IPCP Webinar Series: POPs in plastic and monitoring approaches

Part I: Understanding POPs in plastics; 24/25 April 2023

POPs and selected other chemicals of concern in plastic – human exposure from some plastic use priority sectors

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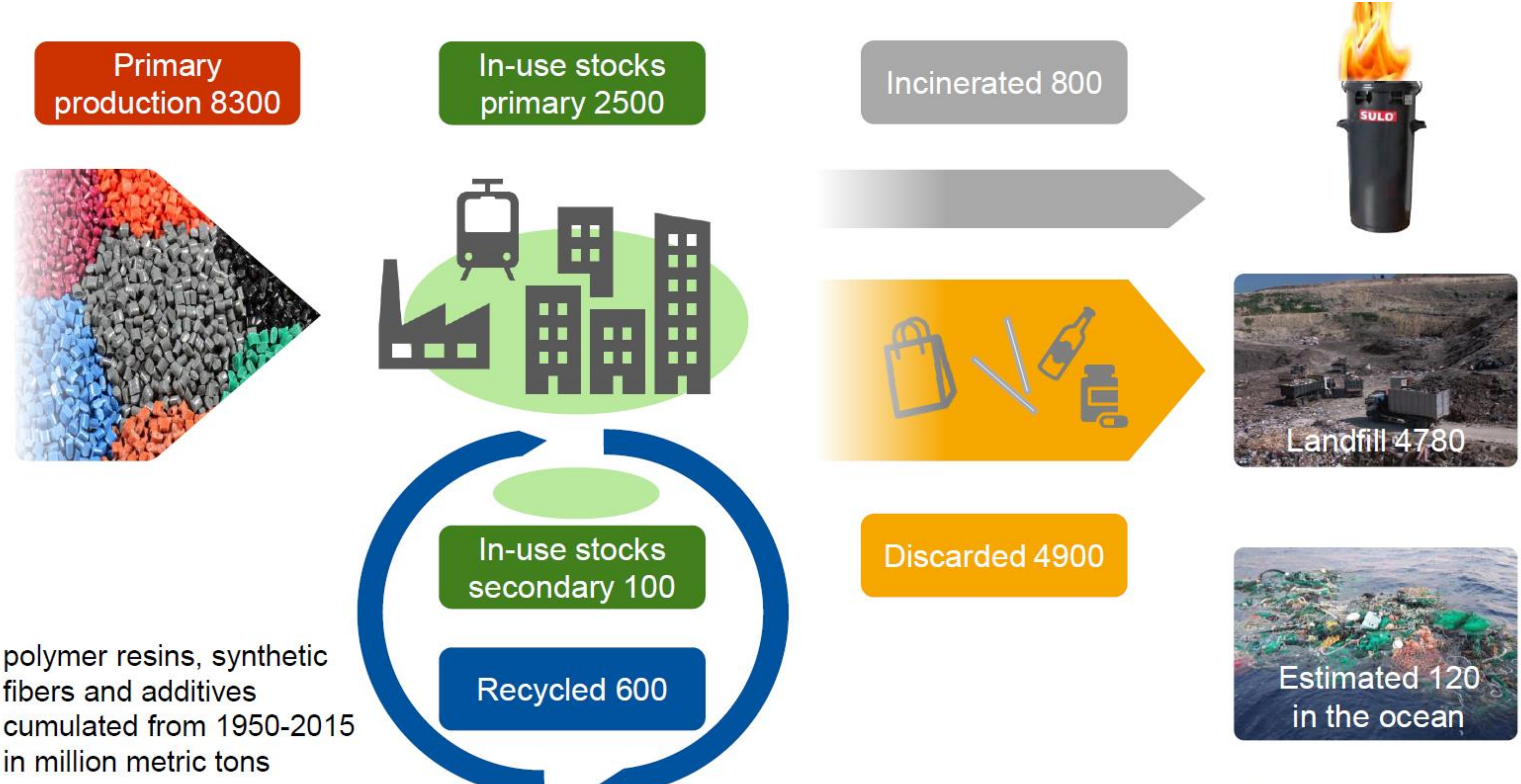
https://scholar.google.com/citations?user=-Cexto4AAAAJ&hl=en

IPCP International Panel on Chemical Pollution
UN environment programme
gef

Content of Presentation

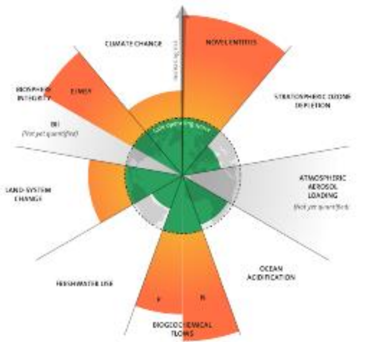
- Plastic and chemical pollution have crossed global boundaries
- Stockholm Convention POPs – which are used in plastic?
- UNEP/WHO POPs in human milk – contamination from plastic additives
- Plastic additive groups of concern and some health effects and related external cost
- Human exposure to POPs and other CoC in plastics in buildings
- Human exposure from POPs in synthetic textiles and carpets
- Additives in toys and child exposure – state of art exposure assessment from plastic

Challenge with huge global production and life cycle of plastic (MT)



[Geyer 2017] [Maximenko 2019] [UBA 2018]

The increasing production & consumption and the linear economy result in a waste/plastics nightmare crossing global boundaries



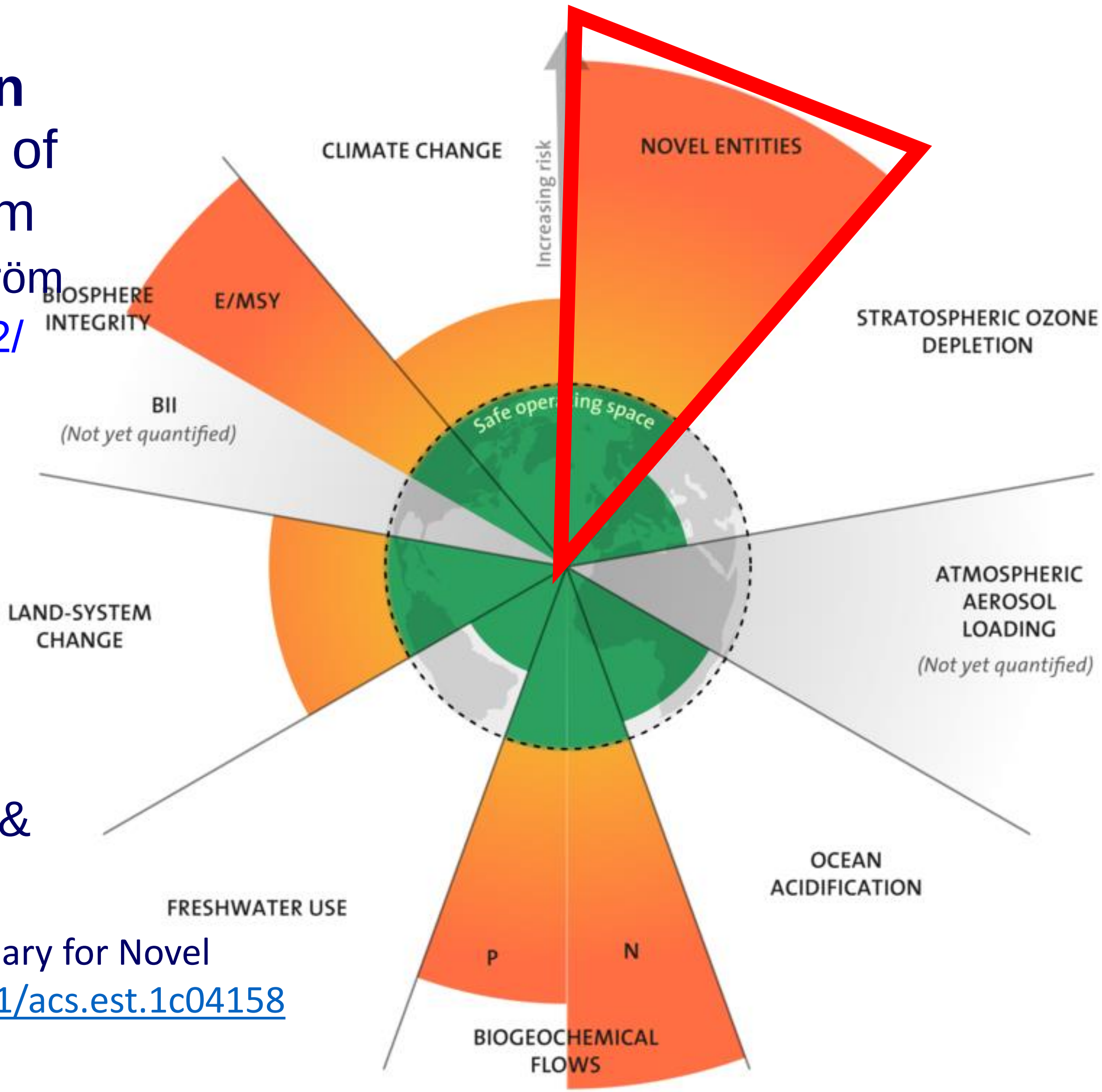
Persson et al. (2022) Outside the Safe Operating Space of the Planetary Boundary for Novel Entities. ES&T 2022, https://doi.org/10.1021/acs.est.1c04158

“New Entities” plastic & chemicals crossed Planetary Boundaries

- The planetary boundaries **– which define the environmental limits within which humanity can safely operate –** have been evaluated for a range of critical anthropogenic pressure on the Earth System (climate, phosphorus, nitrogen; biodiversity; Rockström et al. 2009). http://www.ecologyandsociety.org/vol14/iss2/art32/

- **Also “New entities” including plastic and chemical pollution have crossed planetary boundaries and is therefore a concern for humanity and several ecosystem services.**

- The irreversibility and global ubiquity of chemical and plastic pollution mean that the essential conditions for a planetary boundary threat are met. Increasing chemical & plastic production will further increase the pollution.



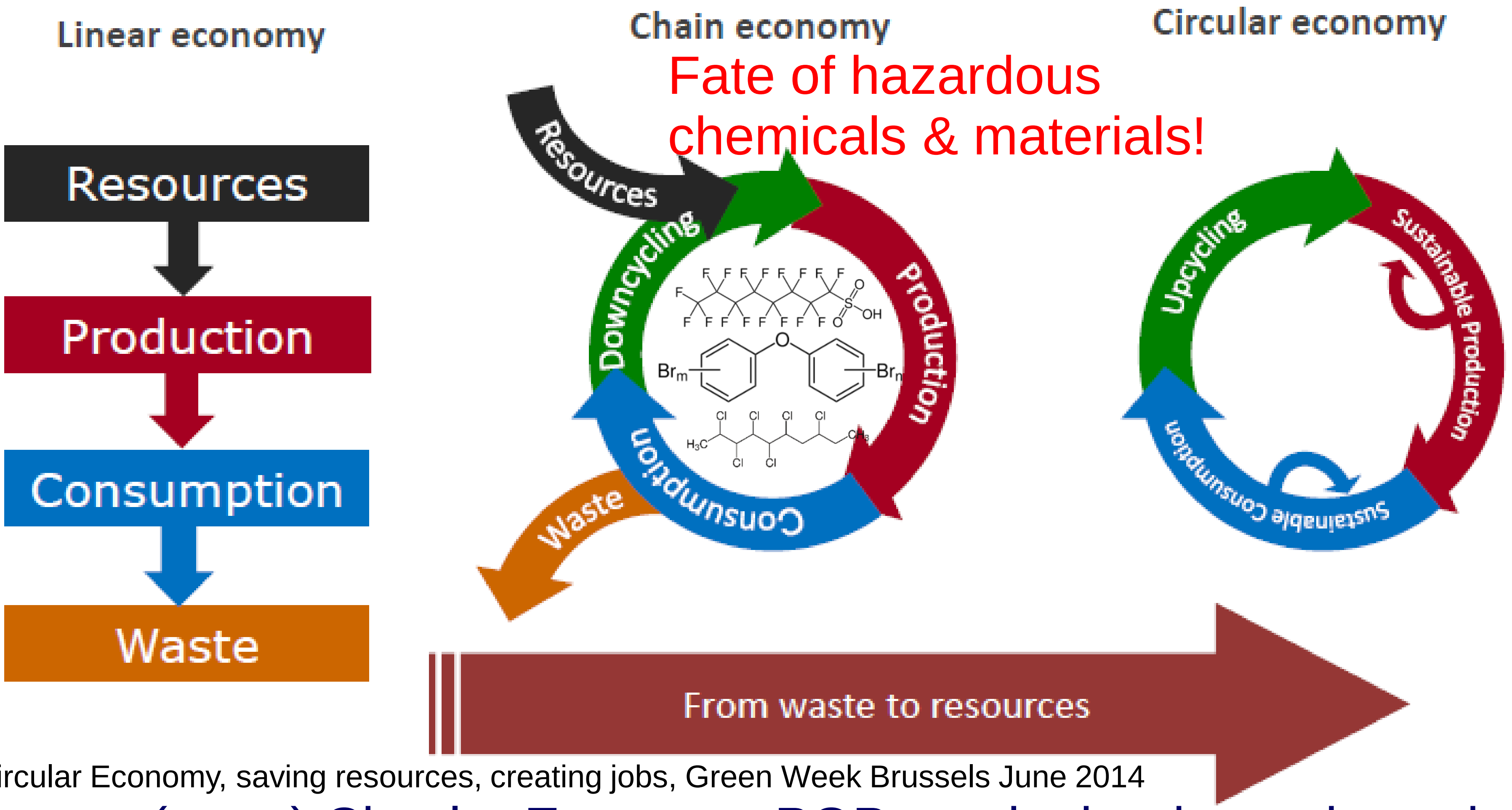
Persson et al. (2022) Outside the Safe Operating Space of the Planetary Boundary for Novel Entities. Environ. Sci. Technol. 2022, 56, 3, 1510–1521. https://doi.org/10.1021/acs.est.1c04158

Rockström et al. (2009) Ecology & Society 14(2): 32
Update post 2015: http://www.post2015hlp.org/wp-content/uploads/2013/06/Rockstroem-Sachs-Oehman-Schmidt-Traub_Sustainable-Development-and-Planetary-Boundaries.pdf

We need to move to a Circular Economy – Fate of hazardous chemicals?

Considering the **waste/plastic crises and the limits of resources**, humanity needs to move to (a more) circular economy (stressed by UN Organisations, GEF, and EU)

https://www.unep.org/news-and-stories/story/plastic-treaty-progress-puts-spotlight-circular-economy



Bonnet (ARC+) Circular Economy, saving resources, creating jobs, Green Week Brussels June 2014

When moving to a (more) Circular Economy, POPs and other hazardous chemicals need to be controlled and phased out. Best within a global approach.

19 new POPs listed in the Stockholm Convention

Chemical	Pesticides	Industrial chemicals	Unintentional production	Annex
Chlordecone	+			A
α- and β- hexachlorocyclohexane	+		By-product of lindane	A
Lindane (gamma HCH)	+			A
Endosulfan, Dicofol	+			A
Pentachlorophenol (PCP)	+	+		A
Commercial PentaBDE		+		A
Commercial OctaBDE (hexa/hepta)		+		A
DecaBDE		+		A
Hexabromobiphenyl (HBB)		+		A
Hexabromocyclododecane (HBCD)		+		A
Perfluorooctane sulfonic acid (PFOS), its salts and PFOSF	+	+		B
PFOA and related compounds		+		A
PFHxS and related compounds		+		A
Short Chain Chlorinated Paraffins		+		A
Hexachlorobutadiene (HCBD)		+	+	A/C
Pentachlorobenzene (PeCBz)		+	+	A/C
Polychlorinated Naphtalene (PCN)				

POPRC: Chlorpyrífos, MCCP, LC-PFAA. **COP:** Methoxychlor; UV328, Dechlorane Plus

Many of the new listed POPs are additives in plastic.

Some of these POPs have or had high production volumes.

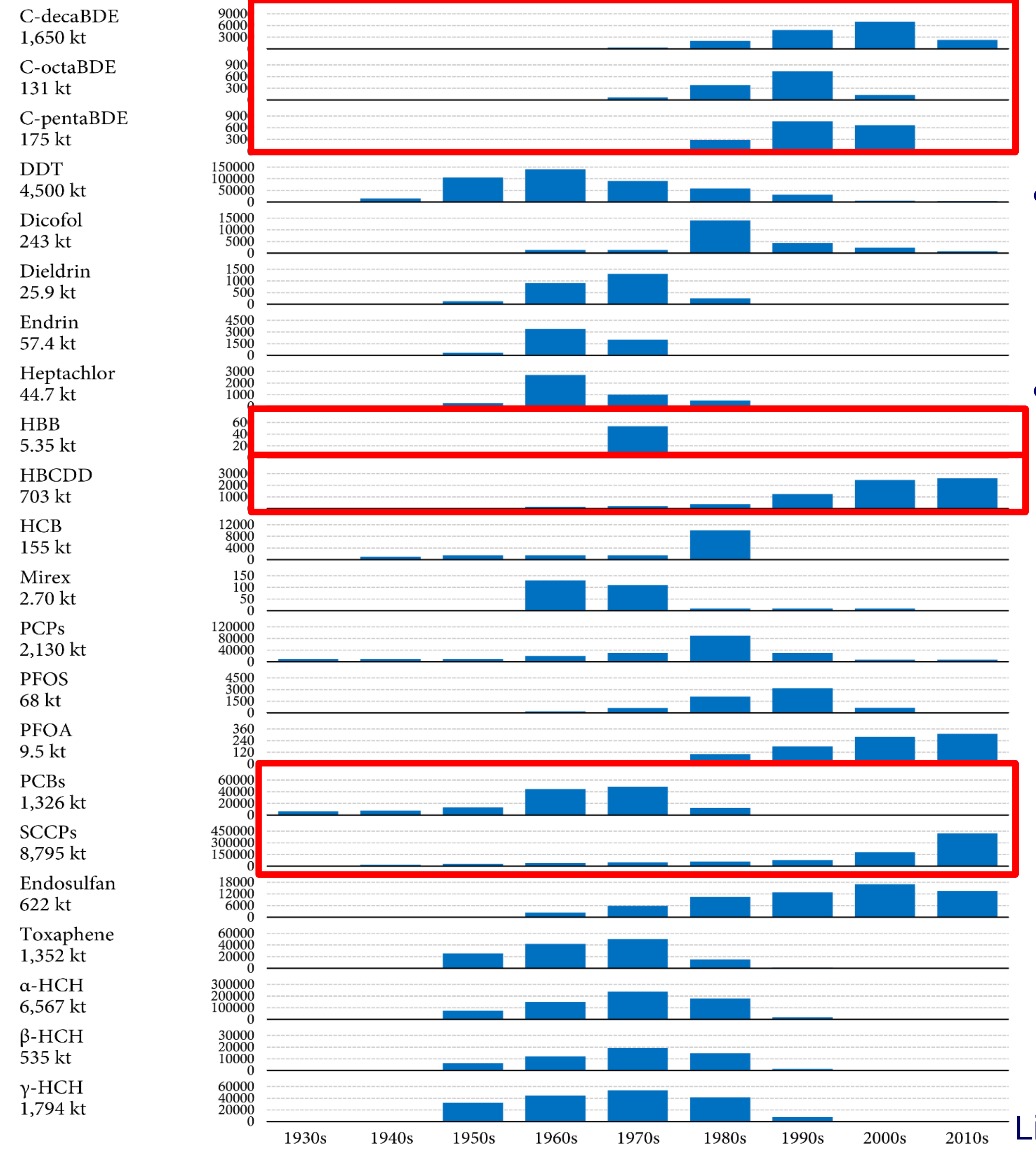
DecaBDE, HBCD, PFOA and SCCP received exemption for continued production.

PFOS/PFOA are/were used in polymer production and are incuded in side-chain fluoropolymers.

Three of the POP candidates are also plastic additives.

Therefore the control and management of plastic containing POPs becomes a major task in implementing the Stockholm Convention and impulse for management of chemicals in plastic.

Some POPs plastic additives used in high volumes with recent use



- Some of POPs plastic additives have been produced in 100,000 tonnes or even million tonne scale and are therefore important for management.
- **The high production POPs plastic additives SCCPs, DecaBDE and HBCD are still produced or have been produced untill recently.**
  - **SCCPs** are the POPs produced in largest amount of all POPs in history (**8.8 MT**; twice of DDT) and still produced today with use exemptions.
  - **1.6 MT DecaBDE** have been produced. With an additive amount of 10%, **~16 MT POP plastic**.
  - **0.7 MT HBCD** has been produced until 2021. 90% used in EPS/XPS at ca. 1.5% resulting in **42 MT** of EPS/XPS largely still present as insulation foam.

Li et al. (2023). Environmental Science: Advances.

UNEP study on chemicals in plastics contributing to Plastic Treaty Process

IPCP scientists prepared for UNEP a report on chemicals in plastics with following key findings:

- More than 13,000 chemicals are present in plastics.
- More than 3,200 are chemicals of potential concern (with certain hazard properties considering GHS/CLP).
- Need of a better life cycle management and control.
- Need of non-toxic alternatives for clean material cycles.

Available online at www.sciencedirect.com
ScienceDirect
Current Opinion in Green and Sustainable Chemistry
ELSEVIER
https://doi.org/10.1016/j.cogsc.2021.100513

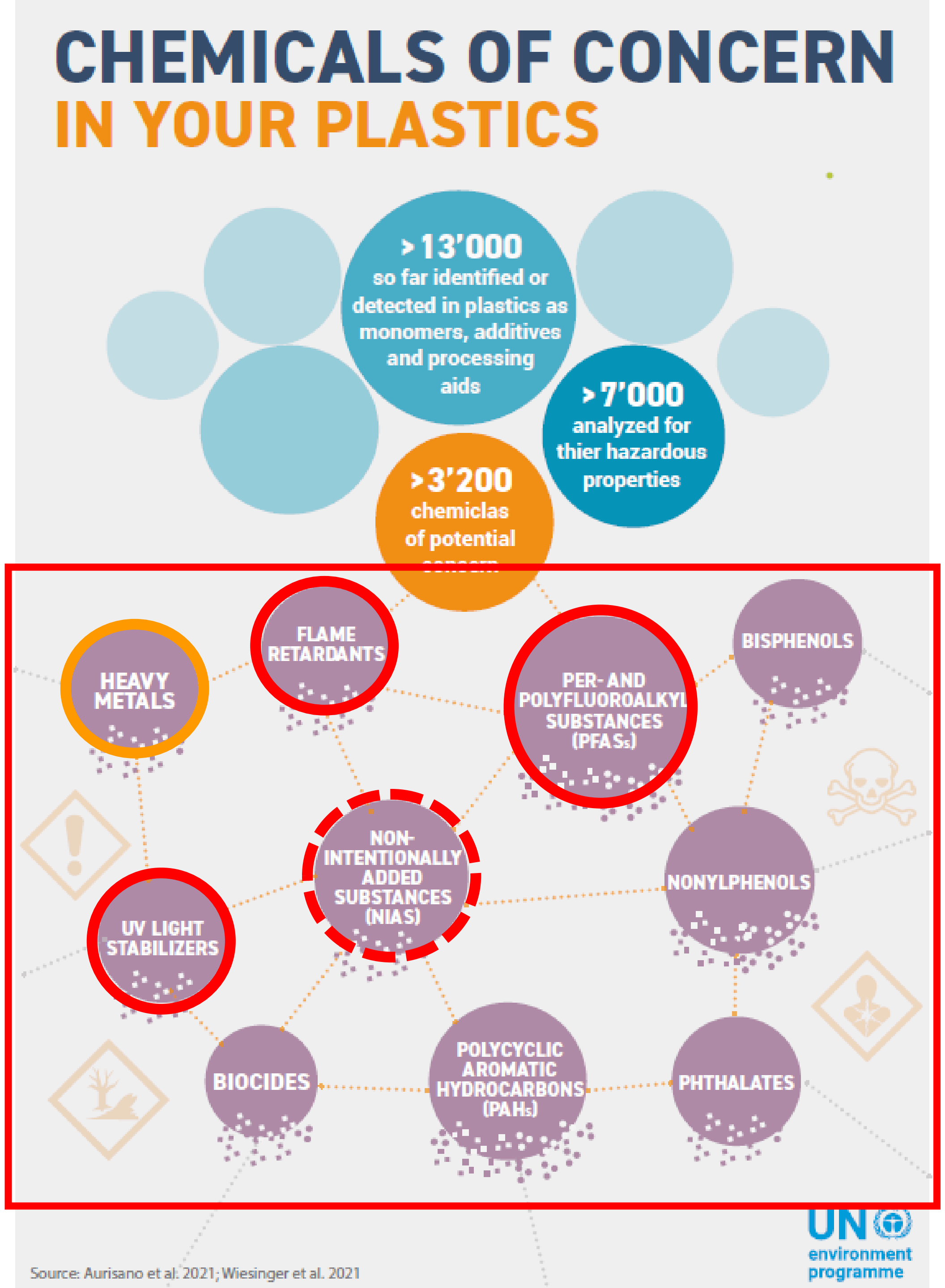
Enabling a circular economy for chemicals in plastics

Nicolò Aurisano[1], Roland Weber[2] and Peter Fantke[1]

Deep Dive into Plastic Monomers, Additives, and Processing Aids

Helene Wiesinger,* Zhanyun Wang,* and Stefanie Hellweg

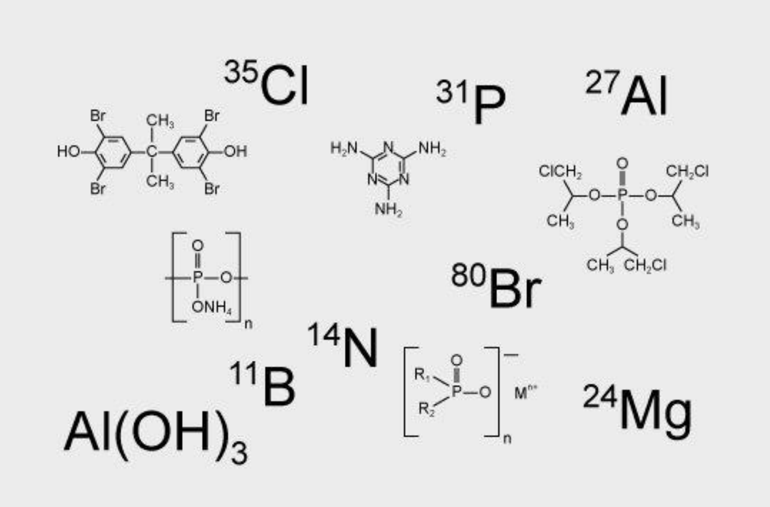
https://doi.org/10.1021/acs.est.1c00976
Environmental Science & Technology

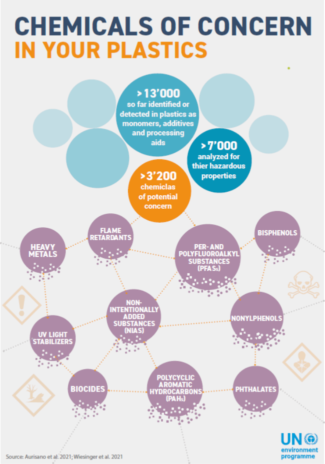


Chemicals Additives (of Concern) in Plastics – halogenated flame retardants (1)

- **Flame retardants**: a wide range of chemicals with large production
  - brominated flame retardants (BFRs), often used with antimony (Sb) as synergist, e.g., **polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD),** tetrabromobisphenol A (TBBPA)
  - Chlorinated flame retardants (CFRs), Short- and medium-chain chlorinated paraffins (**SCCPs/MCCPs**); **Dechlorane Plus (DP)**

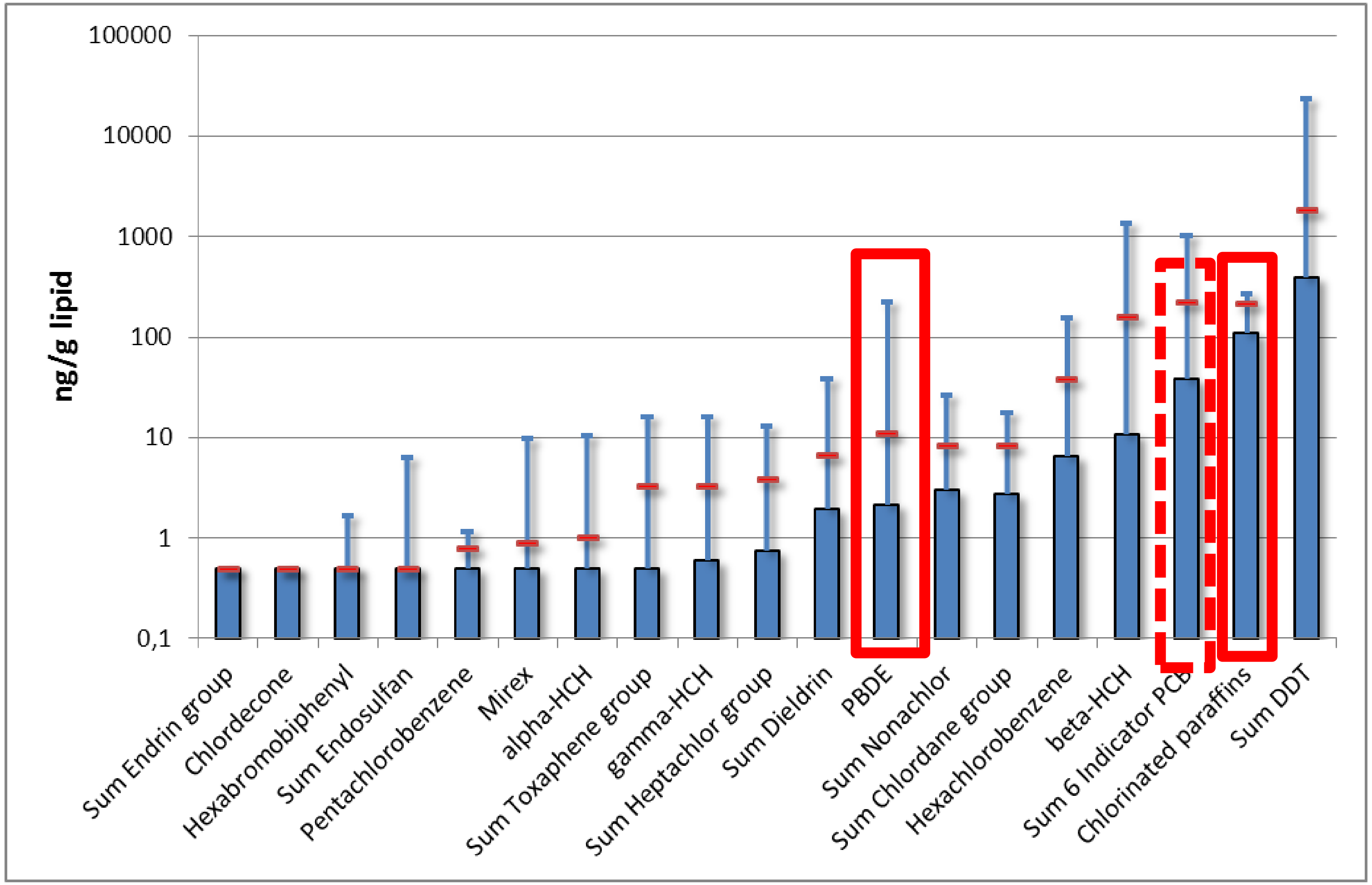
- Functionality: to reduce flammability and reduce the spread of fire, **but** not effective against plastic burning
  - Use in insulation, electrical devices, vehicles, textiles etc.
  - Typical amounts = 2–28 weight%





UNEP/WHO GMP human milk monitoring

POPs plastic additives accumulate in human milk UNEP/WHO study (65 countries; 2000-2012)



Krätschmer et al. (2021) EHP, 129(8) https://doi.org/10.1289/EHP7696

- SCCPs have a lower toxicity compared to PCBs.
- But sensitive endpoint not yet assessed (immuno-, neuro-, and developmental toxicity of children).

PBDEs in global human milk survey of UNEP/WHO

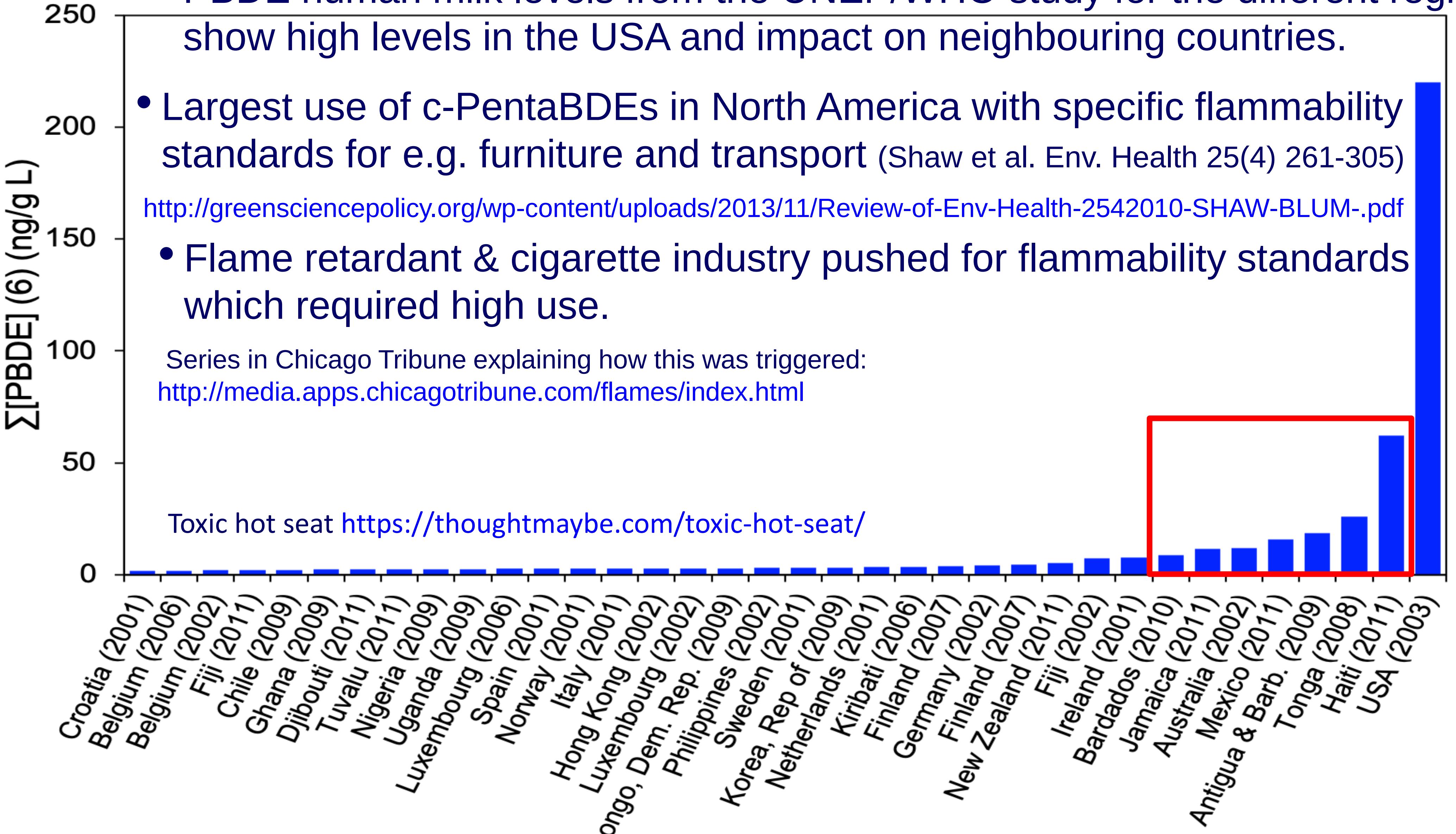
- PBDE human milk levels from the UNEP/WHO study for the different regions show high levels in the USA and impact on neighbouring countries.
- Largest use of c-PentaBDEs in North America with specific flammability standards for e.g. furniture and transport (Shaw et al. Env. Health 25(4) 261-305)

http://greensciencepolicy.org/wp-content/uploads/2013/11/Review-of-Env-Health-2542010-SHAW-BLUM-.pdf

- Flame retardant & cigarette industry pushed for flammability standards which required high use.

Series in Chicago Tribune explaining how this was triggered:
http://media.apps.chicagotribune.com/flames/index.html

Toxic hot seat https://thoughtmaybe.com/toxic-hot-seat/



The cost of IQ loss & intellectual disability in the US due to PBDEs is estimated to $US 266 billion/year (Attina et al 2016 Lancet D&E 4, 996-1003).

UNEP (2013) UNEP/POPS/COP.6/INF/33;
Charbonnet (2020), Emerging Contaminants´DOI: 10.1016/j.emcon.2020.05.002

Industry lobbied with false science for flammability standards

Flame retardant & cigarette industry pushed for flammability standards in the US requiring high use of flame retardants in upholstery furniture, vehicles and even in children's sleep wear

INDUSTRY DECEPTION

Part one: Torching the truth

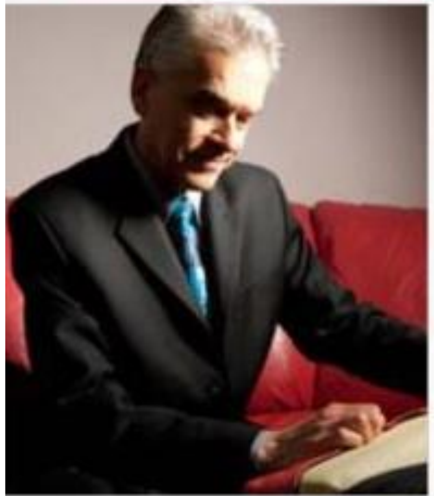
As evidence of health risks piled up, makers of flame retardants created a phony consumer watchdog that misled lawmakers and the public by stoking the fear of fire. **Read »**

- **Tests call effectiveness of flame retardants into question**

Series Chicago Tribune:
http://media.apps.chicagotribune.com/flames/index.html

https://www.chicagotribune.com/investigations/ct-met-flame-retardants-20120506-story.html

DISTORTING SCIENCE



Part three: 'Flat-out deceptive'

Companies that make flame retardants say science shows their products prevent fire deaths and are safe to use, but the research they often cite is either seriously flawed or grossly misrepresented. **Read »**

https://www.chicagotribune.com/investigations/ct-met-flames-science-20120509-story.html

TOBACCO'S CLOUT

Part two: 'Our fire service friends'

With cigarettes starting deadly fires, tobacco companies created a new scapegoat — the furniture going up in flames — and invested in a national group of fire officials that would deliver the message. **Read »**

https://www.chicagotribune.com/lifestyles/health/ct-met-flames-tobacco-20120508-story.html

Toxic hot seat https://thoughtmaybe.com/toxic-hot-seat/

TOXIC ROULETTE

Part four: 'Why do we not learn?'

Regulators have allowed generation after generation of flame retardants onto the market without thoroughly assessing the health risks. One chemical touted as safe is now turning up in wildlife around the world. **Read »**

- **Reform efforts tied up in Washington**

https://www.chicagotribune.com/investigations/ct-met-flames-regulators-20120510-story.html

Annual costs for disorders from endocrine-disrupting chemicals in the USA

	Base case estimate (US$)	Low-end estimate (US$)	High-end estimate or alternative scenario (US$)
PBDE and IQ points loss and intellectual disability	208 billion and 58·2 billion	NA	367 billion and 133 billion
Organophosphate pesticides and IQ points loss and intellectual disability	34·6 billion and 10·1 billion	11·3 billion and 3·0 billion	45·5 billion and 14·0 billion
Dichlorodiphenyltrichloroethane and childhood obesity	29·6 million	NA	57·3 million
Dichlorodiphenyltrichloroethane and adult diabetes	1·8 billion	NA	13·5 billion
Di-2-ethylhexylphthalate and adult obesity	1·7 billion	NA	NA
Di-2-ethylhexylphthalate and adult diabetes	91·4 million	NA	NA
Bisphenol A and childhood obesity	2·4 billion	NA	NA
PBDE and testicular cancer	81·5 million	24·8 million	109·3 million
PBDE and cryptorchidism	35·7 million	NA	NA
Benzylphthalates and butylphthalates and male infertility resulting in increased assisted reproductive technology	2·5 billion	NA	NA
Phthalates and low testosterone resulting in increased early mortality	8·8 billion	NA	NA
Multiple exposures and ADHD	698 million	568 million	1·95 billion
Multiple exposures and autism	1 billion for boys, 984 million for girls	410 million for boys, 393 million for girls	2·1 billion for boys, 2·0 billion for girls
Dichlorodiphenyltrichloroethane and fibroids	259 million	NA	595 million
Di-2-ethylhexylphthalate and endometriosis	47 billion	NA	NA

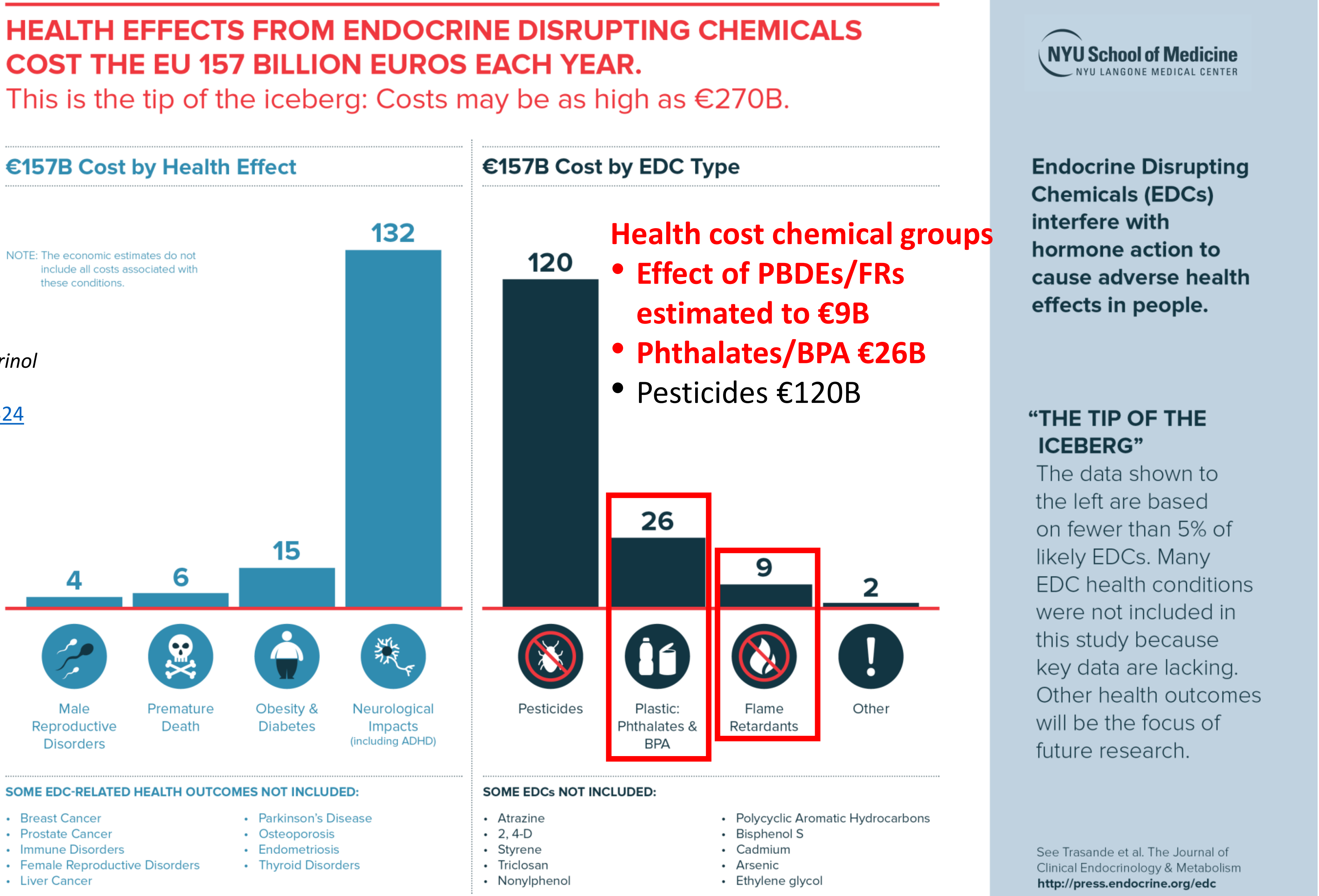
All estimates are for 2010. Estimates are conditional on certainty of causation. PBDE=polybrominated diphenyl ethers. IQ=intelligence quotient. NA=alternative inputs not available to do sensitivity analyses. ADHD=attention deficit hyperactivity disorder.

- External health costs in the US were highest for PBDEs (266B US$/a) due to IQ points loss & intellectual disability (US had highest use of PBDEs).
- Also health costs of DDT (diabetes; obesity) were relevant (2B US$/a).
- Other EDCs with relevant health costs are phthalate plasticizer (DEHP) and Bisphenol A (plastic monomer/additive)
- Also high costs estimated for organophosphate pesticides and IQ point loss and intellectual disability of children (44.7B US$/a).

(Base case estimates)

POPs | OP-Pesticides | Plastic additives

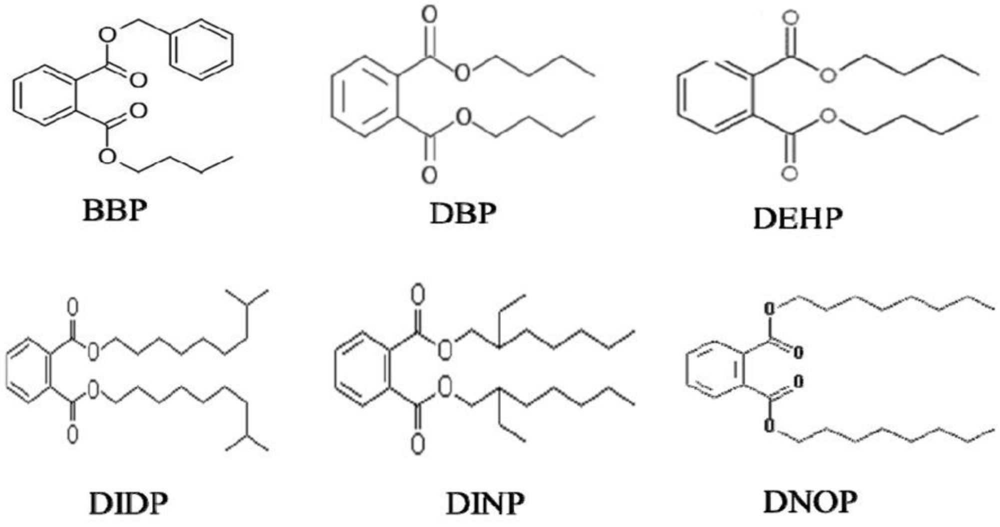
Attina et al. (2016) The Lancet
http://dx.doi.org/10.1016/S2213-8587(16)30275-3

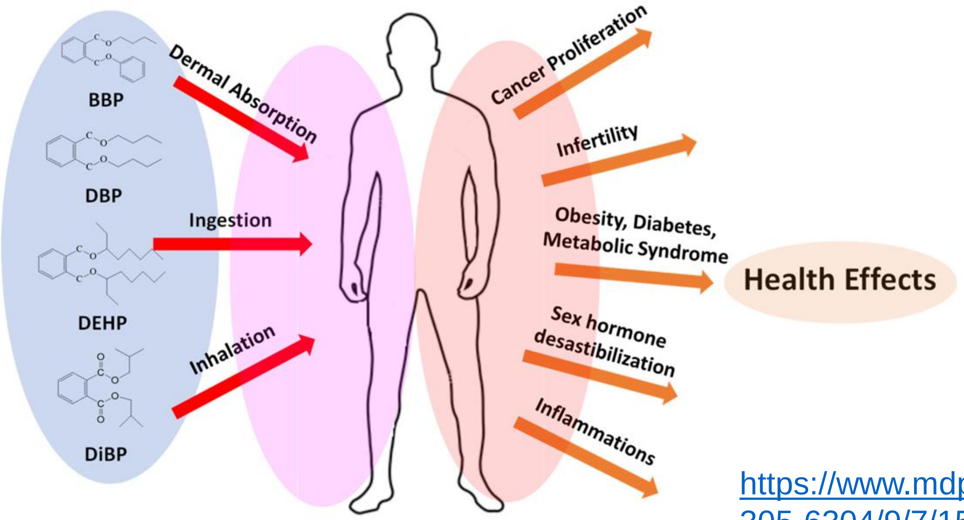


Trasande, et al. (2015). *J Clin Endocrinol Metab*, *100*(4), 1245–1255. https://doi.org/10.1210/jc.2014-4324
Norden (2014) Cost of inaction. TemaNord 2014:557

Chemicals Additives (of Concern) in Plastics (2) – Phthalates

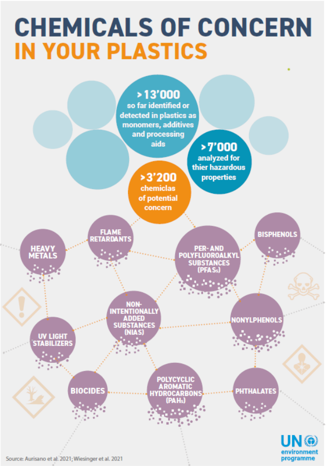
- **Phthalates** are high-production volume chemicals (MT/yr)
  - largely used as **plasticizers** in plastics, particularly in PVC (10–60 weight%)
- Phthalates can be released during the plastic life cycles





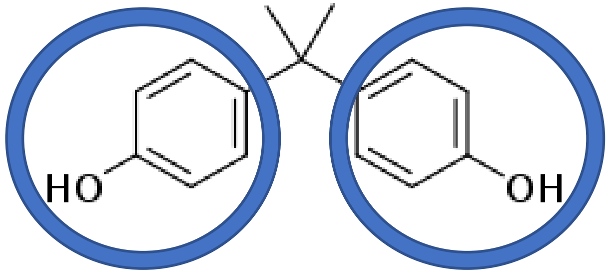
https://www.mdpi.com/2305-6304/9/7/157/htm

- Many are subject to various chemicals legislations, e.g., EU restricted DEHP, DBP, BBP and DIBP in toys and indoor/outdoor articles[1]



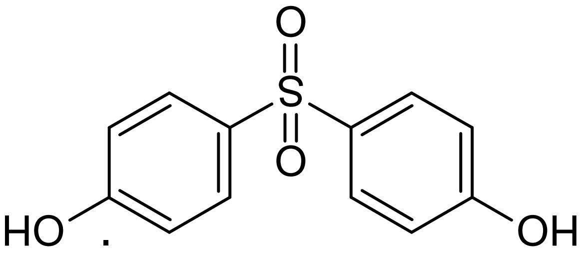
1. https://wedocs.unep.org/bitstream/handle/20.500.11822/33807/ARIC.pdf?sequence=1&isAllowed=y

Chemicals Additives (of Concern) in Plastics (3) – Bisphenols

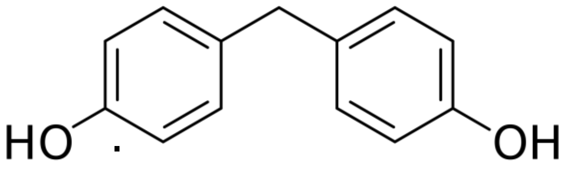


Bisphenol A (BPA)

Bisphenols are a group of aromatics with two hydroxyphenyl groups.

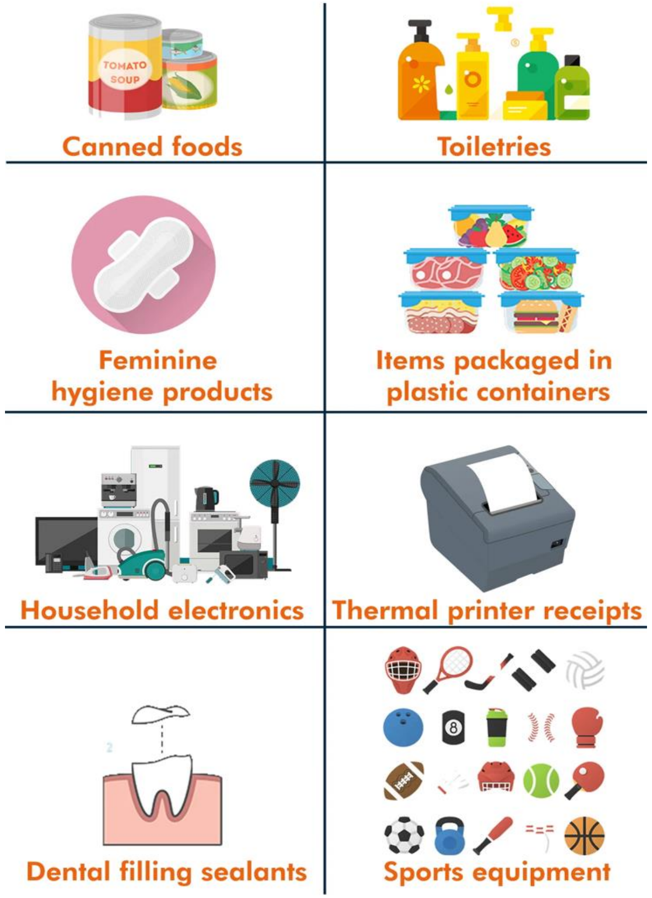


Bisphenol S (BPS)

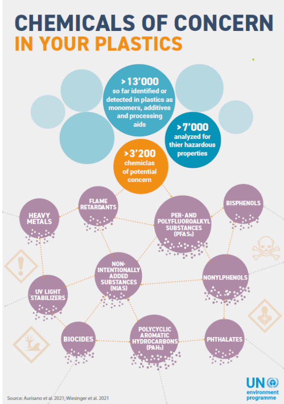


Bisphenol F (BPF)

- **Major uses:** to make polycarbonates, make the epoxy resin liners of cans, as an ink developer in thermal paper, etc.
  - Migration from containers to food and beverages is a primary source of consumer exposure
- **First toxicity evidence in the 1930s**, now it is known to cause immunotoxicity, metabolic effects, neurotoxicity and developmental neurotoxicity, and reproductive and developmental toxicity
- **The safe level is getting lower:** 50 mg/kg/d by the US National Toxicology Program in 1982 → 50 ug/kg/d by US EPA in 1988 and EFSA in 2006 → 4 ug/kg/d by the EFSA in 2015 → **0.04 ng/kg/d** by the EFSA (draft)

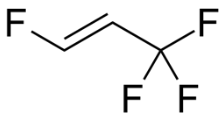


https://aminoco.com/blogs/nutrition/what-is-bpa-and-why-is-it-bad-for-you

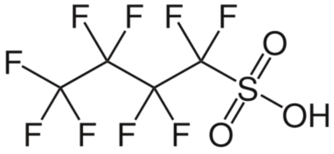


Plastics related chemical group (of Concern) (4) - Per- and polyfluoroalkyl substances (PFASs)

- **Per- and polyfluoroalkyl substances (PFASs)** = fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom[1]
  - Thousands of PFASs on the market, with many uses in plastics

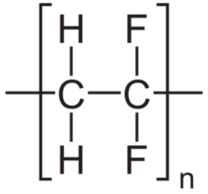


HFO-1234ze, as a blowing agent

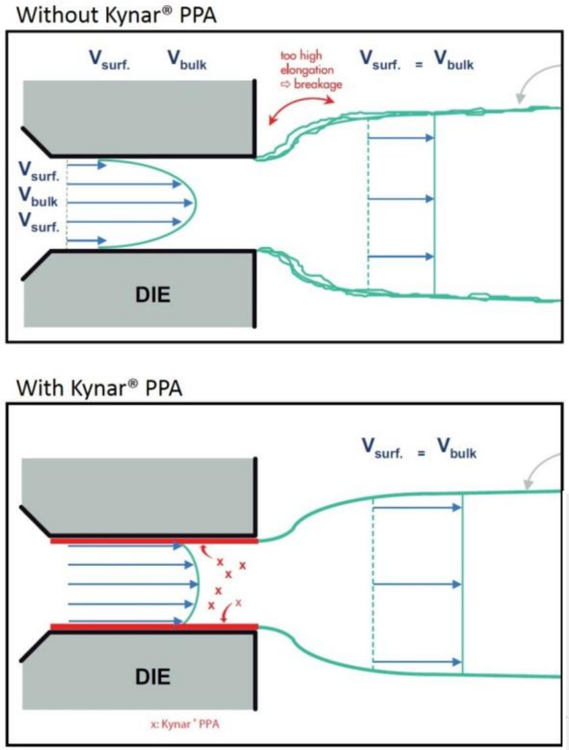


PFBS, as a flame retardant

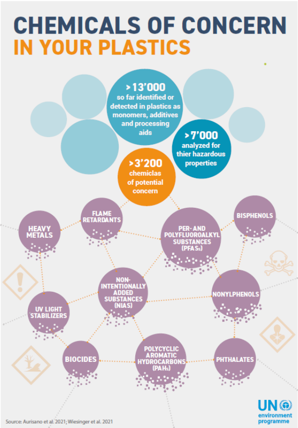
◆Insulation between circuit board and metal housing of notebook PC



PVDF, as a polymer processing aid



- Side-chain fluoropolymer were a major use of PFOS and PFOA (carpet, paper)
- PFASs are a class of highly problematic chemicals[2]
  - highly **persistent** themselves, or can degrade into highly persistent end-products that are still PFASs,
  - may cause various adverse effects on human and ecosystem health
  - Many have been detected ubiquitously in the environment
- Many PFASs are subject to various chemicals legislations, including the **Stockholm Convention** (PFOS, PFOA, PFHxS and related compounds)[3]



1. https://pubs.acs.org/doi/full/10.1021/acs.est.1c06896;
2. https://pubs.acs.org/doi/full/10.1021/acs.estlett.0c00255
3. https://wedocs.unep.org/bitstream/handle/20.500.11822/33807/ARIC.pdf?sequence=1&isAllowed=y

Mixtures of plastic additives in house dust **and** decrease of sperm quality

- **Men's sperm quality in Europe has decreased by 50% in the past 60 years!**

There are 29 chemicals or chemical groups relevant to male reproductive health with a focus on deterioration of sperm quality – a large share of these chemicals are related to plastic:

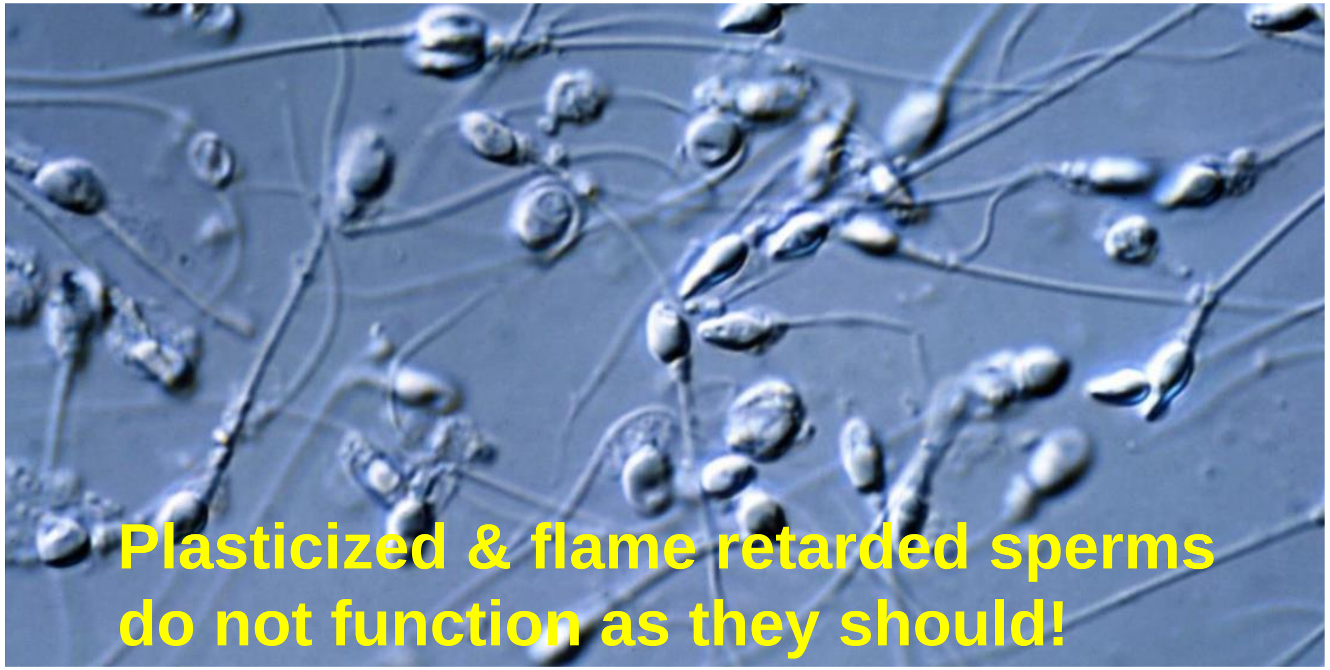
- **Antrogen receptor antagonists: Bisphenols A, F, S;** n-butyl paraben; **PBDE 99, 100, 183, 209; PCB 118, 126;** chlorpyrifos, vinclozolin, procymidone, fenitrothione
- **Suppression of testosterone synthesis**: **Phthalates DEHP, DnBP, BBzP, DiNP**; acrylamide
- **Disruption of prostaglandin signaling and InsL3 production**: Paracetamol
- **Inhibition of steroidogenic enzymes**: linuron
- **AhR activation:** Dioxins (PCDD/Fs), **Polychlorinated biphenyls: PCB 118, 126, 169.**

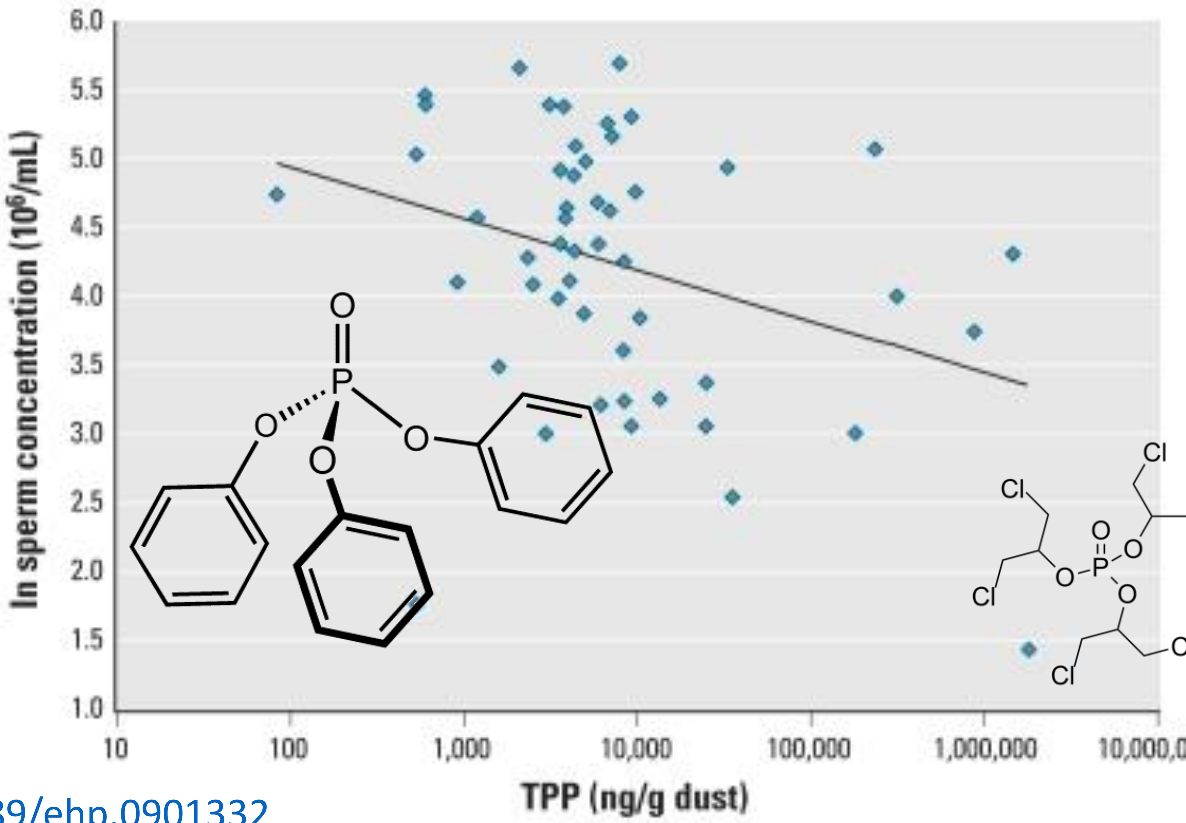
- Further chemicals with effects on the sperm quality related to plastic/polymer materials with unknown mode of action: **PFOS/PFOA, organophosphorus esters**

Kortenkamp et al. (2022) Environ. Int. 165, 107322.
https://doi.org/10.1016/j.envint.2022.107322

Sperm quality decrease with certain indoor plastic additives in house dust

- **Also sperm quality in the United States decreased.**
- A study in the US assessed the concentration of organophosphorus flame retardants and sperm quality. An increase of organophosphorus flame retardants (TPP; TDCPP) in house dust was associated with a 18.8% and 13.6% decline in sperm concentration (When adjusting for age, BMI, and abstinence period)
- PFRs/OPEs are uses in building insulation foams, textiles and electronics.

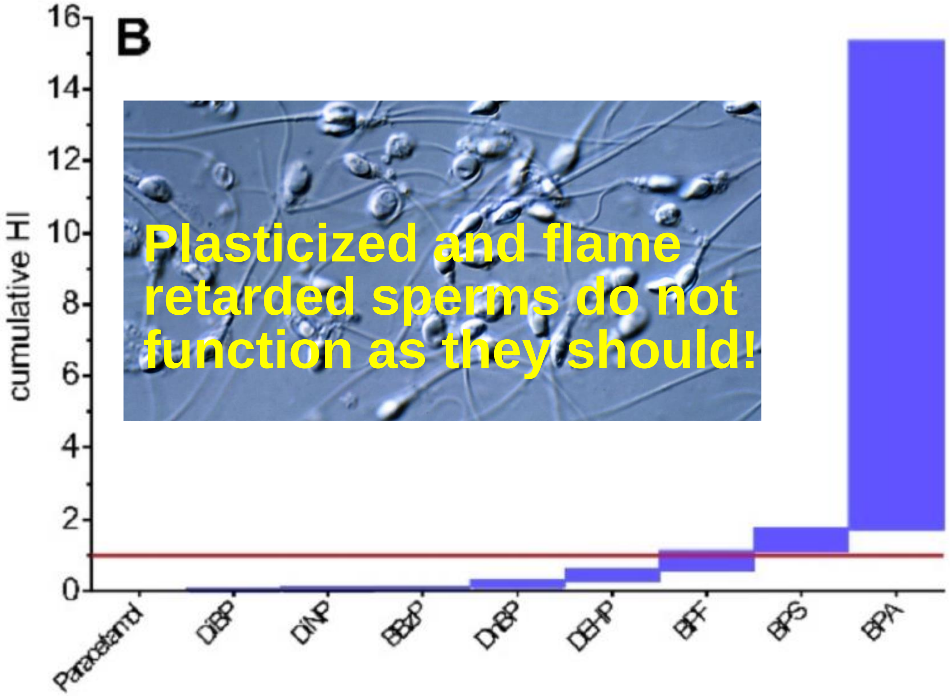


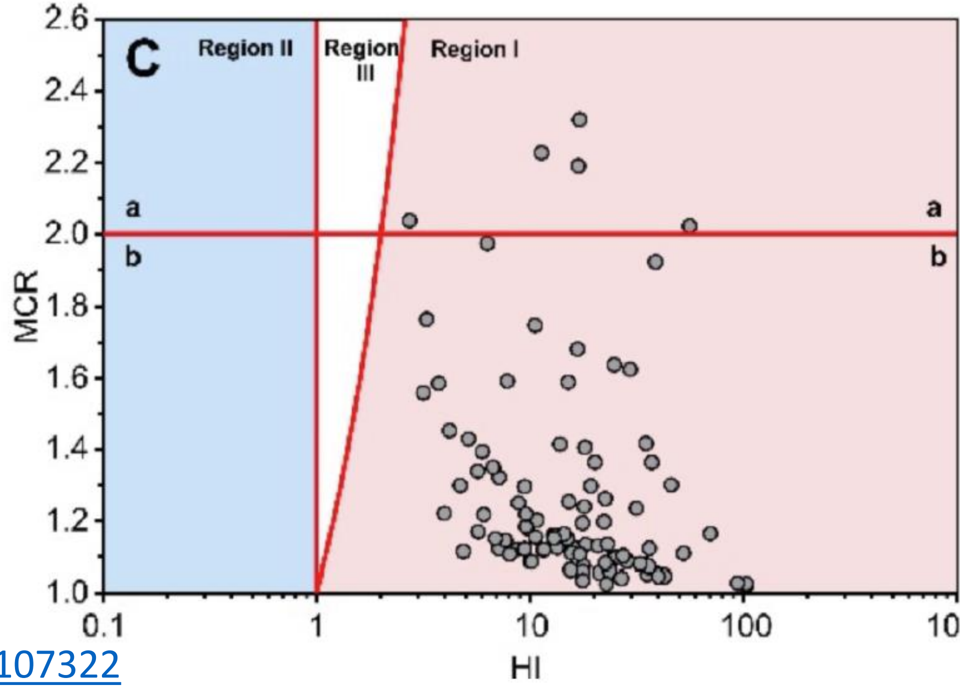


Meeker JD, Stapleton HM (2010) EHP 118 (3), 318-323 https://doi.org/10.1289/ehp.0901332

Assessment of mixture toxicity in young men and risk for sperm quality

- In a study 98 young Danish men where monitored for chemicals affecting semen quality including assessment of mixture toxicity.
- For this the Hazard Index (HI) which utilises risk quotients (RQs) of daily intakes (DI) and reference doses (RfD) for relevant health endpoints. By summing up the risk quotients of all chemicals included in the mixture risk assessment, the HI examines fold-exceedances of "acceptable" mixture exposures relative to an index value of 1.
- All 98 men were above a HI value of 1. **Highly exposed men had a combined exposures that exceeded the index value by more than 100-fold; the median was a 17-fold exceedance**.
- **Bisphenol A had the largest contribution followed by BPF and BPS.** The phthalates had in average a contribution below 1.
- **Mixture toxicity of plastic additives is a risk to sperm quality in Europe and contributes to the continued sperm decrease!**

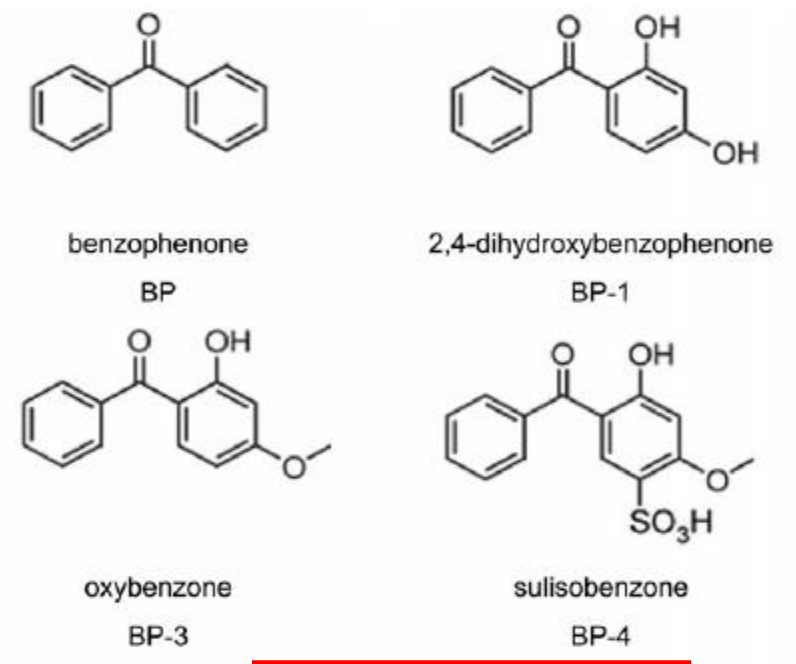




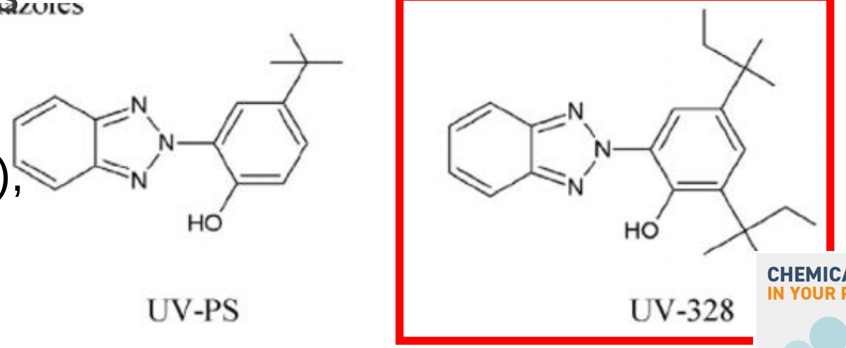
Kortenkamp et al. (2022) Environ. Int. 165, 107322. https://doi.org/10.1016/j.envint.2022.107322

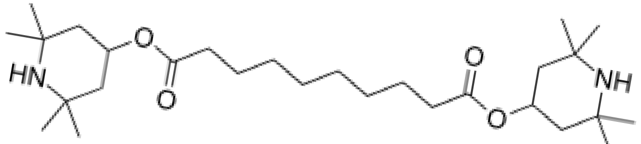
Chemicals Additives (of Concern) in Plastics (5) – UV Stabilizer

- **UV stabilizers** protect plastics from photo-degradation initiated by UV light, and thus decrease plastic weatherability.
  - **Benzophenones (BPs):** for polyolefins and PVC (absorb between 290–340 nm, i.e., most UVB and some UVA light)
  - **Benzotriazoles (BZTs):** transparent plastic materials such as ABS, HIPS, PVC, PES, PC, POM, PMMA, polyvinylbutyral (PVB), and PUR fibers (absorb between 290 and 350 nm)
  - **Hindered amine light stabilizers (HALS):** polyolefins, styrenics, polyamides, polyurethanes, polyacetals, adhesives, and sealants.

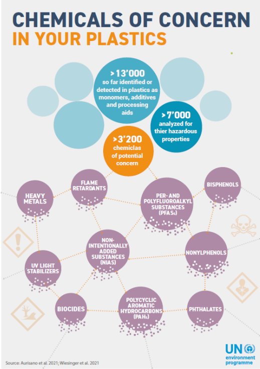


- **Some BZTs are SVHCs in EU** (UV-320, UV-327, UV-328, & UV-350), **UV-328 is a candidate POP for the Stockholm Convention.** **BPs are ecotoxic and have potential to induce allergies**, and **HALS are classified as very toxic (class III)** → EU and US regulates some HALS for food contact materials, and





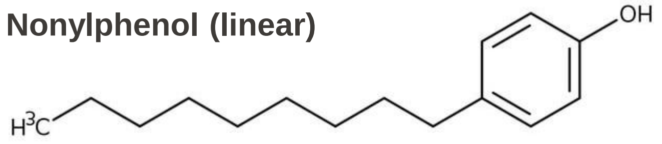
Example of a commercial HAL



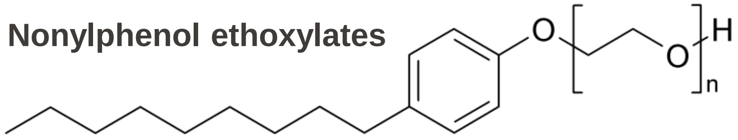
Chemicals Additives (of Concern) in Plastics (6) - Alkylphenols

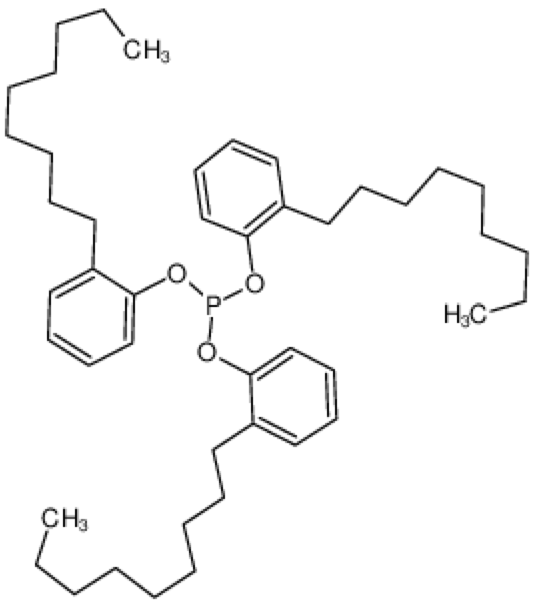
- **Nonylphenol (NP)** is used as a catalytic diluent in epoxy resins, and an intermediate to produce
  - Nonylphenol ethoxylates: surfactants in various applications, dispersing or stabilizing agents in plastics and rubber
  - TNPP: an antioxidant in rubber, vinyl, polyolefins (PE and PP), polystyrenes; a stabilizer in plastic food packaging
  - Barium and calcium salts of NP: heat stabilizers
- Thus, NP can be present in plastics and rubber as a residual and degradation product. → can be released during the plastic life cycles
- NP is an endocrine disruptor, and is restricted, e.g., in the EU[1]

Nonylphenol (linear)

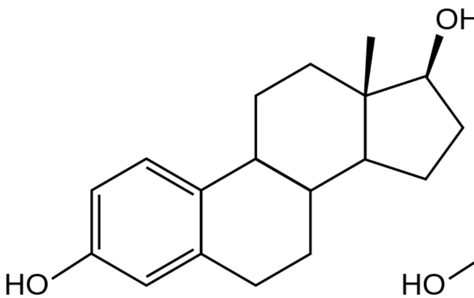


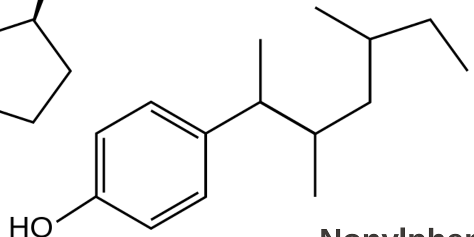
Nonylphenol ethoxylates





17beta-estradiol





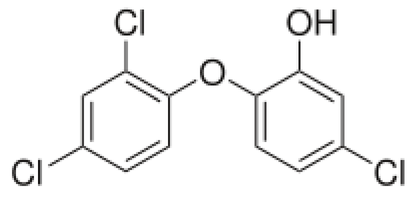
Nonylphenol (branched)

TNPP (CASRN 26523-78-4)

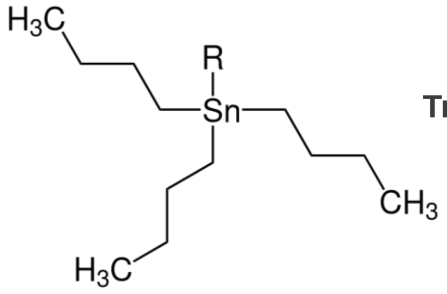
1. Substances restricted under REACH - ECHA (europa.eu)

Chemicals Additives (of Concern) in Plastics (7) - Biocides

- **Biocides** are antimicrobial substances to protect the plastics from attack and degradation by microorganisms, e.g.,
    - triclosan: in PE, PP, PVC, polyester and polyamide fibres
    - organic tin compounds such as tributyltin (TBT) and bis(tributyltin)oxide: PUR foam and PVC
    - arsenic compounds: PUR; PVC, LDPE and polyesters
- Biocides are problematic, e.g., causing health and environmental hazards, since they can strongly interact with living organisms, including causing allergic contact dermatitis and asthma.
    - E.g., TBT is very toxic for aqueous organisms, genotoxic and a endocrine disruptor.
- **Biocides in packaging are regulated in industrial countries**. In the US, it is done by In the Federal Food, Drugs, and Cosmetics Act, § 348, and in the EU, by the Biocidal Products Regulation.



triclosan



Tributyltin compounds

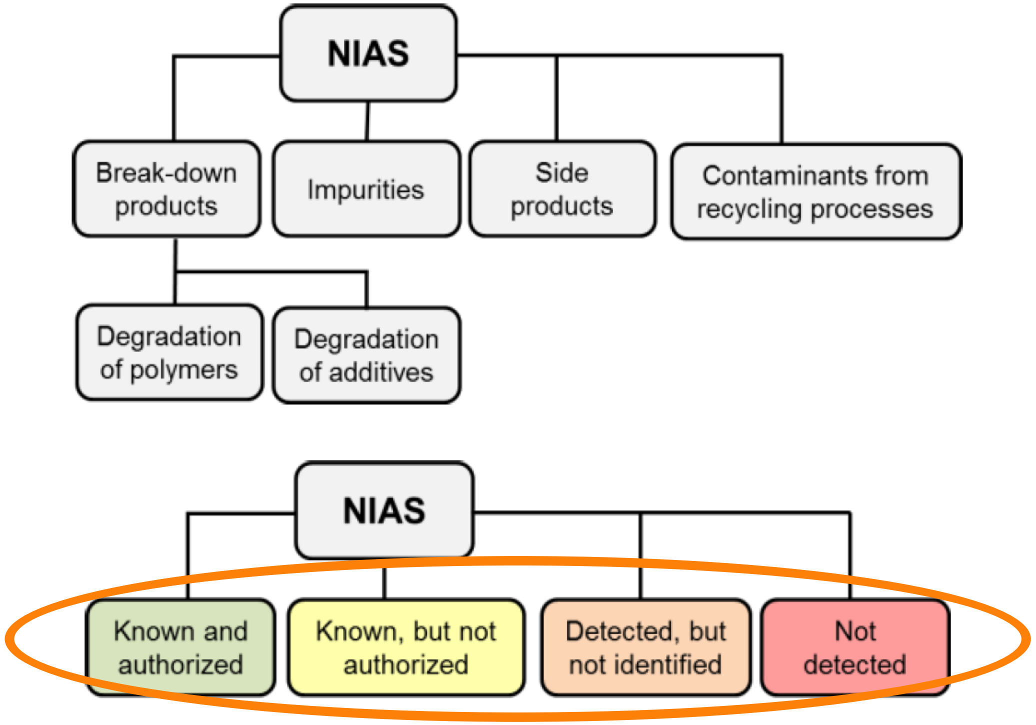
Chemicals Additives (of Concern) in Plastics (8) – Metal(loid)s

Metal(loid)s	Functions	Type of polymers	Effects on Human Health
Antimony (Sb)	Flame retardants, biocides, catalyst	Various	Breast cancer
Zinc (Zn)	Heat stabilizers, flame retardants, anti-slip agents, pigments	PVC, PE, PP	-
Cadmium (Cd)	Heat stabilizers, UV stabilizers, pigments	PVC	Changes in metabolism; DANN methylation, promotion of carcinogensis, etc.
Cooper (Cu)	Biocides	-	Formation of reactive oxygen species; inducing DNA strand breaks
Mercury (Hg)	Catalyst, Biocides	PUR	Mutagen or carcinogen; brain damage
Arsenic (As)	Biocides	PVC, LDPE and polyesters	Congenital disabilities; carcinogen
Tin (Sn)	UV stabilizers, biocides	PUR foam, PVC	Breast cancer, skin rashes, endocrine disruption (certain organotins)
Lead (Pb)	Heat stabilizers, UV stabilizers, pigments (particularly red)	PVC and others that need red pigments	Hypertension, miscarriages, disruption of nerve systems, infertility
Titanium (Ti)	UV stabilizers, pigments	PVC	Cytotoxicity on human lung and colon cells
…	…	…	…

IJERPH | Free Full-Text | A Detailed Review Study on Potential Effects of Microplastics and Additives of Concern on Human Health (mdpi.com);
https://wedocs.unep.org/bitstream/handle/20.500.11822/33807/ARIC.pdf?sequence=1&isAllowed=y

Other Chemicals (of Concern) in Plastics - Non-intentionally added substances (NIAS)

- **Non-intentionally added substances (NIAS)** = chemicals co-present in plastics but are not intentionally added during the production and processing, including
  - unreacted residuals of raw materials and intermediates
  - impurities in raw materials
  - reaction by-products
  - break-down/degradation products
  - contaminants during production and processing
  - Additives might become NIAS in recycling
- NIAS can include **unintentional POPs such as PCDD/PCDF, PCB, or hexachlorobenzene (from e.g. pigments additives)** which are regulated in some countries with unintentional trace limits.

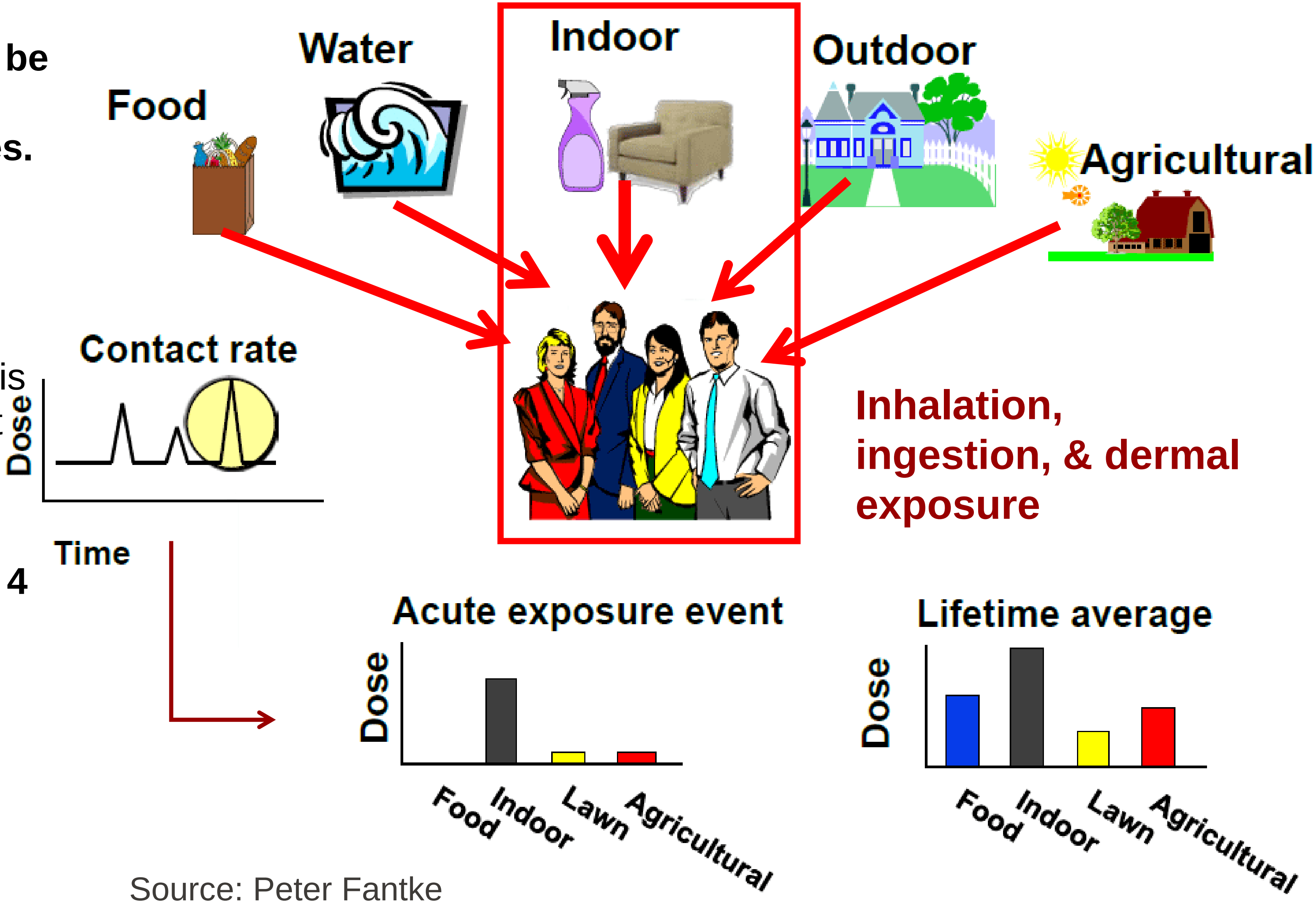


Source: Geueke B (2013a) Dossier – Non-intentionally added substances (NIAS). Dossier of the Food Packaging Forum. DOI: 10.5281/zenodo.33514

UNEP (2023) Chemicals in plastics: a technical report, in press.

Human exposure sources – Indoor contribution

- **Indoor environment contributes greatly to human exposure and can be major contributor for certain chemicals including plastic additives.**
- **In Northern Hemisphere the time spent indoor is approx. 90% (home, workplace and transport)** (Leech 2002).
- For Southern Hemisphere countries this is likely lower. No robust data on spent indoor time in African countries.
- **WHO estimates that indoor air pollution is responsible for close to 4 million death/year** (large share from indoor cooking/heating using low tech stoves. With increasing plastic use as fuel).

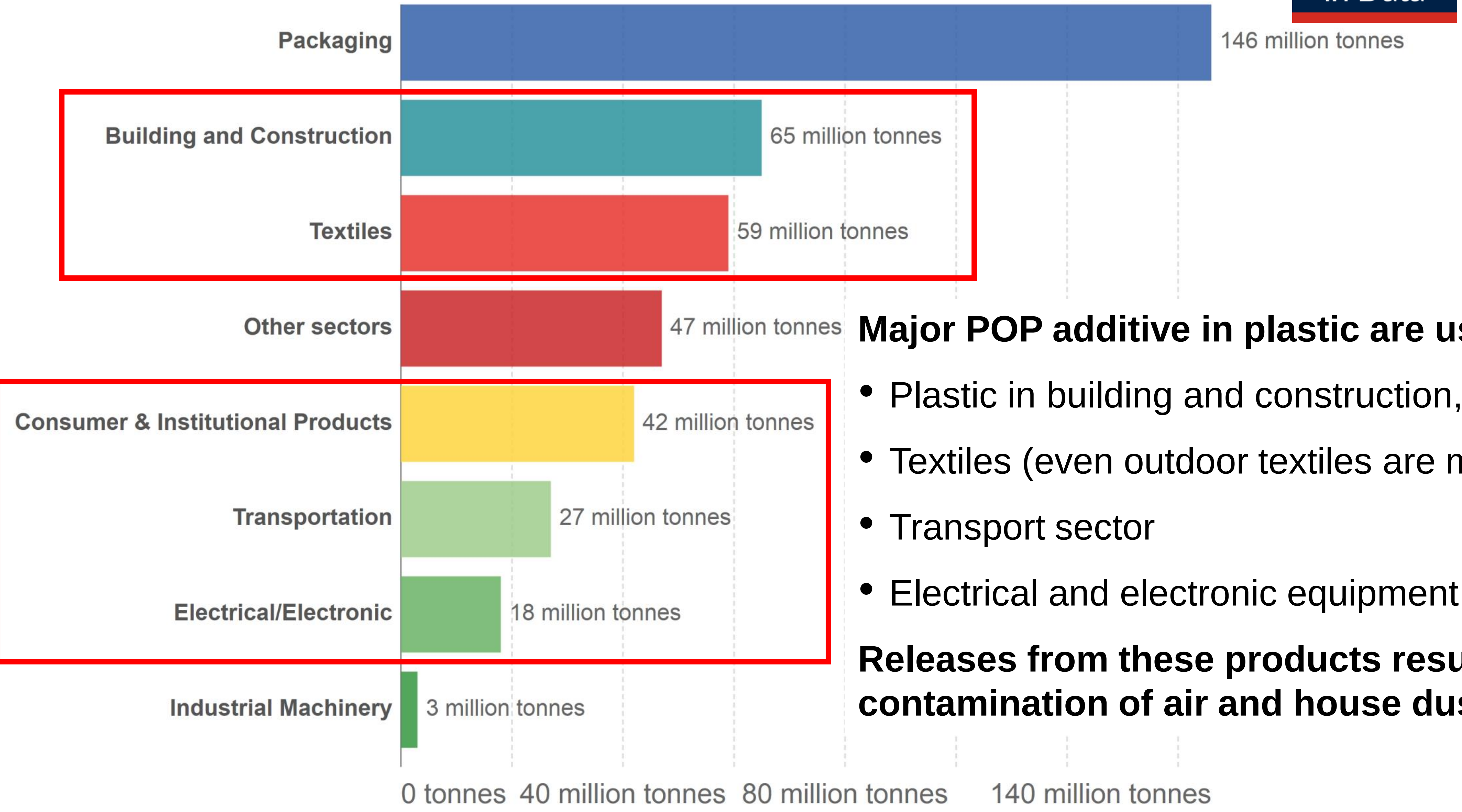


Source: Peter Fantke

WHO. Household Air Pollution and Health.
Leech (2002). J. Expo. Sci. Environ. Epidemiol. 12, 427–432
Fantke, et al. 2016. Environment International 94, 508-518. doi:10.1016/j.envint.2016.06.010

Indoor exposure major POP by industrial plastic sector use

Primary global plastic production by industrial sector (tonnes/year)



Major POP additive in plastic are used indoor in:

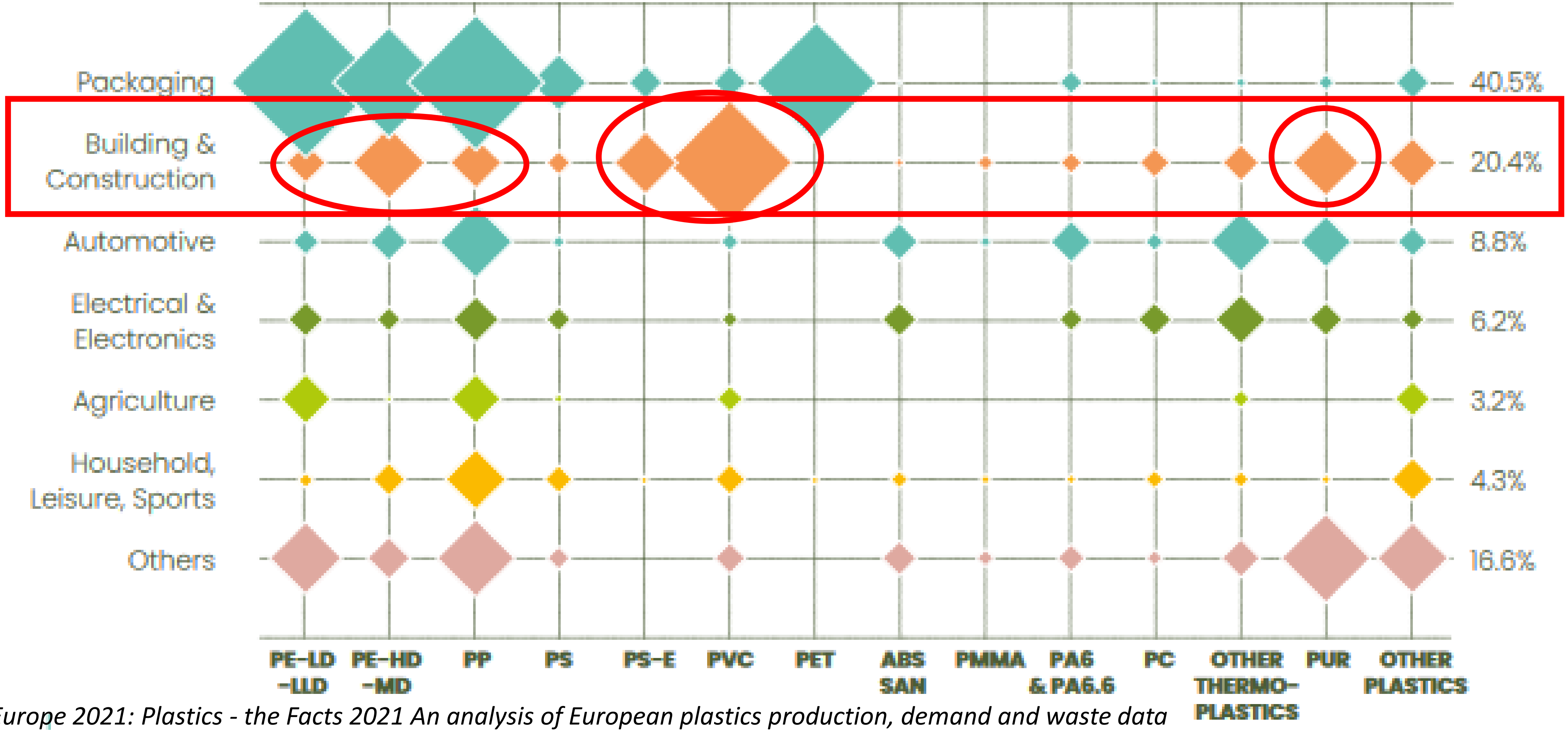
- Plastic in building and construction,
- Textiles (even outdoor textiles are major time indoor)
- Transport sector
- Electrical and electronic equipment.

Releases from these products result in indoor contamination of air and house dust with exposure.

Based on Geyer et al (2017) Sci. Adv. 2017;3: e1700782

Plastic demand by segment and polymer (EU 2020)

- Major plastics in buildings are PVC, expanded and extruded polystyrene (EPS/XPS), polyethylene and PUR.
- PVC often contains large amount of additives (up to 60%) including EDCs (e.g. DEHP; DBP) or POPs (SCCP, PCBs).
- Other plastics (EPS/XPS; PUR) in buildings are frequently flame retarded with POPs (PBDEs, HBCDD) or other hazardous chemicals like phosphorous flame retardants (PFRs) or treated with pesticides/biocides (e.g- silicone).

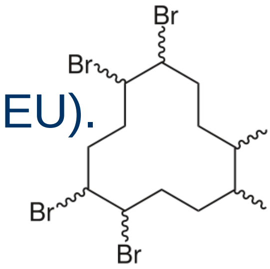


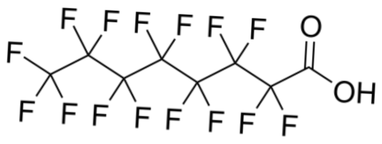
Plastics Europe 2021: Plastics - the Facts 2021 An analysis of European plastics production, demand and waste data

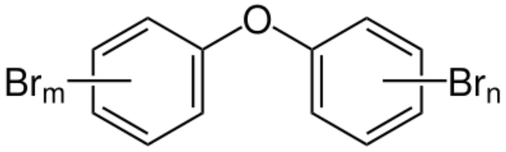
Additives of concern in polymers in buildings and textiles

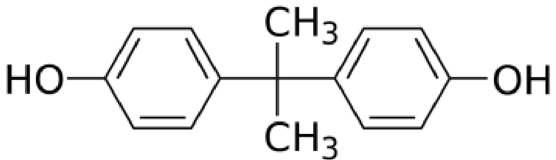
A range of additives of concern were and are used in plastics in buildings & textiles. Some major additives including some legacy additives which were restricted but are still present due to long service life are:

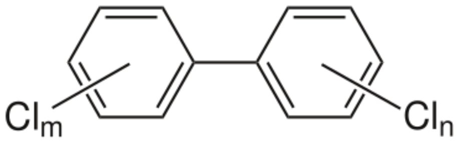
- **PCBs (POP):** Has been used in polymer sealants (Thiokol) and PVC coatings/paints and cables (1950 to 1980).
- **HBCD (POP):** Flame retardant in expanded/extruded polystyrene (EPS/XPS) insulation (until ca. 2017) and textiles.
- **PBDEs (POPs) and other brominated flame retardants:** Used in PE/PP foils, PUR/XPS and PE insulation, rigid PUR spray foam and insulation, roller blinds and curtains.
- **Short-/Medium-chain chlorinated paraffins (MCCPs/SCCPs) (POPs):** plasticizer and flame retardants in **PVC** (e.g. flooring, roofing, cables, foils, wall covering), sealant materials (**rigid PUR foam**) and adhesives.
- **UV-328** (POP candidate): UV-filter to reduce polymer degradation in plastics (PE, PC, PVC, PS) & textiles (PES/PET)
- **Phosphorus** flame retardants/organophosphorus esters (**PFR/OPE**): Flame retardants in PUR, textiles and furniture.
- **Phthalates** (e.g. **DEHP, BBP, DBP**) used primarily as plasticizer in **PVC** (e.g. roofing, sealants, flooring, wall covering)
- **Bisphenol A (BPA)** is the monomer of polycarbonate. Polycarbonate has high optical clarity and is used for windows and skylights, wall panels and roof domes. Also a minor use is as an additive in PVC and polyurethane.
- **Cadmium and lead:** Stabilizer mainly in PVC window frames and doors (meanwhile restricted e.g. in the EU).







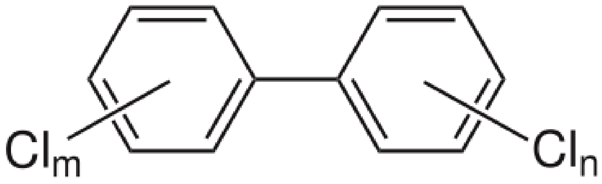




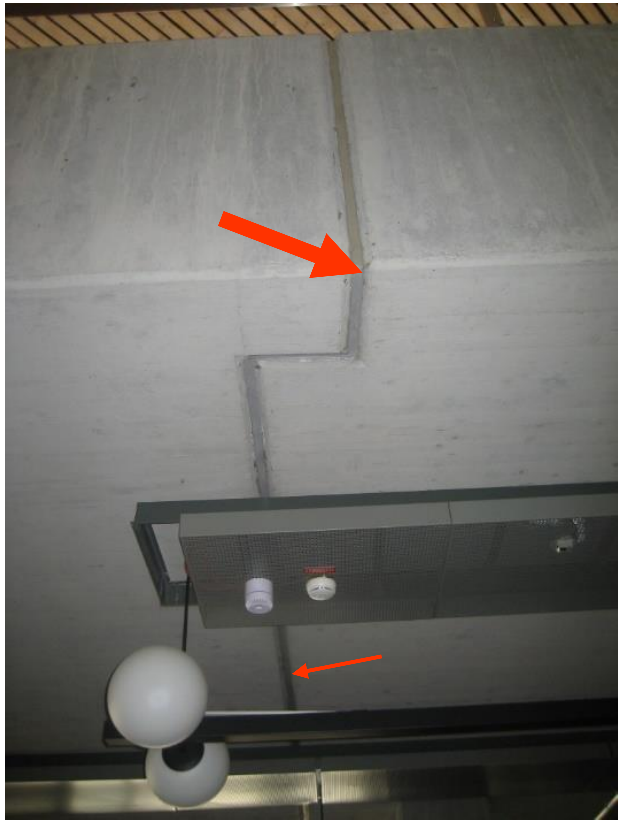
Learning from the past: PCBs in plastics in buildings - indoor pollution

PCBs use in polymers in buildings resulting in indoor contamination:

- **Sealants, PVC-coating/paints and adhesives in buildings** and other constructions have been major "open applications" for PCBs. In total about **250,000 tonnes of PCBs have been used from 1950s to 1970s mainly in industrial countries (expensive sealants and paints).**



- The buildings with a large amount of sealants are (prefabricated) concrete where sealants were/are used as joints. Typical PCBs sealants (conc. 5 to 35%) were **polysulfide sealants** (e.g. Thiokol). **In Germany 33% of kindergarten and schools were affected.**
- **Due to the long lifetime of sealants in buildings of 30 to 60 years and longer, a considerable share of these sealants is still present.**
- Also PCB coatings/paints were used in buildings from the and are still present but often repainted.



PCB exposure indoor and need of remediation action (experience)

Germany's experience with PCBs in indoor air pollution from polymer sealants and coatings

- Between 1953-1972, in West Germany about 24,000 t of PCB were used in the building sector, mainly in sealants. Largest open PCB use in the world (360 g/person). 40%-70% of PCB materials are still present.
- German PCB regulation (1995) (based on a **Tolerable Daily Intake (TDI)** of **1000 ng** PCB/kg bw-day):
  - TDI exceeded when PCB air concentration >3,000 ng/m^3 (60 kg person; 20 m^3 air/day)

  ⇒ Building remediation required for PCB air conc. >3,000 ng/m^3.

- **In 2003 the WHO reevaluated the tolerable daily intake (TDI)** for PCBs and WHO set it to **20 ng per** kg body weight per day; Now, remediation would be necessary if PCB air concentration **>60 ng/m^3.**
- However, in PCB-contaminated buildings it is practically impossible to remediate below 60 ng PCB/m^3. **No regulation change**. So the situation was/is challenging and since 2003 children, students and adults are exposed >TDI in PCB buildings. Implementation would likely cost billions (closure & reconstruction).
- **So PCBs are the first plastic additives which result that buildings need remediation and today buildings are sometimes broken down due to PCB contamination. Kindergarten and school children, students and academia are still exposed in thousands of buildings in Europe and USA.**

Liability of PCB producers for health effects

Monsanto/Bayer (responsible for approx. 70% of all PCB produced in the past) face recent legal cases and litigation risks in the US and still need to compensate. (**https://www.pcbinschools.org/**)

Global

This is Bayer | Health | Agriculture | Products | Innovation | Sustainability | Media | Investors | Career

Home > Managing and Mitigating the U.S. PCB Litigation Risk

https://www.bayer.com/en/resolving-us-pcb-litigation

Managing and Mitigating the U.S. PCB Litigation Risk

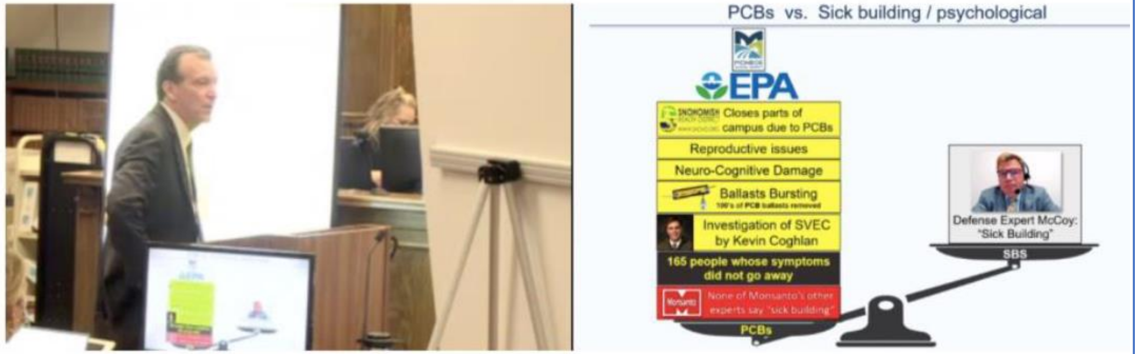
Polychlorinated biphenyls (PCBs) are chemicals that were produced until the 1970s and were used in a wide array of industrial products and building materials, especially to reduce fire risk in electrical components. Monsanto voluntarily ceased manufacturing PCBs in 1977, two years before the EPA banned their production. Nevertheless, the Company currently faces legacy PCB-related litigation in the U.S. and has a clear strategy to manage and mitigate these risks, which relate to actions that date back more than four

Jury Hits Monsanto With $275M Verdict In Latest Trial Over PCB Exposure in Washington State School

Posted by *David Siegel* on Oct 17, 2022 12:56:06 PM

Tweet | Share

https://blog.cvn.com/jury-hits-monsanto-with-275m-verdict-in-latest-trial-over-pcb-exposure-in-washington-state-school



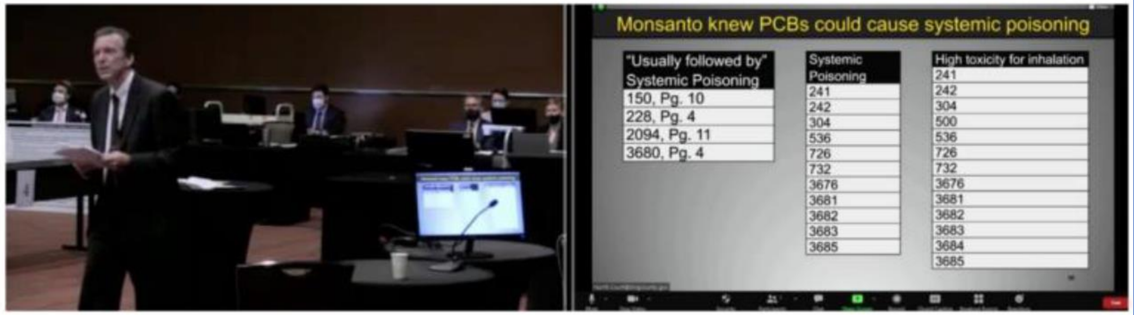
CVN screenshot of plaintiffs' attorney Rick Friedman delivering his closing argument

BREAKING: Monsanto Hit With $185M Verdict Over Teachers' PCB-Related Brain Damage

Posted by *David Siegel* on Jul 28, 2021 1:28:46 AM

Tweet | Share

https://blog.cvn.com/breaking-monsanto-hit-with-185m-verdict-over-teachers-pcb-related-brain-damage



PCB in polymer release contaminate indoor & outdoor environment

PCB-Emission from buildings/open applications:

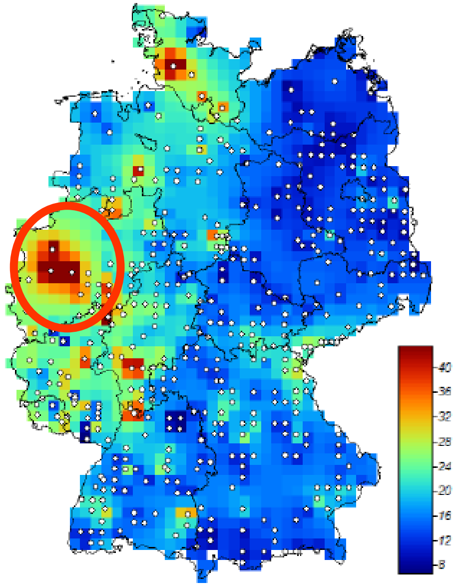
- Thomas et al. (2012) estimated PCB emissions of several building sealants based on chamber tests at 23°C, e.g.:
  - Length 6.4 m; 14.2% PCB; Emission: 320 µg PCB/h **(2.8 g PCB/year)**;
  - Length 110 m; 24.3% PCB; Emission: 3100 µg PCB/h (27.2 g PCB/year).

- Investigation at a university building in Germany (Weber et al. 2015): **PCB inventory: 500 kg PCB in paint of ceiling tiles (10,000 m²) and 500 kg PCBs in joint sealants. Annual PCB release via room ventilation: 600 g PCB! This is 6 times above the PRTR reporting for an industrial plant.**

  → PCB Emission rate: 0.06% annually

- For a building in Sweden (Sundahl et al. 1999):
  PCB inventory: 90 kg in sealants. PCB emission: 60 g/year

  → PCB Emission rate: 0.07% annually (>1000 years release)



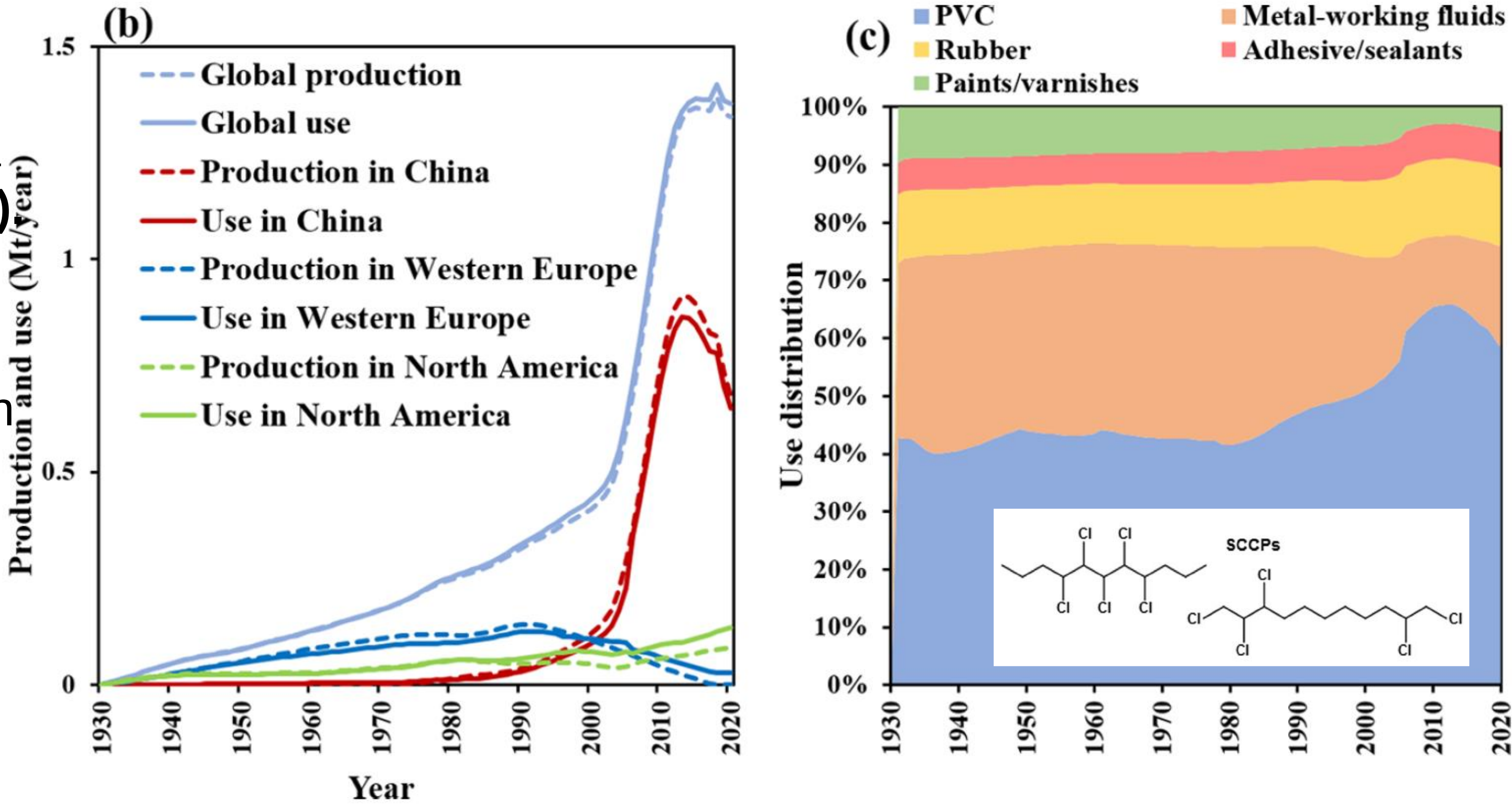
Auflage (O-Horizonte) (ng/g TM)

Thomas et al. (2012) EPA/600/R-12/051;
Guo et al. (2012) EPA/600/R-11;
Weber et al. (2015) UBA Dokumentationen:114/2015; Anhang I;
Sundahl et al. (1999) J Environ Monit 1 (4):383–387

Chlorinated paraffines in buildings - regrettable substitutes for PCBs

PCBs were substituted by SCCPs/MCCPs in the 1970s (e.g. flame retardants in cables; **sealants, paints).**
In 2017 SCCPs were listed as POP in the Stockholm Convention and MCCPs are proposed as POP.

- CP production strongly increased since 2000. Today ca. 1.4 Mt/a are primarily produced in China & India **(more than total PCB production)**
- Largest share of SCCP/ MCCPs is **used in PVC (70%)** and rigid PUR spray sealant mainly in construction (Chen et al. 2021; 2022) and in rubber.



Source: Chen et al. (2022) Environ. Sci. Technol. https://doi.org/10.1021/acs.est.2c00264

Chen et al. (2021) Environ. Sci. Technol. 55, 7335–7343. https://doi.org/10.1021/acs.est.0c07058
Guida, Capella, Weber (2020) Emerg. Contam. https://www.sciencedirect.com/science/article/pii/S2405665020300111

What are sources of SCCPs/MCCPs indoor contamination

- The main uses for SCCPs/MCCPs in China (main CP producer) are products used indoor in particular PVC (wall paper, floor, panels, cables), sealants/adhesives (PUR and others) and paints.
- And consumer products made from soft PVC plastics: e.g. PVC-curtains, PVC stroller rain cover, backing oven (cable), cables, PVC & rubber toys, rubber hand rail; mats etc.

Excercise mat

Adhesive PUR

Electical cable with PVC sheathing

Soft plastic curtain (Brit Berlin Pixelio)

CP-containing sealant

CP-containing PVC floor

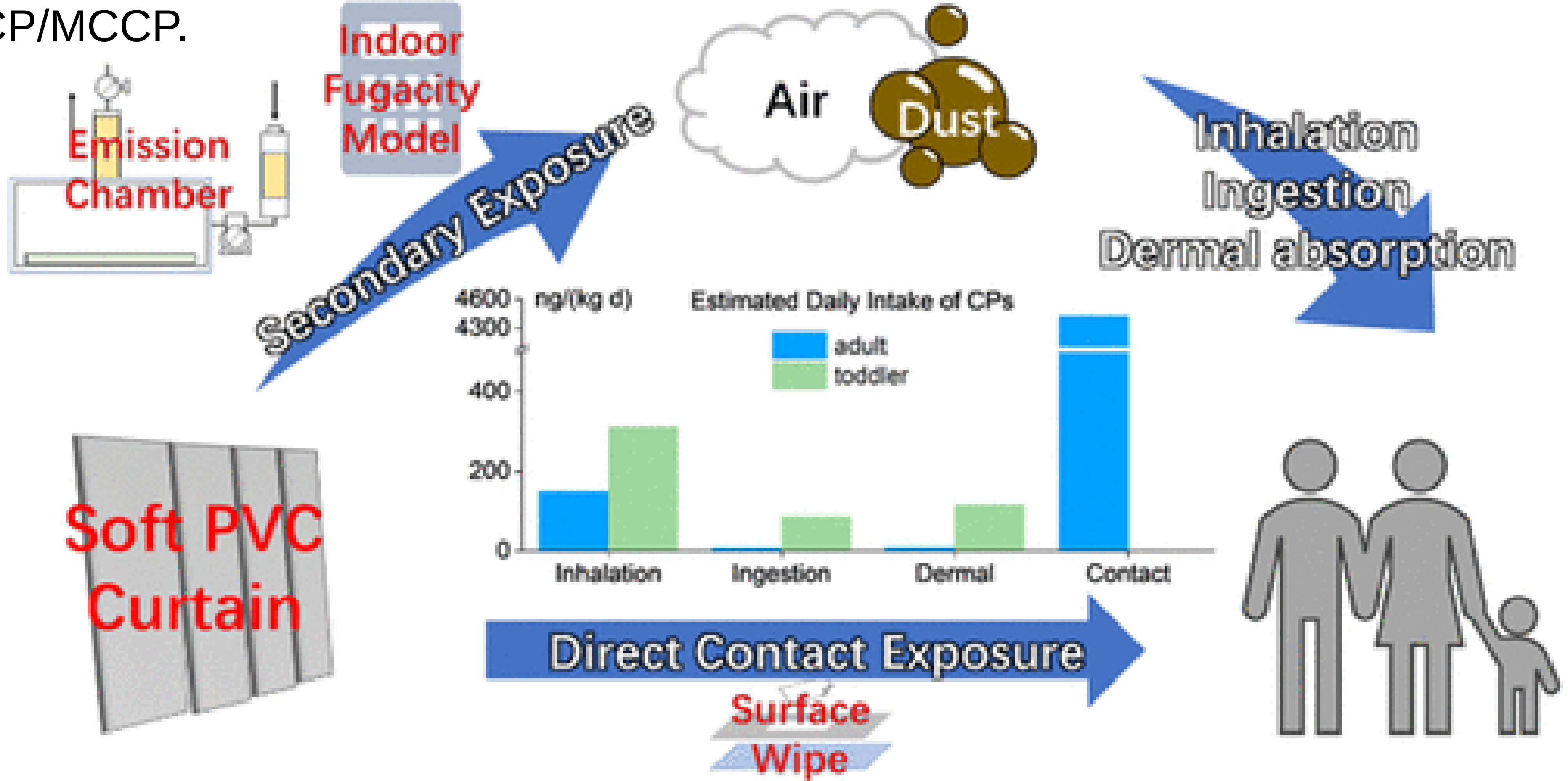
paint on radiator

Electical cable in oven

Sources pictures: Chen et al (2021) Environ. Sci. Technol. 55, 7335–7343; https://www.eti-swiss.com/bauschadstoffe/chlorparaffine/; and Christine Herold

High SCCP/MCCP exposure from PVC curtains

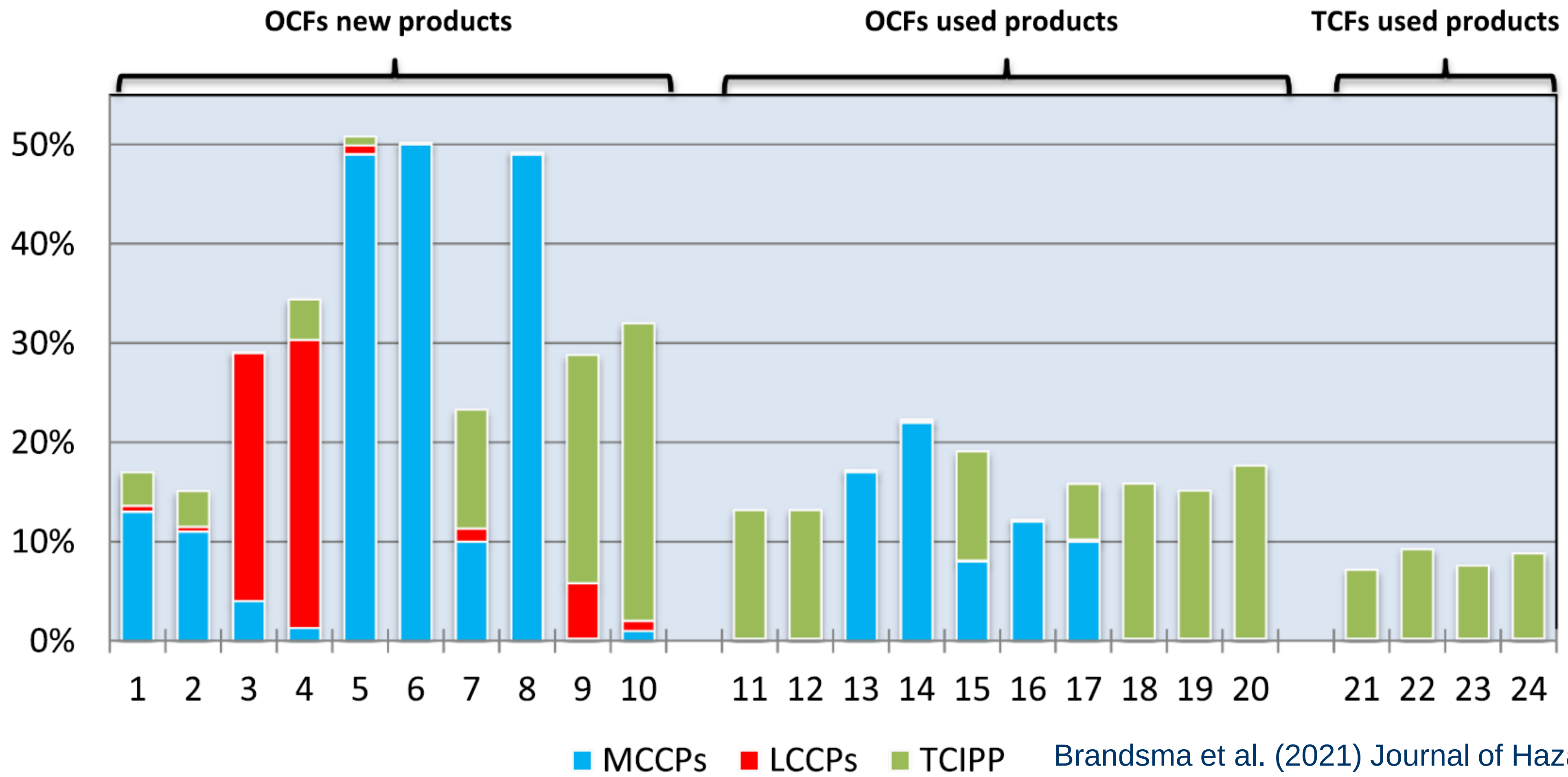
- Short-chain and medium-chain CPs accounted for 30% by weight of the PVC curtains.
- High CP emission rate to air (7 ng/(cm2 h) with estimated SCCP/MCCP concentrations in indoor air of 583 and 95.3 ng/m3 and total daily intakes from air and dust were 165 ng/(kg day) for an adult and 514 ng/(kg day) for a toddler.
- The results indicated that curtains could pose considerable health risks through inhalation of and dermal contact to SCCP/MCCP.

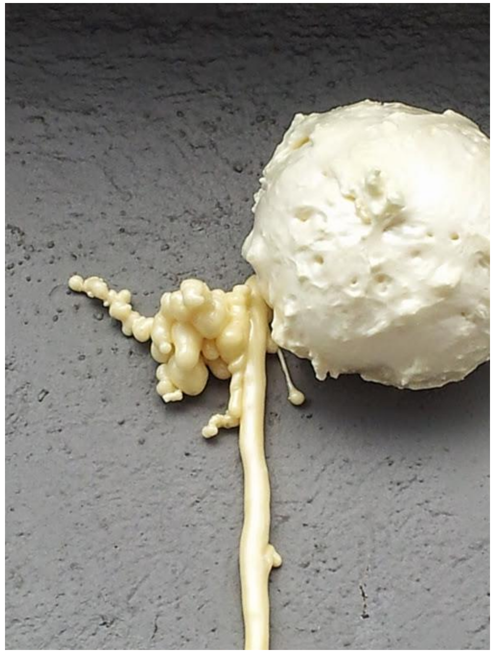


Weng et al. (2023) Environ Sci Technol https://doi.org/10.1021/acs.est.2c07040

High CP and PFR use & release from PUR foam

- Up to 50% flame retardants (particular CPs) in one- and two-component spray polyurethane foams (OCF; TCF) with major use of CPs and PFRs.
- Lower levels of CPs and phosphorous FRs (PFRs) in PUR foam in use indicate that a share of FRs were released during lifetime.
- High PFR levels in indoor air in CP in dust also indicate high releases from products.



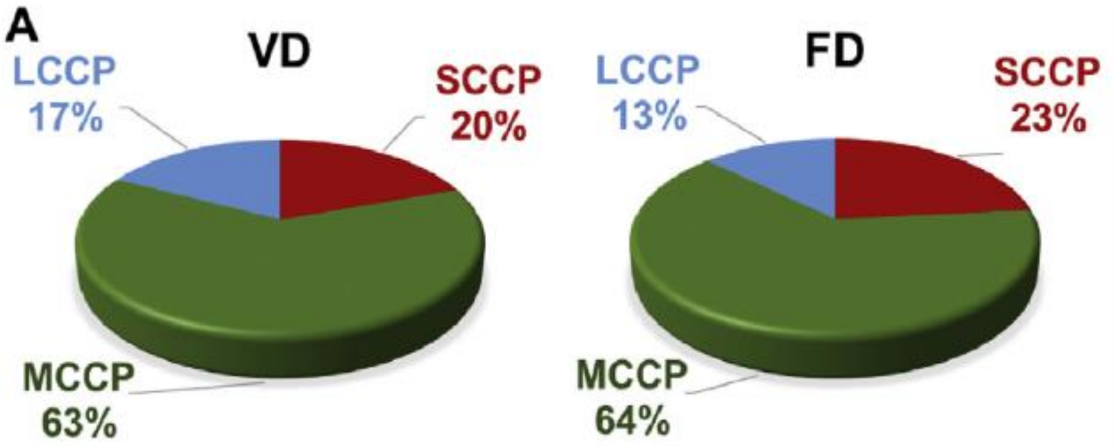


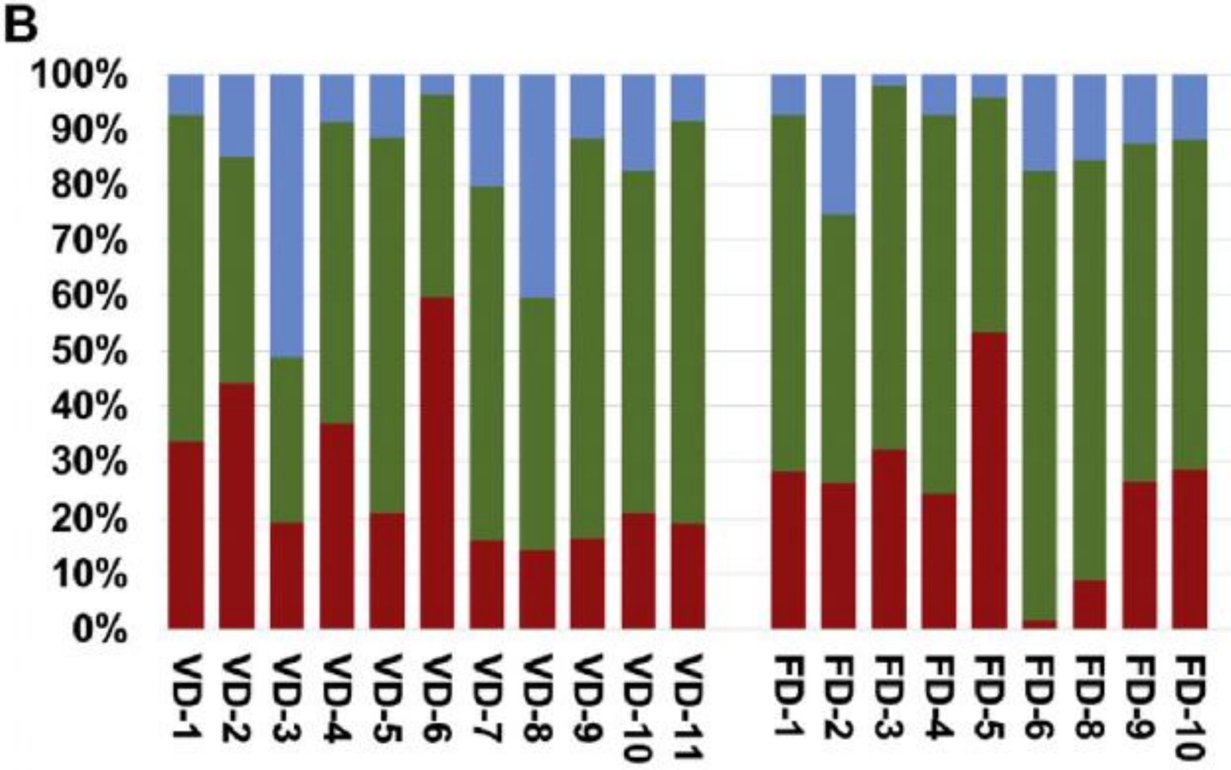
Source Kencf0618

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

High SCCPs, MCCPs and LCCPs levels in South African house dust

- High SCCPs, MCCPs, and LCCPs levels were detected in all house dust samples in South Africa with a **mean conc. of 130 to 230 mg/kg in dust** with maximum of 660 mg/kg!
- MCCPs were the dominant CP group followed by SCCPs.
- This indicates large SCCP/MCCP sources in African private houses **and high indoor exposure to SCCPs and MCCPs**.





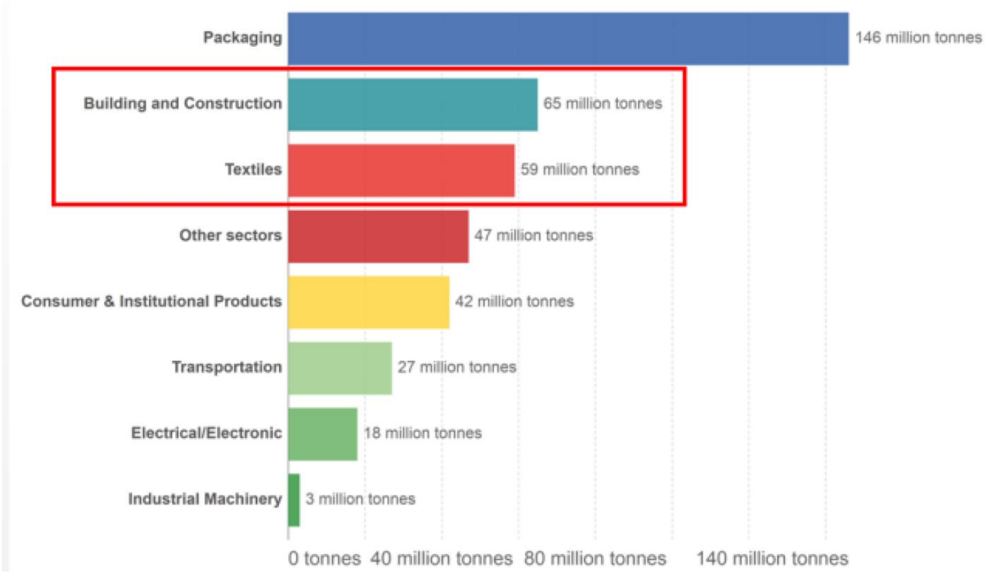
Brits et al. (2020) Chemosphere 238, 124643.

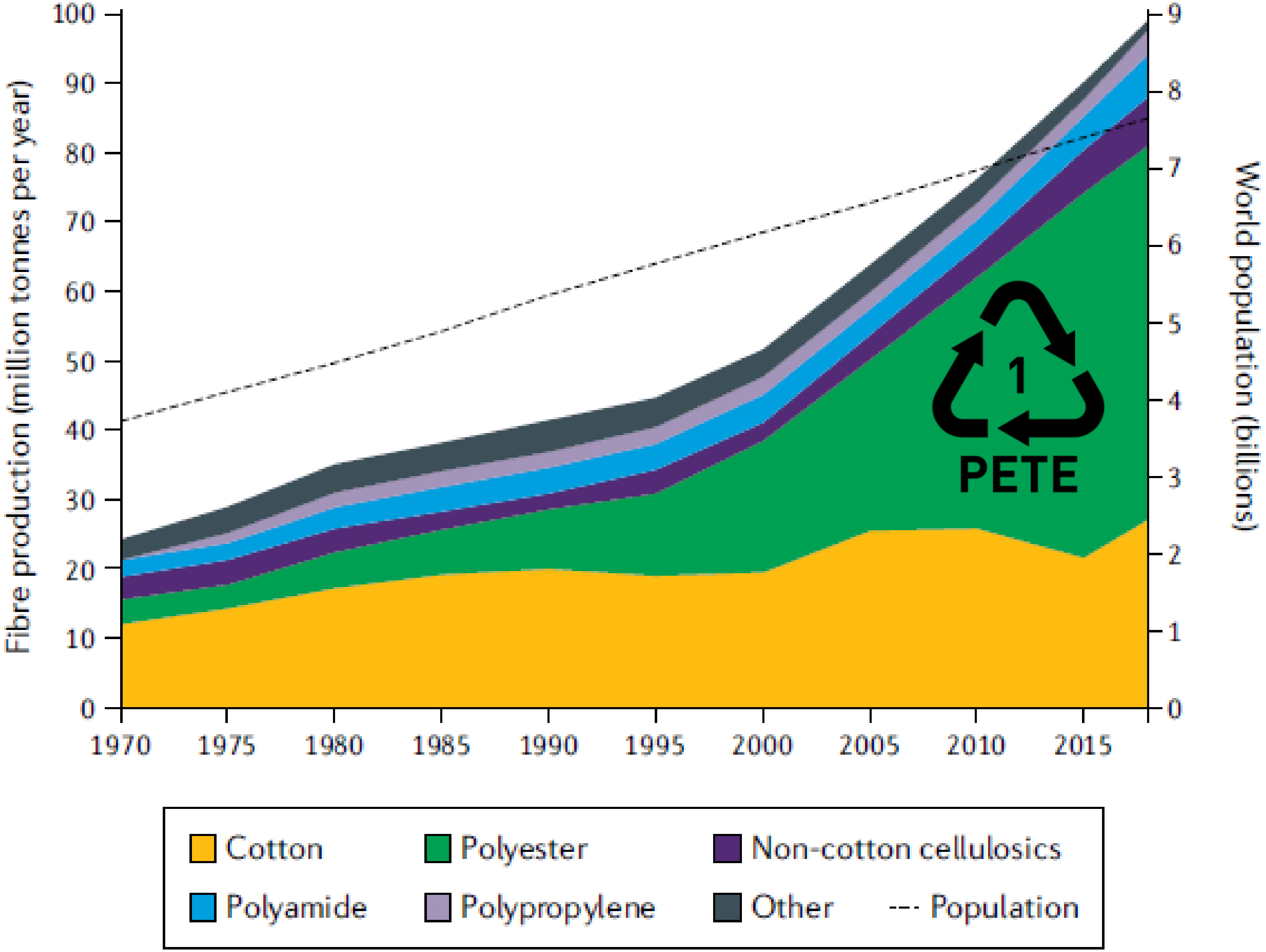
C

Congener group		VD (µg/g)				FD (µg/g)			
		Mean	Median	Min	Max	Mean	Median	Min	Max
ΣSCCP	(red)	48	14	5.1	214	62	17	5.4	353
ΣMCCP	(green)	69	46	13	200	142	47	21	498
ΣLCCP	(blue)	17	13	4.3	74	24	9.4	1.9	108
ΣCP		135	68	36	488	228	94	33	663

Strong growth of global textile fibre production – a major plastic use

- Fast fashion results in strong increase of textile fibre production now above 100 million tonnes/year **with ca. 70% of synthetic fibres (plastics!).**
- Polyester (PES or PETE) is meanwhile the most used fibre (ca. 50% of all) far exceeding cotton.

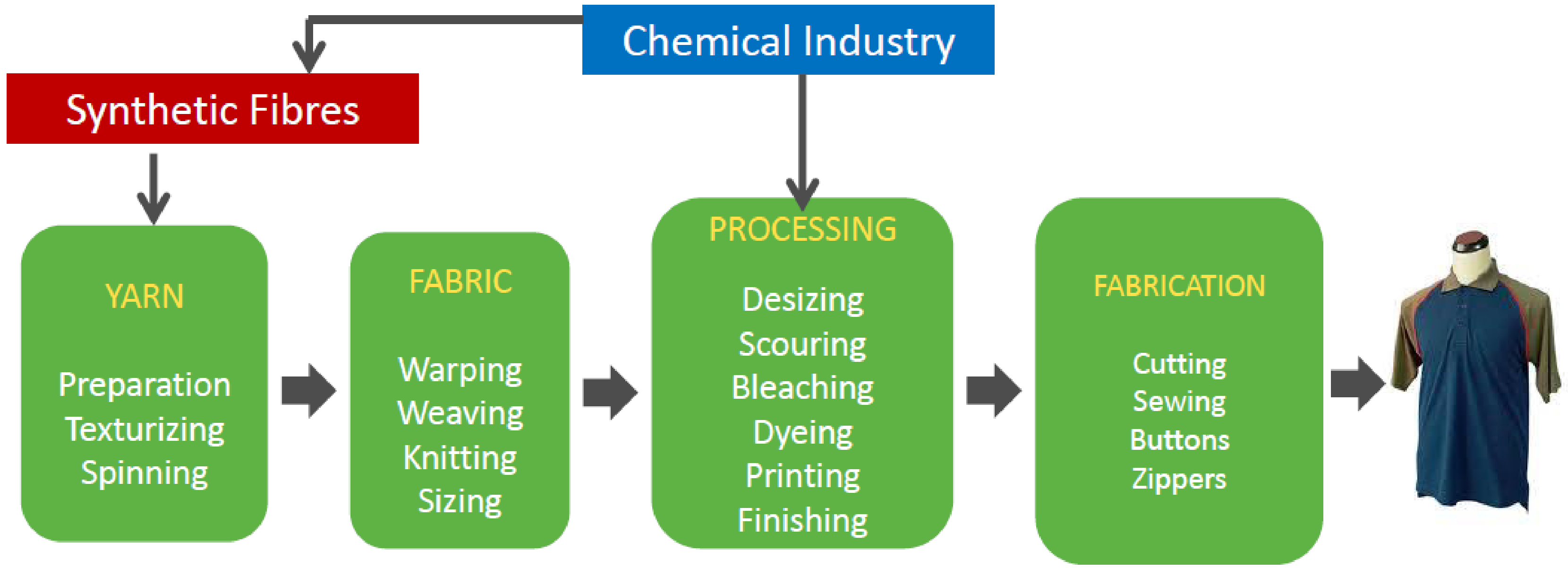




Niinimäki, et al. , (2020) Nature Reviews | Earth & Environment Vol. 1, 189-200

Chemical use in textiles in the indoor environment

- **More than 5000 chemicals are used in the production of textiles at different stages.**
- **Particular high use of additives in synthetic textiles (“plastics”)** as well as process chemicals partly remaining on the fibre and in the textile products.



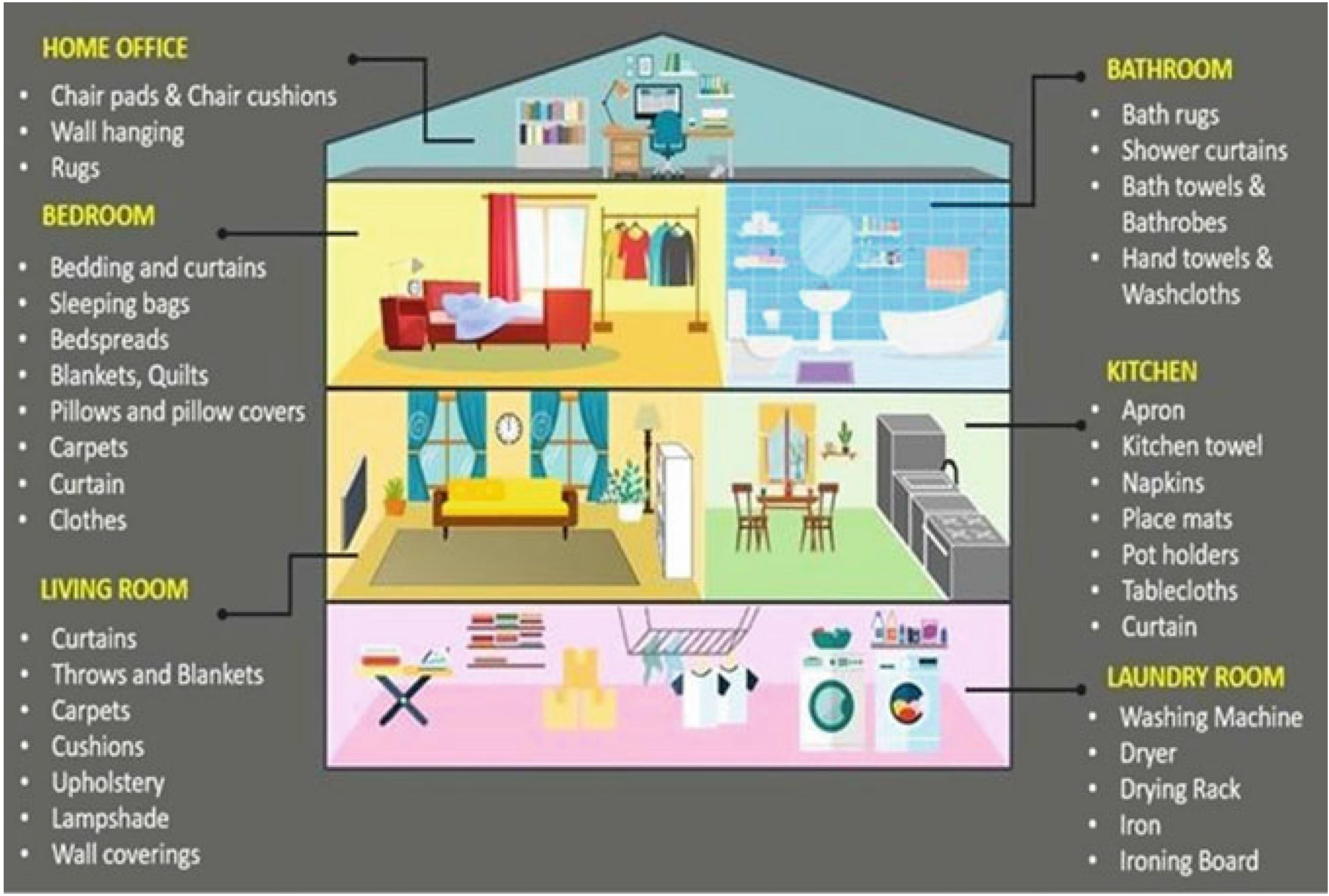
>5000 Chemicals are used at all stages

NIMKARTEK

Illhas Nimkar (2018) INPLASTIC Webseminar

Textiles and related additives in the indoor environment

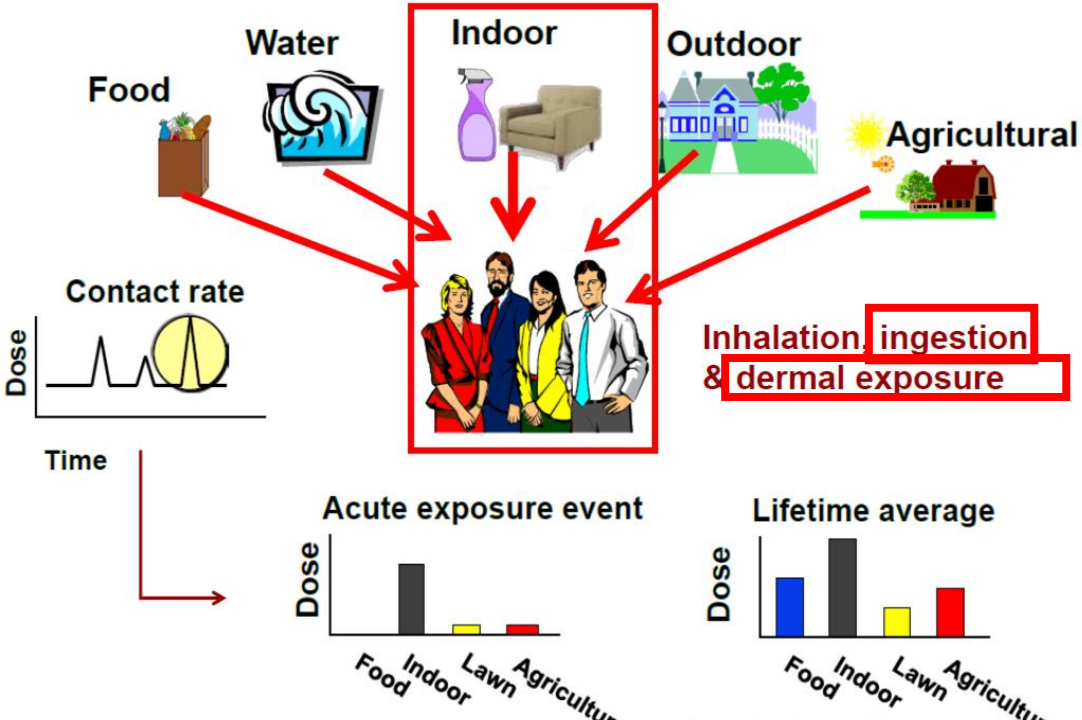
- **A wide range of textiles are present indoors in private households and offices.**
- **Additives from textiles are released to the indoor environment as well as fibres containing additives are released into the indoor environment constituting a share of the house dust.**



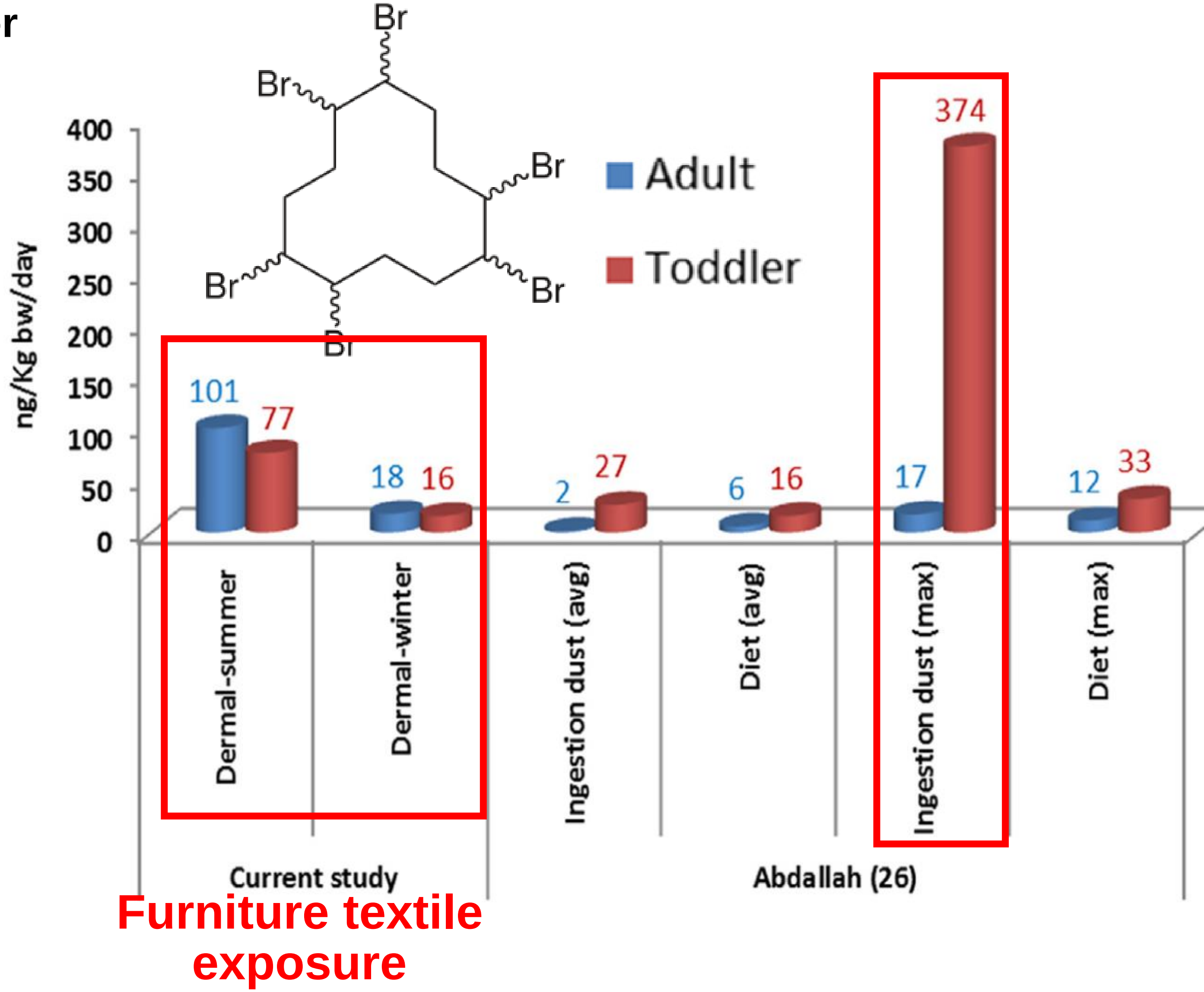
Bhat et al. (2022). Ecological and Health Effects of Building Materials. Springer, Cham. https://doi.org/10.1007/978-3-030-76073-1_27

Exposure to brominated flame retarants (BFRs) from textile - HBCDD

- **Furniture textiles** is a **major exposure pathway for the POP HBCDD to humans via dermal uptake.**
- **High exposure risk of HBCDD for toddlers** from **house dust ingestion** and skin uptake. **This HBCDD stem also largely from textile fibres.**
- The exposure via food from environmental pollution is considerable smaller than textile/dust exposure.

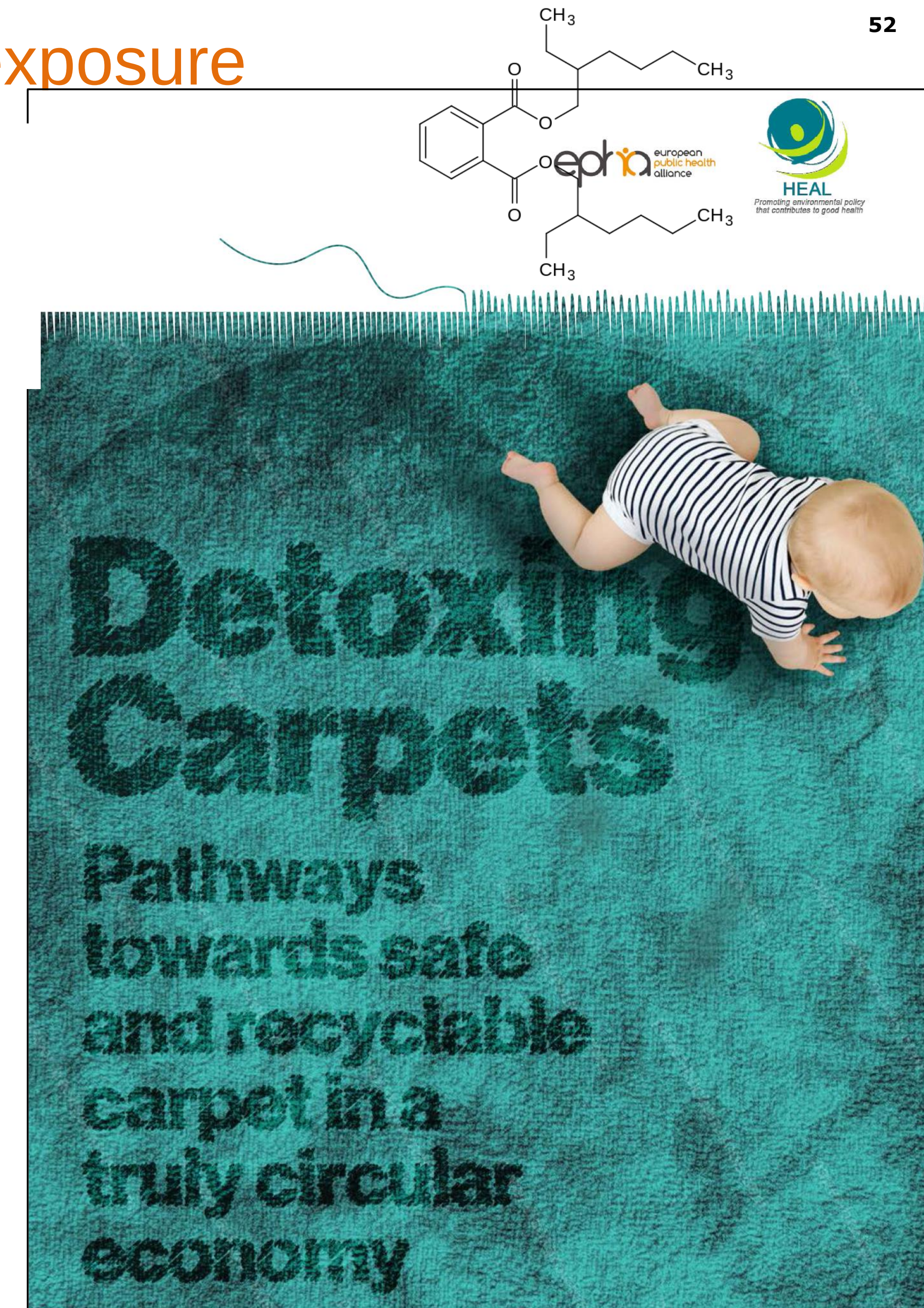


Source: Peter Fantke



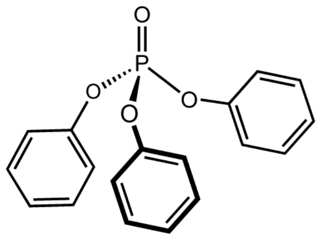
Abdallah & Harrad (2018). Environment international, 118, 26-33.

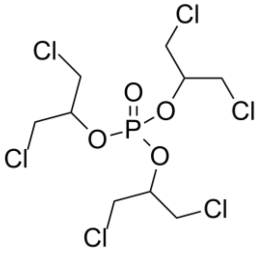
Hazardous chemicals in carpets and human exposure

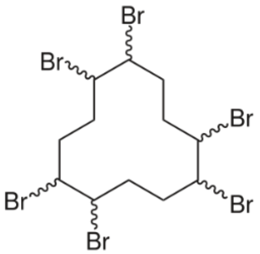


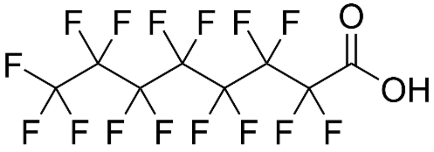
- **Carpets in the EU can contain >59 hazardous substances** including e.g. **BFRs/PFRs, PFAS, phthalates.**
- Among the identified substances are carcinogens, mutagens, chemicals toxic for reproduction and EDC.
- Of the 59 identified substances, **10 are identified by the EU as substances of very high concern (SVHC), and 4 are on the Authorisation List and banned.**
- Exposure to toxic substances from carpets can take place via inhalation, ingestion and dermal contact.

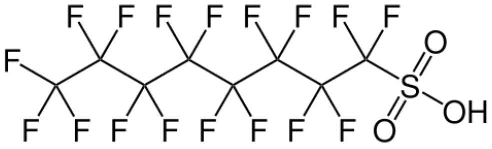
https://changingmarkets.org/portfolio/carpet-recycling/

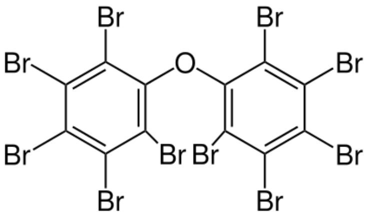






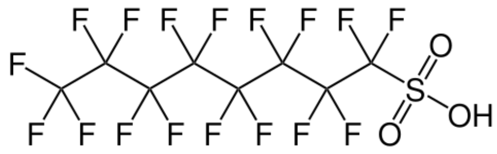


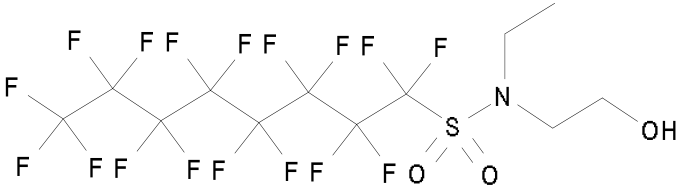


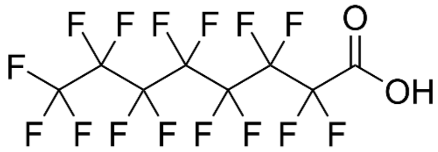


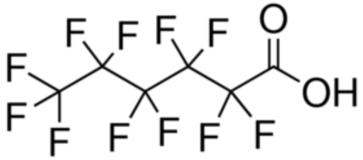
Hazardous chemicals in synthetic carpets and human exposure - PFAS

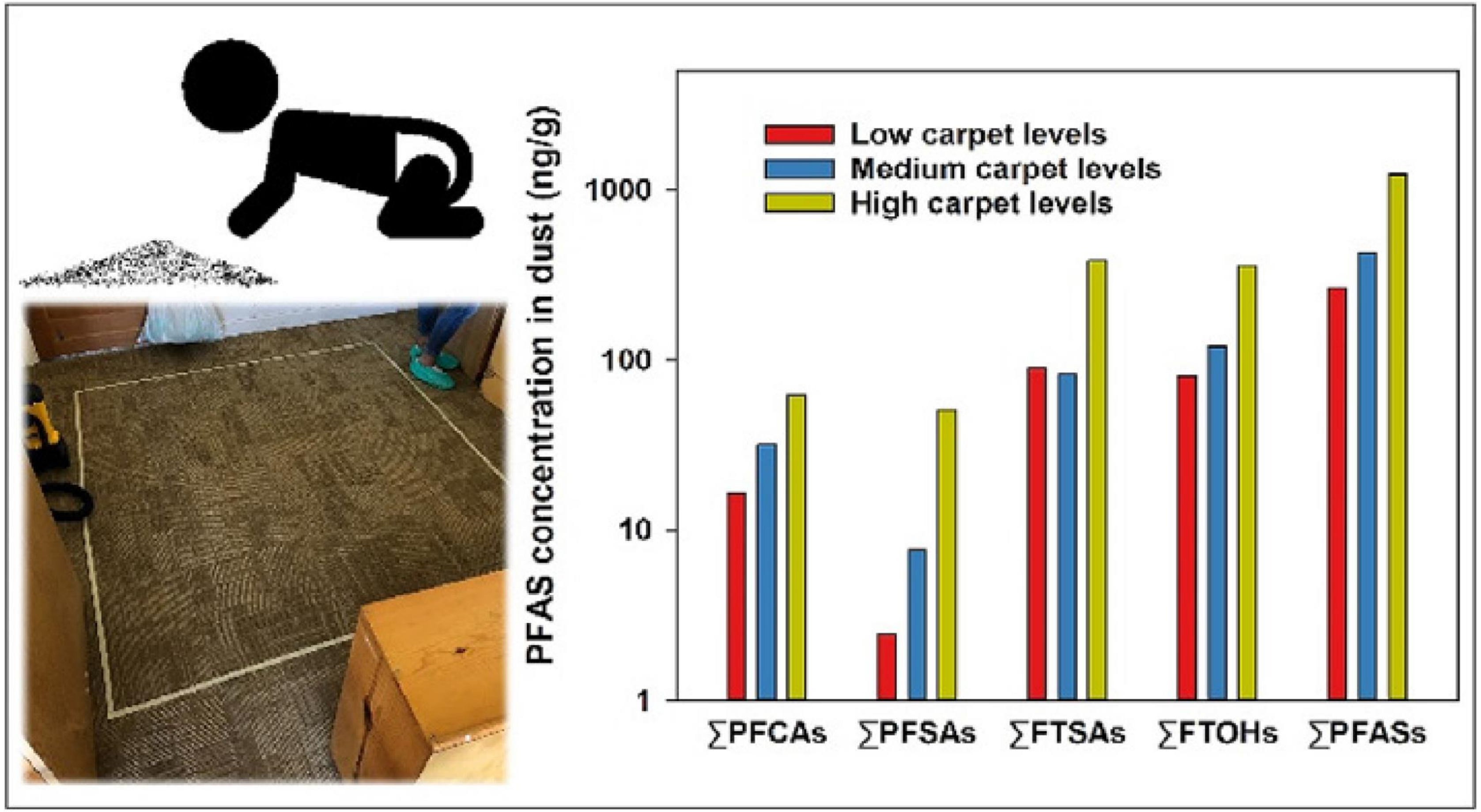
- Synthetic carpets (e.g. polymer nylon) have been found to be a relevant source for PFAS exposure for babies/children sitting on the floor. **Study conducted in child care centers in the USA**.
- **The data suggest that PFASs from carpets are playing an important role for indoor exposure.**











Source: Wu et al. (2020) Chemosphere 251, 126771.

Indoor release of chemical mixtures from major product sectors

- **In addition to pollutant release from building polymers and textiles/carpets**, a range of other consumer products result in releases of POPs and other plastic additives of concern **such as electronics and furniture** (Lucattini et al. 2018)
- Other non-plastic pollution sources are cleaning products and cosmetics

Class of chemicals	Carpets, textiles &clothing	Electronics	Furniture	Building materials/ flooring	Cleaning products	Health/personal care products & cosmetics
PBDEs	Green	Green	Green	Green		
EBFRs	Green	Green		Green		
other BFRs	Green	Green		Green		
OPFRs	Green	Green	Green	Green		Green
PFASs	Green	Green	Green	Green	Green	Green
PEs	Green	Green	Yellow	Green	Green	Green
PCBs		Green		Green		
PAHs				Yellow		
Pesticides	Yellow					
Synthetic musks					Green	Green
Chlorinated paraffins	Yellow	Green	Yellow	Yellow		
Siloxanes	Yellow	Yellow	Yellow	Green	Yellow	Green
Parabens					Yellow	Green
Dechlorane plus		Green		Yellow		

Green: data on concentrations available; **Yellow**: information available of use without concentration.

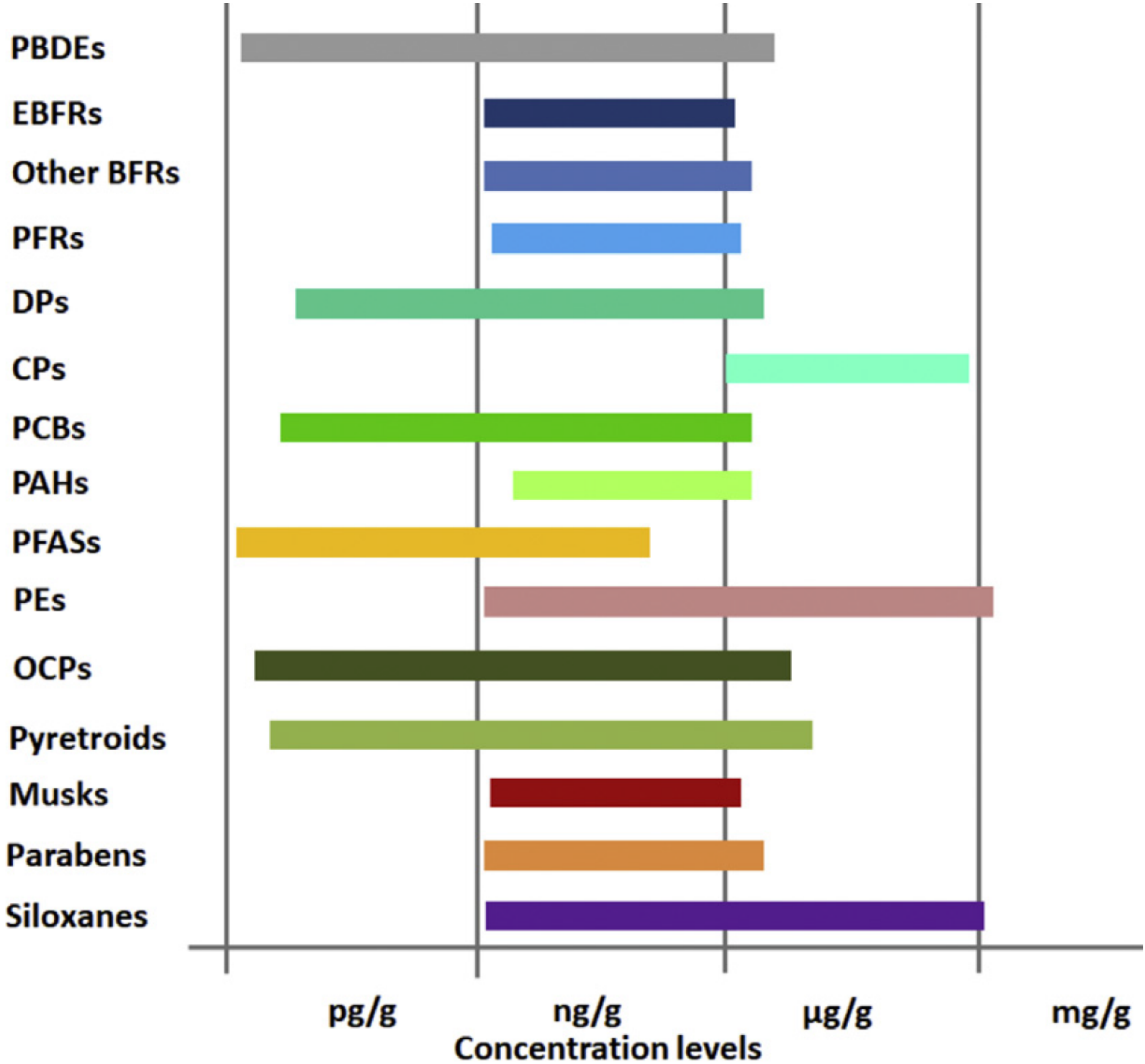
White: No information if the SVOC additive is used.

Lucattini et al. (2018) Chemosphere 201, 466-482

Exposure to mixture of plastic additives in indoor dust

Building materials, textiles et al. result in a mixture of additives in house dust and related exposure:

- CPs highest contamination in indoor dust.
- PFRs frequently detected in high levels.
- PBDEs frequently detected at different levels
- Novel BFRs increasingly detected at similar levels as PBDEs
- Also pesticides detected from use in e.g. pets, sealants/textiles and other indoor use
- Also siloxanes used in sealants and in personal care products.
- What are the combined health effects to the exposure of this mixtures of plastic additives and other chemicals indoors.



Lucattini et al. (2018) Chemosphere 201, 466-482

Exposure to hazardous chemicals in plastic toys

- **The toy industry is a plastic intensive industry: 90% of the toys on the market are made of plastic".**
- **Children, in particular, those below the age of 36 months, are considered particularly vulnerable to chemical exposure, due to physiological differences, development and different exposure patterns, such as hand-to-mouth behavior.**
- **Chemical additives in plastic toys can be absorbed by skin contact, can volatilize into the air & inhaled, can be ingested during mouthing and from dust particles.**
- **A comprehensive study of chemicals in plastic toys and exposure was conducted by Prof. Peter Fantke & group.**

Environment International 146 (2021) 106194

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/envint

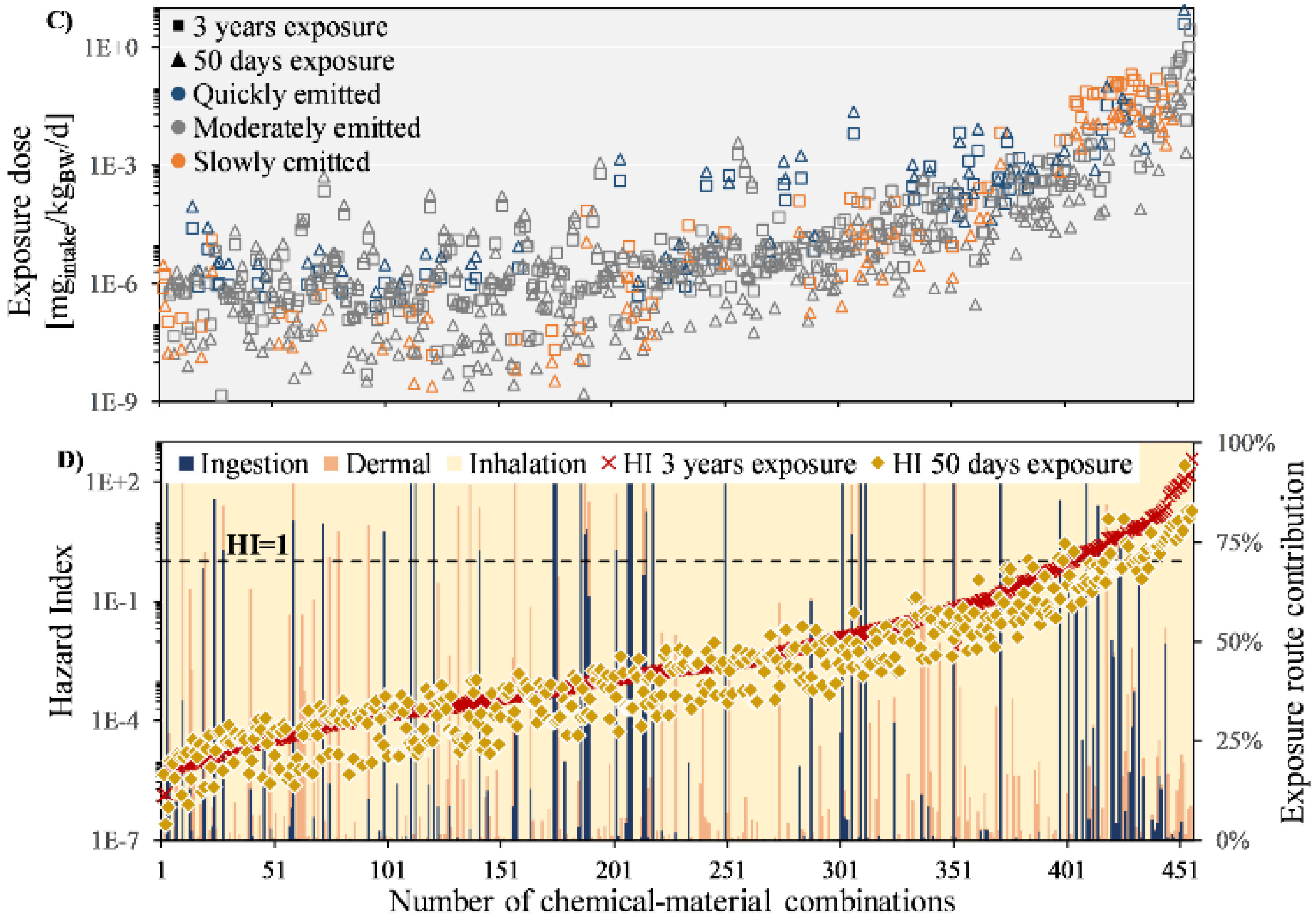
ELSEVIER

https://doi.org/10.1016/j.envint.2020.106194

Chemicals of concern in plastic toys

Nicolò Aurisano [a], Lei Huang [b], Llorenç Milà i Canals [c], Olivier Jolliet [b], Peter Fantke [a,*]

Linking exposure doses with toxicity data – Calculating Hazard Index (HI) for plastic toys



Linking exposure doses with toxicity data

Out of 456 chemical-material combinations, for 55 HI > 1

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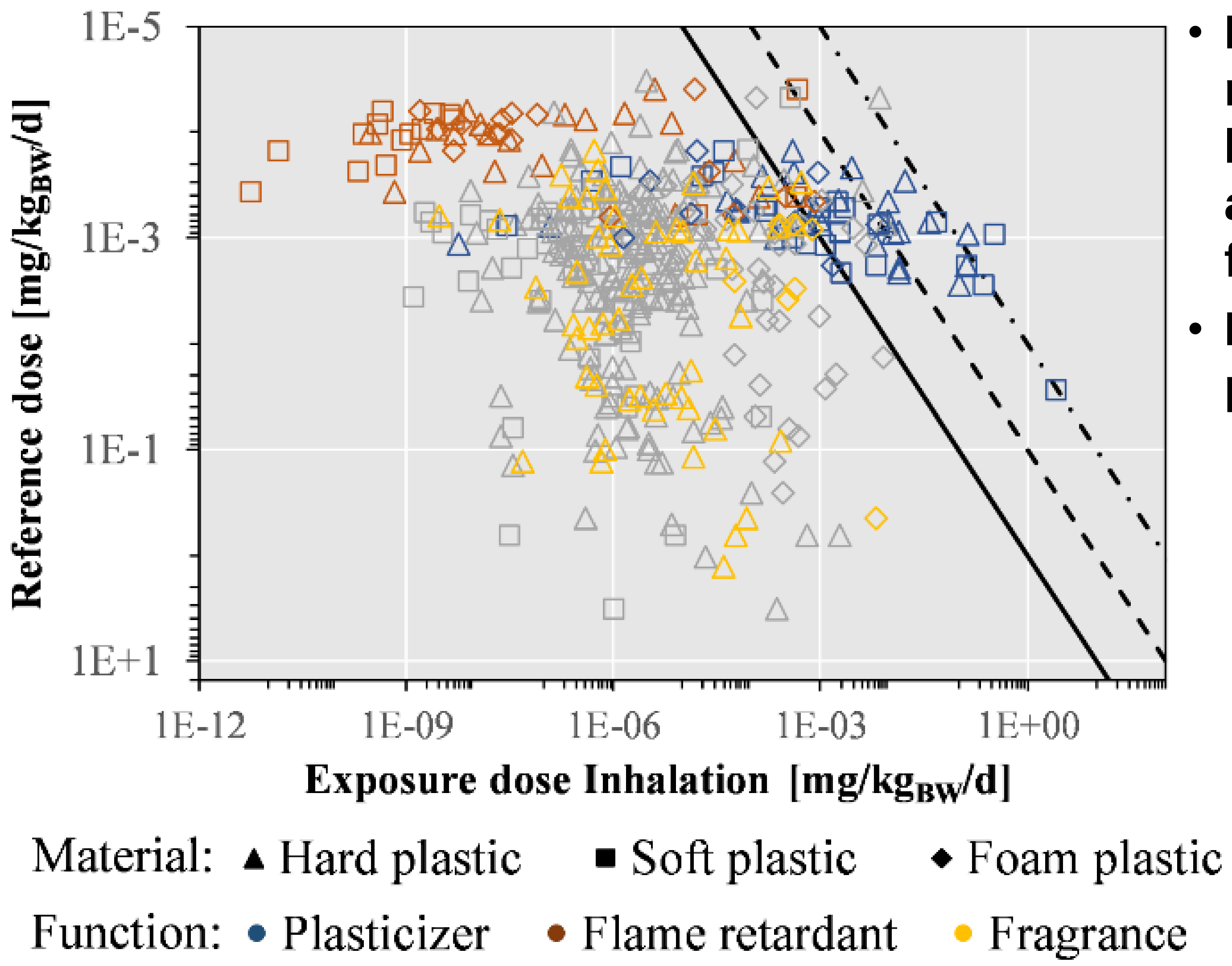
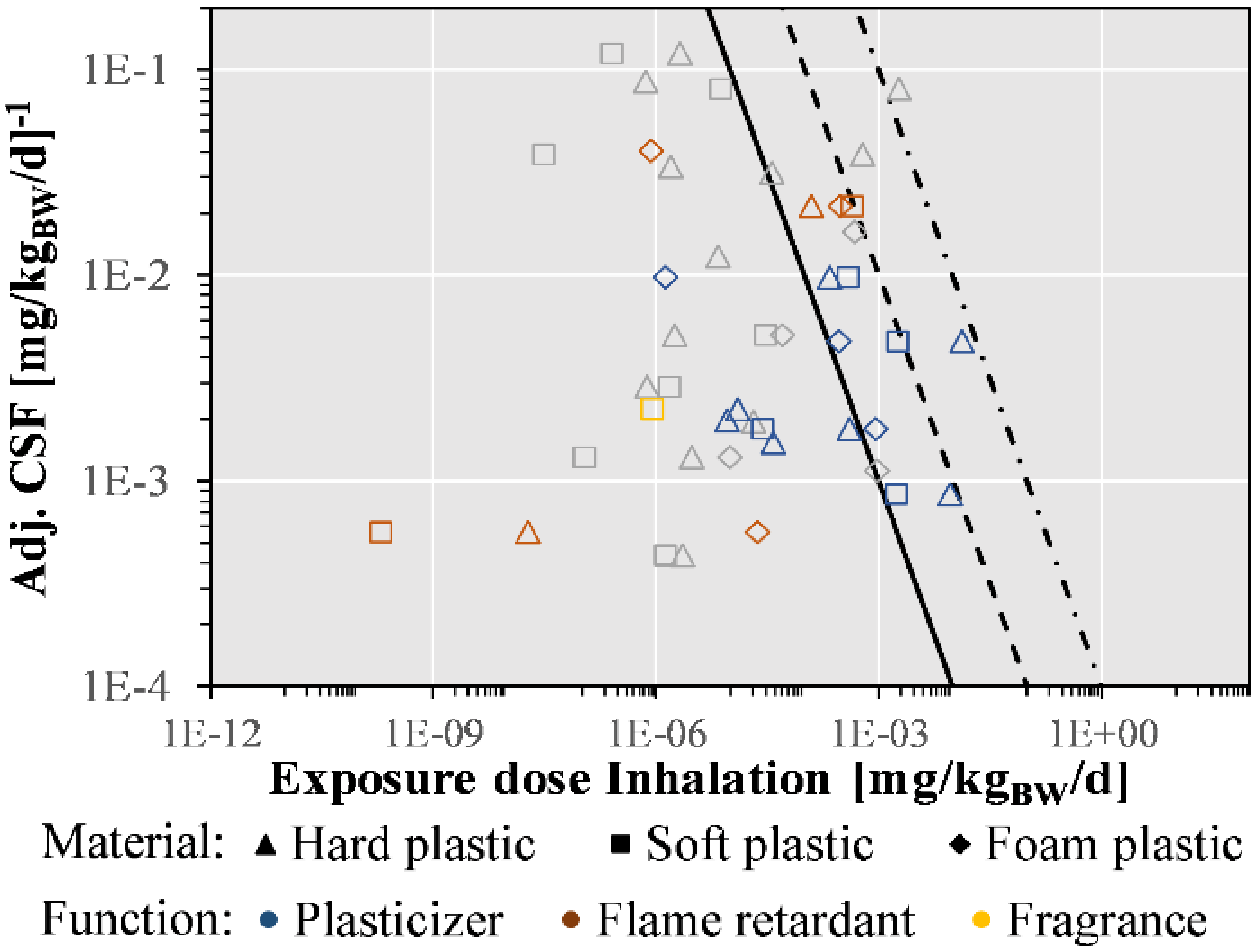
Linking exposure doses to plastic toys with toxicity data – Non-cancer risk assessment



- Exposure and toxicity results per exposure route for non-cancer risk show that HQ is larger than 1 for many plastics and even above 10 for a range of plastics and for a few the HQ is even above 100.
- Risk is driven by plasticizers mainly in soft plastic toys

Aurisano et al. (2021) Environment International 146, 106194 https://doi.org/10.1016/j.envint.2020.106194

Linking exposure doses to plastic toys with toxicity data – Child Cancer Risk (CCR) assessment

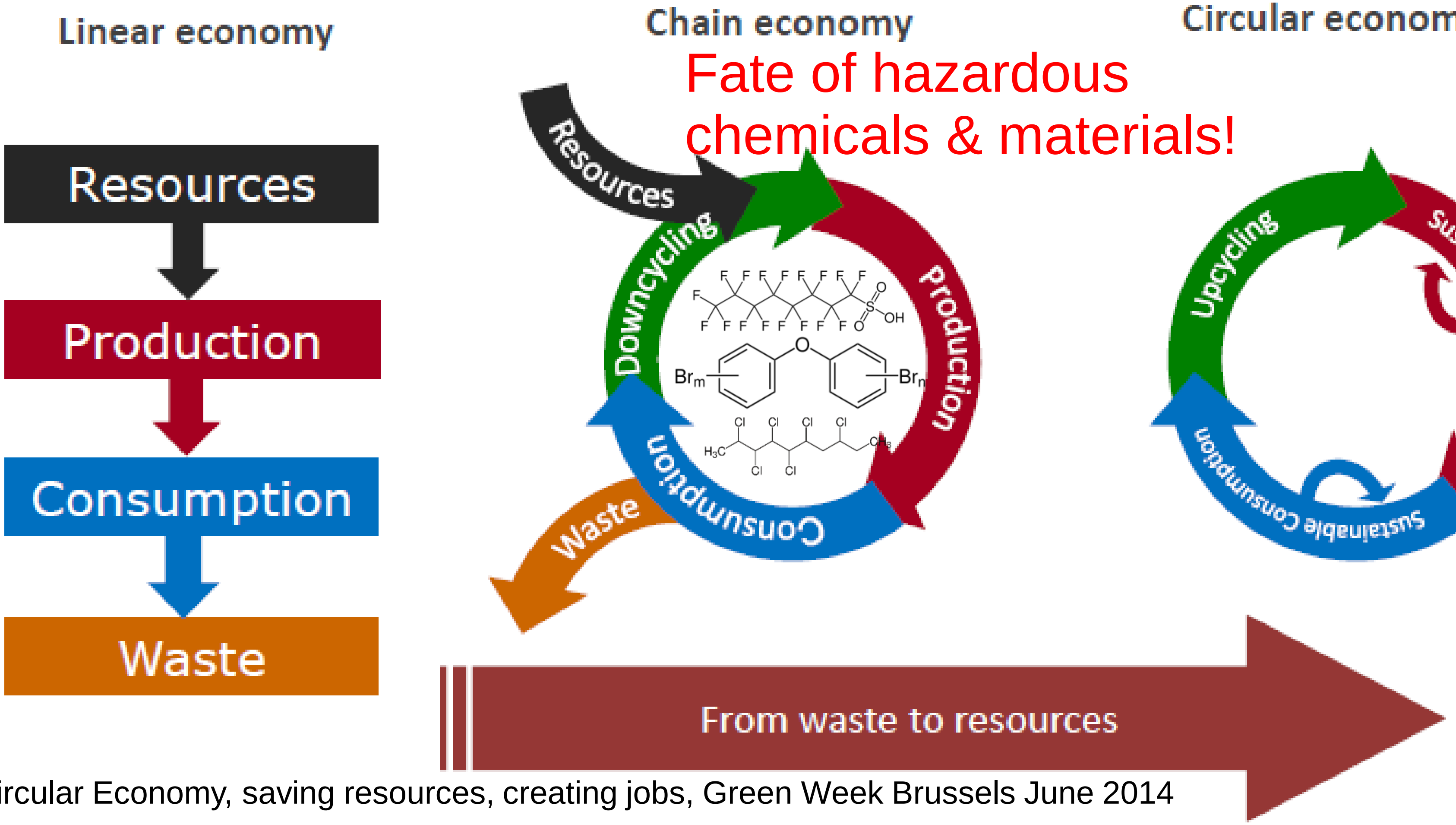


- **Cancer data were available for 47 chemical-material combinations**
- **Again the risk is driven by plasticizers in soft plastic toys**

Aurisano et al. (2021) Environment International 146, 106194 https://doi.org/10.1016/j.envint.2020.106194

We need to move to a Circular Economy – Fate of hazardous chemicals?

Considering the **waste/plastic crises and the limits of resources**, humanity needs to move to (a more) circular economy (stressed by UN, GEF, EU) http://ec.europa.eu/smart-regulation/impact/planned_ia/docs/2015_env_065_env+_032_circular_economy_en.pdf



Bonnet (ARC+) Circular Economy, saving resources, creating jobs, Green Week Brussels June 2014

When moving towars a Circular Economy, POPs and other hazardous chemicals in plastic need to be controlled and phased out. Need a global assessment & control.

PBDEs & PBDD/F in Consumer Products Made of Recycled Plastic from 7 African Countries

IPEN Screened 244 consumer products for bromine found 47 positive: toys, 18 hair accessories, 10 kitchen utensils, 4 office supplies

Car toy (Kenya): 269 ppm of PBDEs;
6590 pg TEQ/g of PBDD/Fs

Knife (Gabon): 182 ppm of PBDEs;
1430 pg TEQ/g of PBDD/Fs

Hair headband (Morroco): 315 ppm of PBDEs
885 pg TEQ/g of PBDD/Fs;
263 ppm of nBFRs; 29 ppm TBBPA;

Waste incineration fly ash ~1000 pg TEQ/g

Limit of 500 ppm for PBDEs in recycled products = high levels of PBDD/Fs

Budin et al (2020) Chemosphere, 251, 126579.
https://ipen.org/sites/default/files/documents/ipen-toxic-plastic-products-africa-v1_3wo.pdf

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/

BASEL CONVENTION

STOCKHOLM CONVENTION

saicm

IPCP International Panel on Chemical Pollution

UN environment programme

gef