni, As, Cd, Hg
Stabilizers: Cd, Pb, Zn, Ba, Sn → XRF

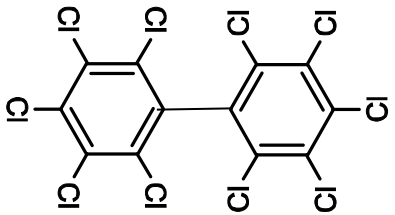
Biological activity — Cytotoxicity, ROS generation, endocrine activity, genotoxicity → Bioassays

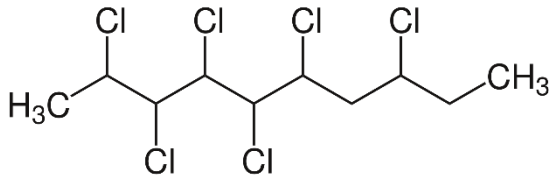
Limitations:

- Not represenative sampling: uncertainties about the market
- Some substances may not be detected by our methods

Monitoring of PCBs in building sealants in Switzerland

- **Switzerland did a nation-wide comprehensive screening of PCB in polymer sealants in buildings.**
- **1348 samples of joint sealants** from concrete buildings built between 1950 and 1980 were **analyzed**. **568 samples (42%) exceeded the limit of 50 mg PCB/kg.** PCB concentrations were **above 10,000 mg/kg in 21% of samples**, and **above 100,000 mg/kg in 9.6% of samples.**
- The study revealed: • The use of PCBs in joint sealants was a common construction practice in Switzerland between **1955 and 1975**. • The sealants represent a significant stockpile of PCBs.
- In a **subset of 85 samples,** it was investigated whether wavelength-dispersive X-ray fluorescence spectrometry (WD-**XRF**) can be used as a rapid screening method for joint sealants.
  - Detection limit for PCBs: 10 to 25 mg/kg.
  - Detected chlorine concentrations were between <1 g/kg and 200 g/kg
  - However, chlorine sources other than PCBs, in particular chlorinated paraffins, other chlorinated organic compounds, and inorganic chlorine, need to be considered.
    - Chlorinated paraffins were detected in about one-third of the samples of the subset.
    - Therefore, low specificity of WD-XRF for PCBs. Since SCCPs/MCCPs are POPs/POP candidates their detection is also appreciated today.

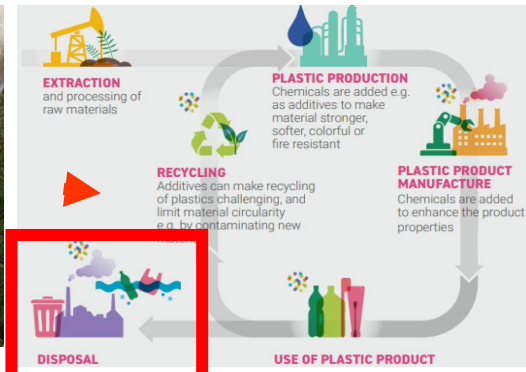




Kohler et al., Environ. Sci. Technol. 2005, 39, 1967-1973

Monitoring POPs in C&D waste and recycling: PCBs

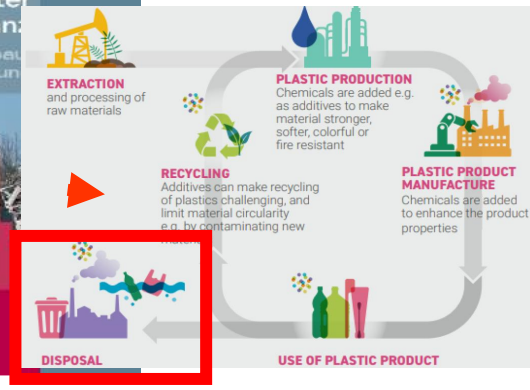
- PCB-sealants and paints can contaminate construction debris if not removed.
- Contamination of surroundings.
- Contamination of cattle when construction debris was used on farms for landscaping.
- **Recycling material is PCB-contaminated (PCB limit for recycling Germany 1 mg/kg Switzerland 0.5 mg/kg)**



Weber et al (2018) Environ Sci Pollut Res Int. 25, 16325-16343.

Monitoring of POPs in the construction and demolition waste

- POPs need to be monitored and managed when demolishing or renovating buildings.
- Monitoring of POPs in buildings (PCBs, HBCD, SCCP/MCCP) need to be integrated in the overall management of pollutants in buildings (e.g. asbestos, mineral fiber, lead).
- Guidance documents on the assessment, deconstruction of buildings containing pollutants, were published e.g. by the Swiss and the Bavarian State Ministry (Germany).



Priority use sector and specific sampling campaigns

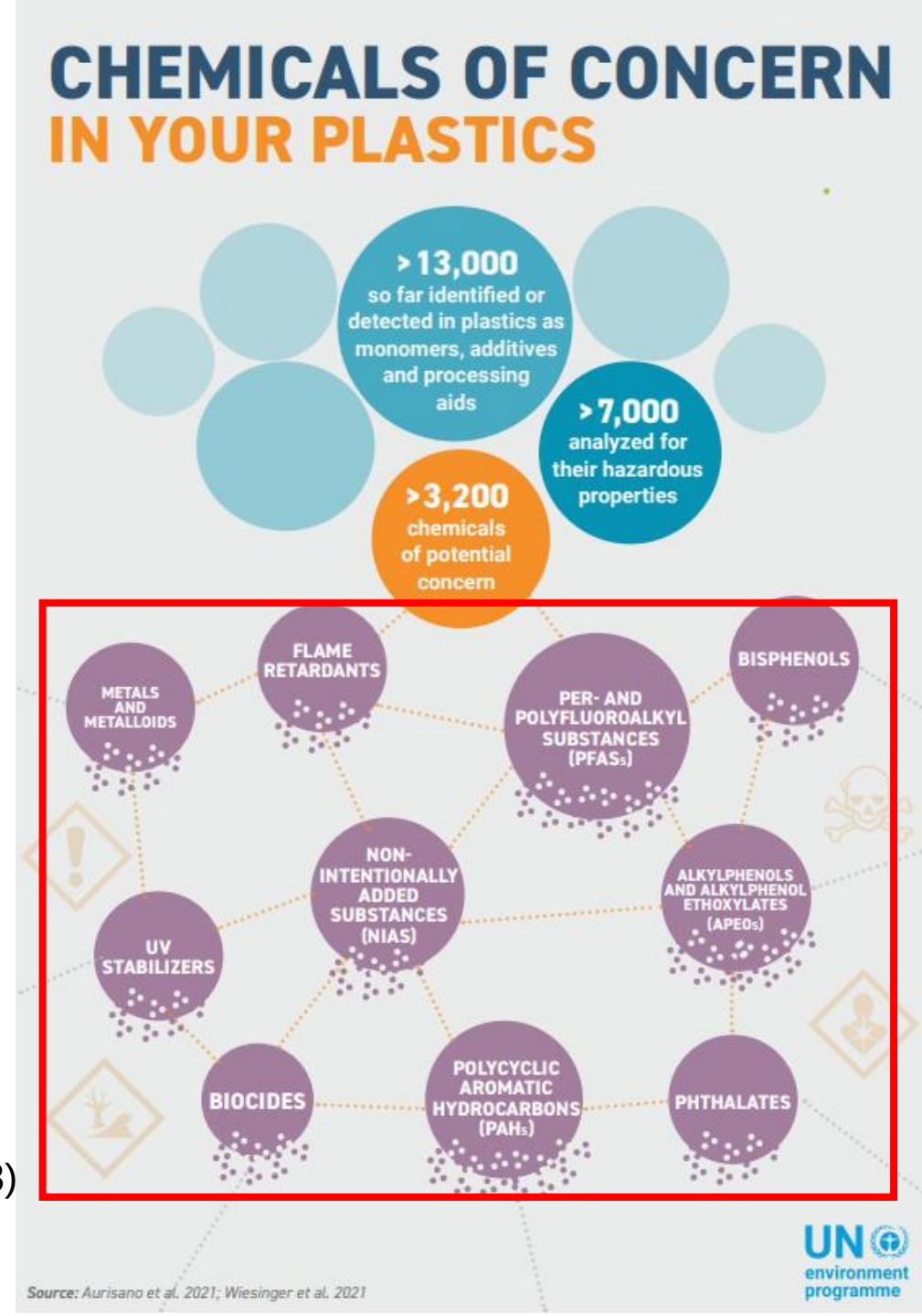
In addition to the major use sectors there are some further sectors with particular exposure risk which can have a priority for monitoring such as toys, furniture or medical devices

UNEP and Secretariat of the Basel, Rotterdam and Stockholm Conventions (2023). Chemicals in plastics: a technical report. Geneva. https://www.unep.org/resources/report/chemicals-plastics-technical-report

Need of an overall assessment of chemicals of concern in plastics

POPs are only the tip of the iceberg!

- In a technical report on chemicals in plastic for UNEPs and BRS Secretariat we have compiled that over 13,000 substances are associated with plastics and that 3200 of them are of potential concern.
- Ten groups of chemicals are identified as being of particular concern due to their hazardous properties.
- They need to be considered in monitoring and management efforts of chemicals in plastic.



UNEP and Secretariat of the Basel, Rotterdam and Stockholm Conventions (2023) Chemicals in plastics: a technical report. Geneva.
https://www.unep.org/resources/report/chemicals-plastics-technical-report

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

gef