UNITAR TRAINING WORKSHOP – Waste Management 13. September 2023

Short-Chain and Medium-Chain Chlorinated Paraffins (SCCP/MCCP) regrettable POP-substitutes of PCBs in open application

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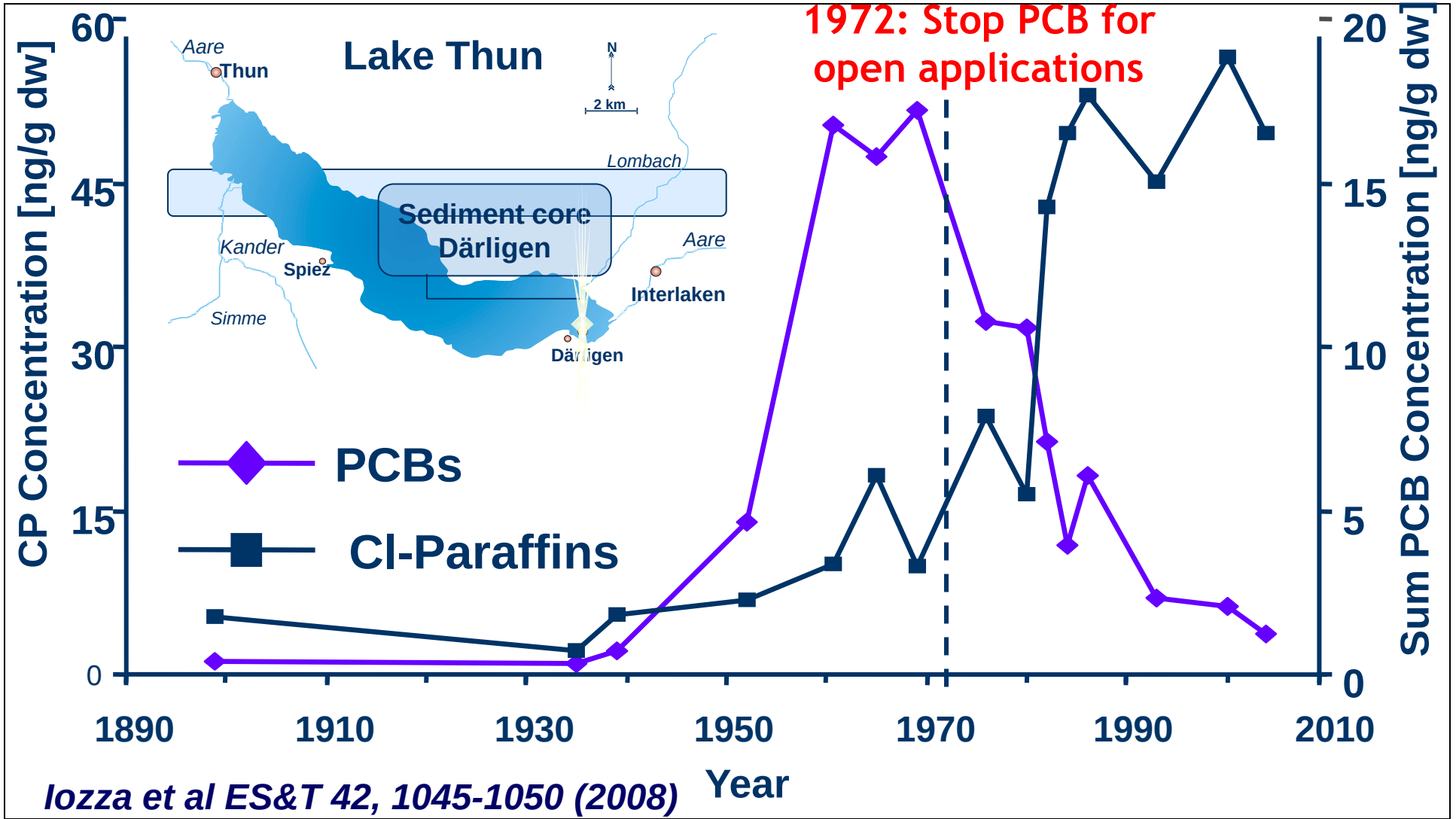
https://scholar.google.com/citations?user=-Cexto4AAAAJ&hl=en

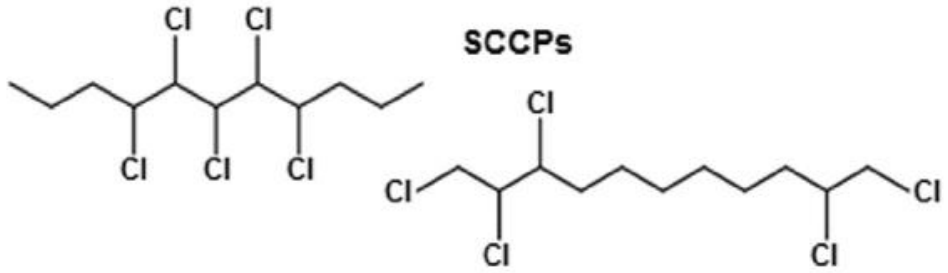
Chlorinated Paraffines in Sediment - PCB substitutes

- Chlorinated paraffins (CPs) have substituted PCBs in many „open PCB application“ early 1970s!
- Sediment contamination by chlorinated paraffins increased strongly in the 1970s and 1980s reaching 3 times the levels compared to peak PCB contamination.



Chlorinated paraffines products – defined by chain length and chlorination degree

- Chlorinated paraffins (CPs), are complex mixtures of chlorinated alkanes ($C_nH_{2n+2}-xCl_x$.)
- According to their chain length, CPs are subdivided into short-chain CPs (**SCCPs, C10–C13),** medium-chain CPs (**MCCPs, C14–C17**) and long-chain CPs (LCCPs, C18–C30),
- Chlorinated paraffins are produced with different chlorination degree varying from 30% to 70% (w/w). The variation option in chain length and chlorination degree make them versatile and approx. 200 commercial CP formulations are in use.



34 POPs listed in the Stockholm Convention (2023)

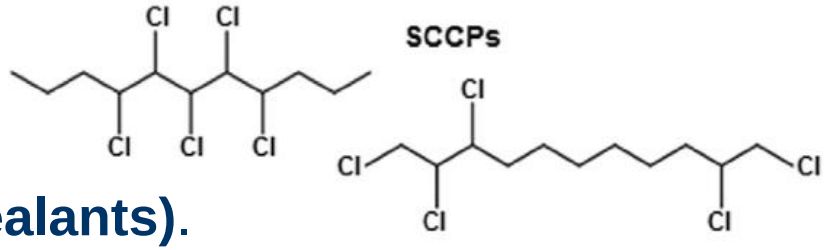
Chemical	Pesticides	Industrial chemicals	Unintentional production	Annex
DDT	+			B
Aldrin, Dieldrin, Endrin, Chlordane, Chlordecone, Toxaphene	+			A
	+			A
Alpha-, Beta-, Gamma-HCH	+		By-product of lindane	A
Endosulfan, Heptachlor, Mirex	+			A
PCP, Dicofol, Methoxychlor	+	+		A
Commercial PentaBDE		+		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				
PFHxS and related compounds		+		A
Short-chain chlorinparaffins SCCPs		+		A
UV-328Dechlorane Plus		+		A
PCB, PeCBz, HCB, PCN, *HCBD*	**+**	**+**	+	A/C
PCDD, PCDF			+	C

- **Stockholm Convention listed SCCPs with a chlorine content >48% as POPs.**
- **Also CP mixtures** with **≥1% of SCCPs are considered SCCPs/POPs.**

MCCP are evaluated by the POPs Review Committee: Annex D POPs criteria were acknowledged; now Annex F; MCCPs might be listed in 2025.

Stockholm Convention exemptions for SCCPs

- The listing in the Stockholm Convention is with a **range of exemptions (basically all major uses):**
  - Secondary plasticizers in **flexible PVC**, except in toys & children's products.
  - Additives in **rubber transmission belts** in the natural and synthetic rubber industry;
  - Leather industry, in particular **fatliquoring in leather**;
  - **Lubricant additives**, in particular for engines of automobiles, electric generators and wind power facilities, and for drilling in oil and gas exploration, petroleum refinery to produce diesel oil;
  - **Metal processing**;
  - **Waterproofing and fire-retardant paints**;
  - Tubes for outdoor decoration bulbs;
  - **Adhesives (countries might also then continue use sealants).**



⇒ Therefore SCCPs will likely be further produced, used and released.

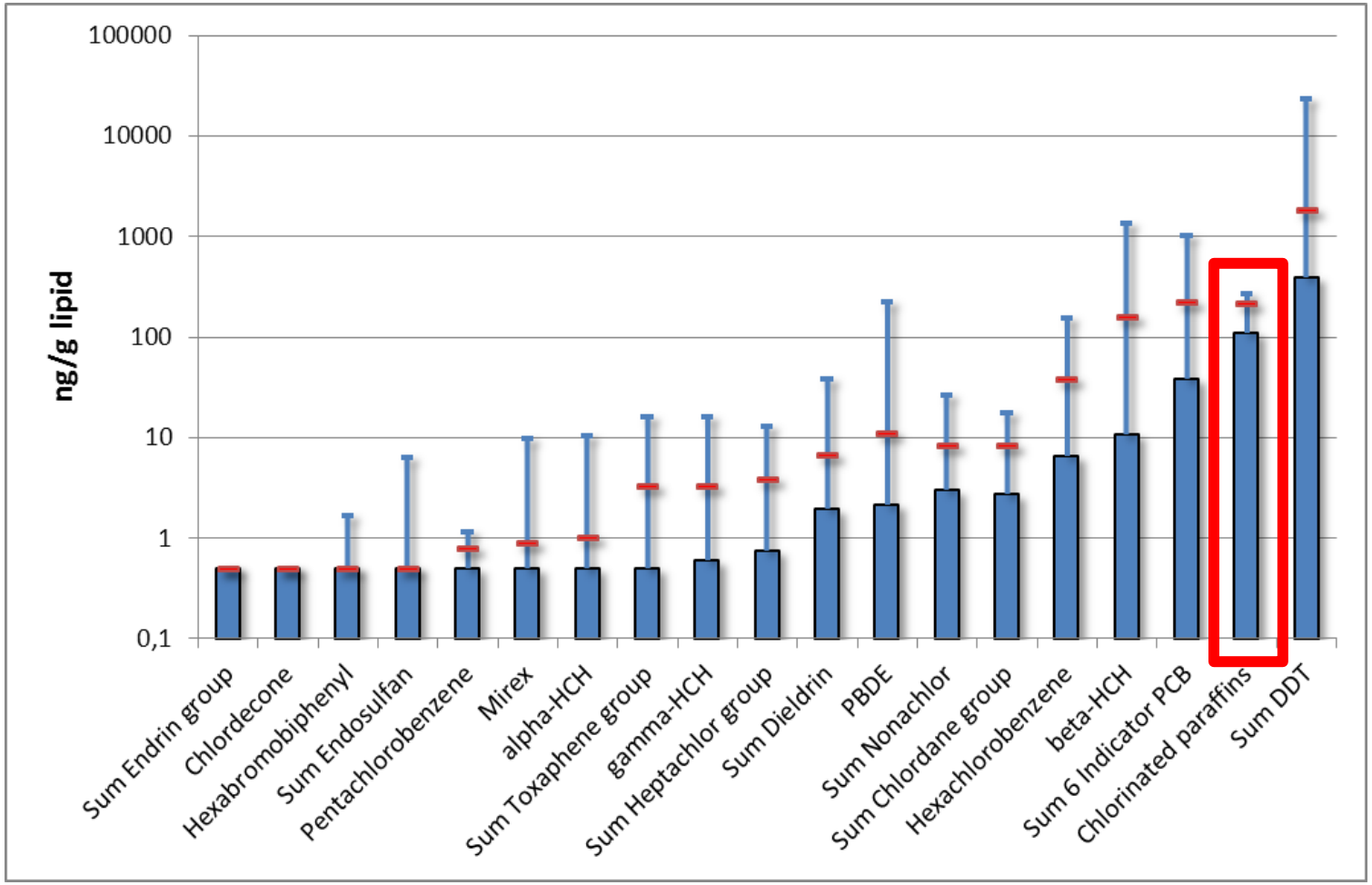
⇒ **Hence assessment of current use (to assess the need) and assessment of alternatives and substitution is needed.**

⇒ Currently only Vietnam has registered exemption for the use of 15,000 t SCCP. Other countries most likely do not know that they are using large amount of SCCPs or get it imported. Even some producers might not be aware that they are producing SCCPs or CPs containing SCCPs.

Decision SC-8/11: Listing of short-chain chlorinated paraffins

SCCP/MCCP levels in UNEP/WHO human milk

SCCP/MCCP high in human milk in the global UNEP/WHO study (65 countries; 2000-2012)

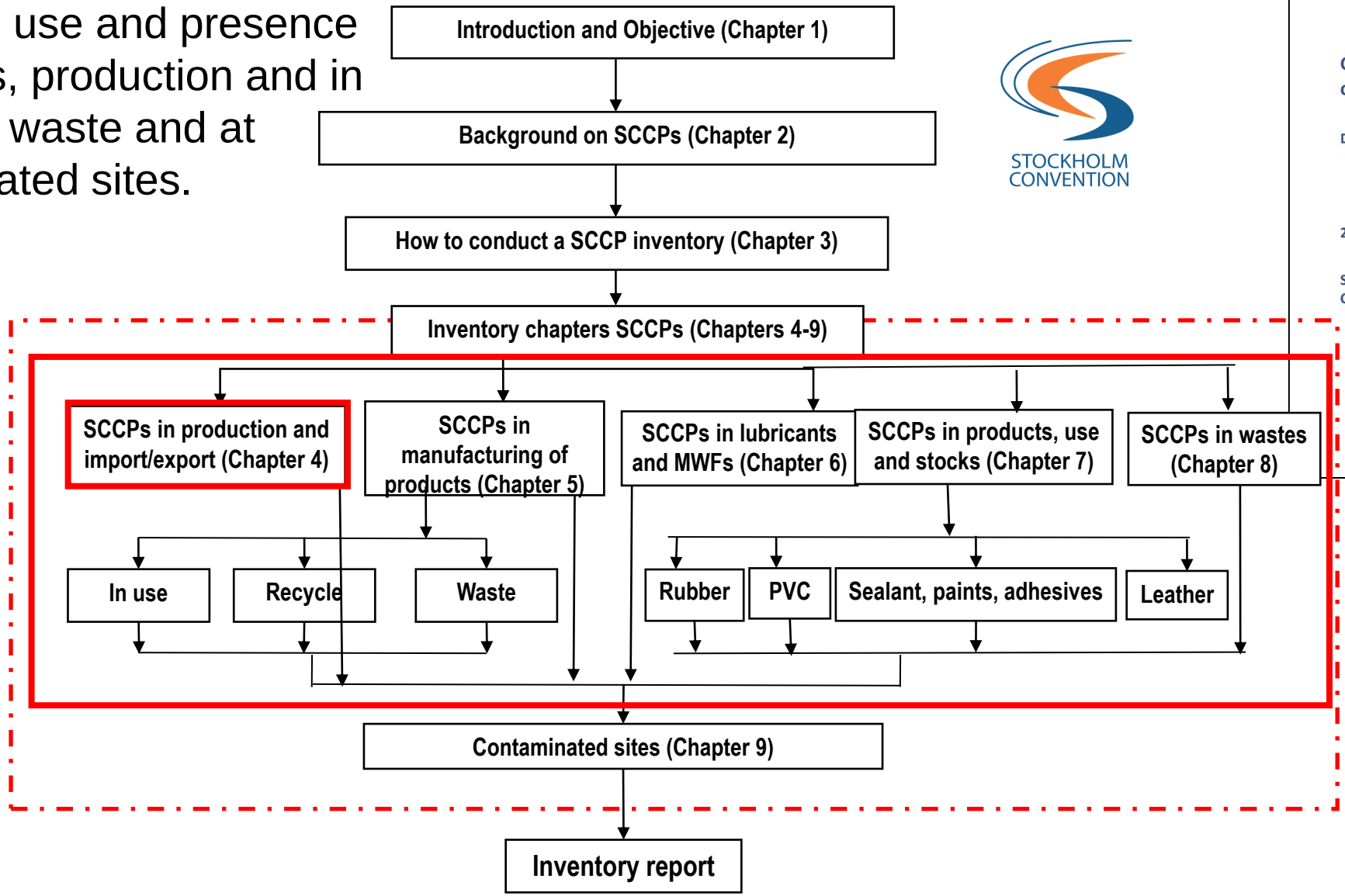


Krätschmer et al. (2021) EHP, 129(8) https://doi.org/10.1289/EHP7696

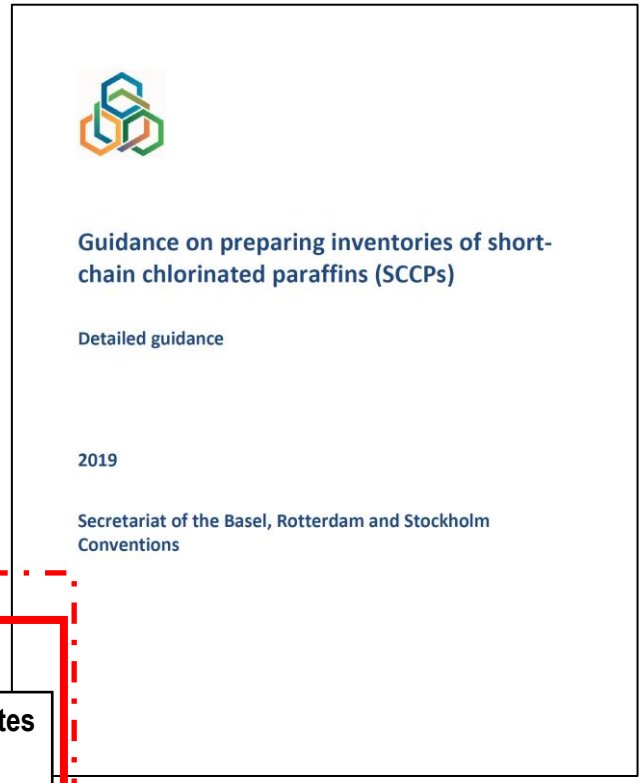
- SCCPs have a lower toxicity compared to PCBs. EFSA evaluated the data and concluded that the margin of exposure (MOEs) is 3 to 5 × 10^3.
- But sensitive endpoint not yet assessed (immuno-, neuro-, and developmental toxicity of children).

Content of the detailed SCCP inventory guidance of the Stockholm Convention

Development of inventories for SCCP use and presence in imports, production and in products, waste and at contaminated sites.

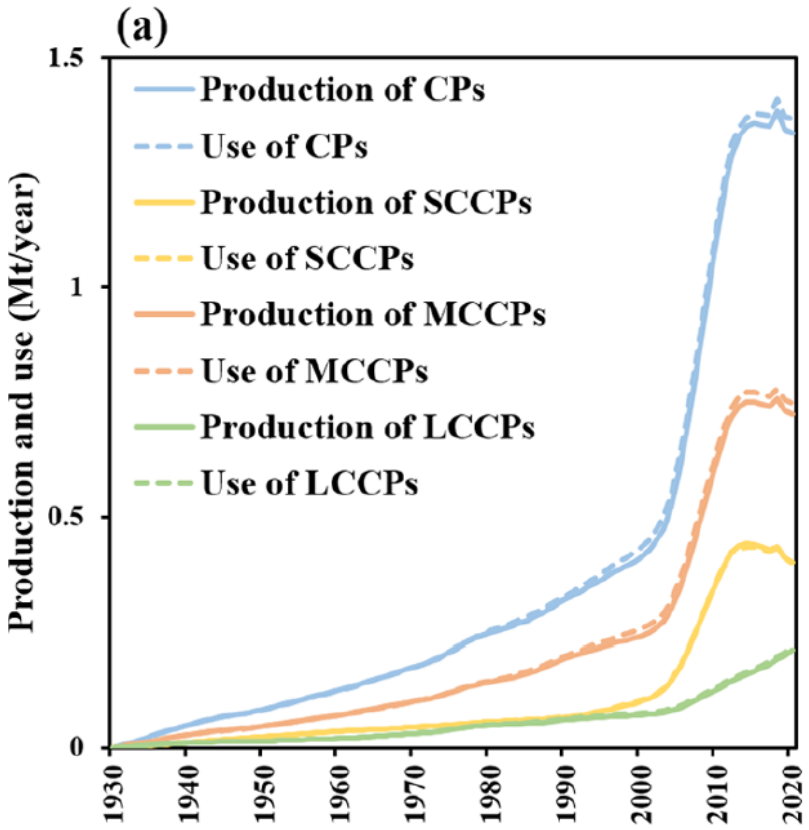


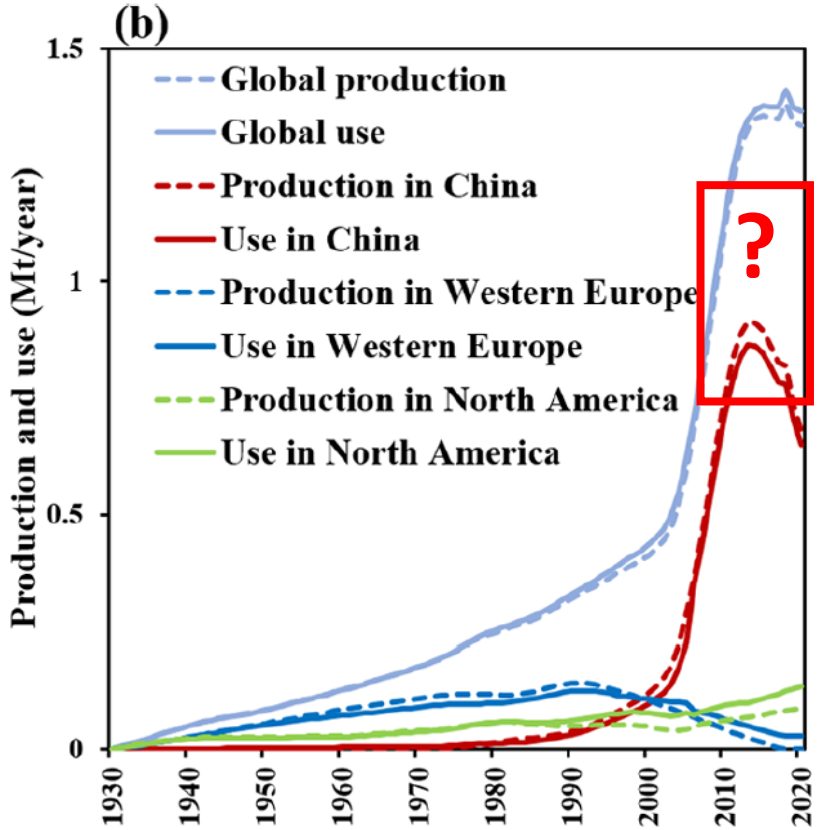
STOCKHOLM CONVENTION

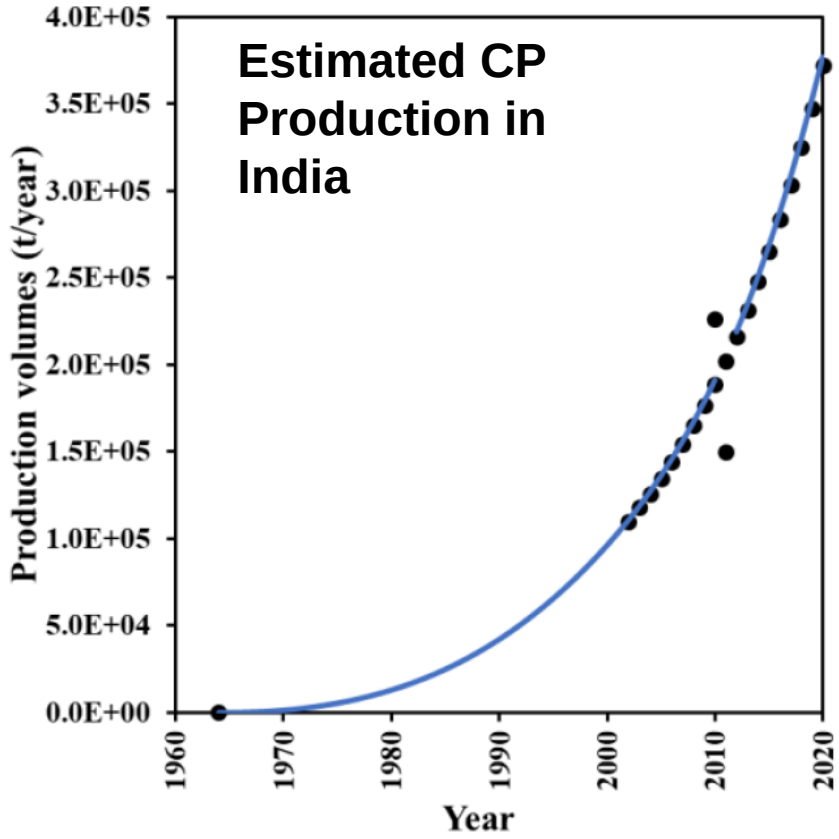


Estimate of global production of CPs

- Global production of CPs increased drastically over past 20 years and is **since ~2010 above 1 Mt/a**. Current production ~1.4 Mt/y (Chen et al 2022). **Global production capacity is above 2 Mt/a.**
- Total production of **SCCPs** estimated to 400,000 t/a but often in CP-mixtures. Therefore the **total amount of CPs containing SCCPs ≥1%** (rather ≥10%) **is ~900,000 t** (Guida et al. 2022; Xia et al. 2021).
- China & India are the largest CP producers with estimated 700,000 t and 375,000 t (Chen et al2022).







Chen et al. (2022) ES&T https://doi.org/10.1021/acs.est.2c00264

Use of SCCPs in the manufacturing of products

Stockholm Convention inventory guidance Chapter 5.1 Assessment if SCCPs or other CPs with unknown SCCP content is used in production sector:

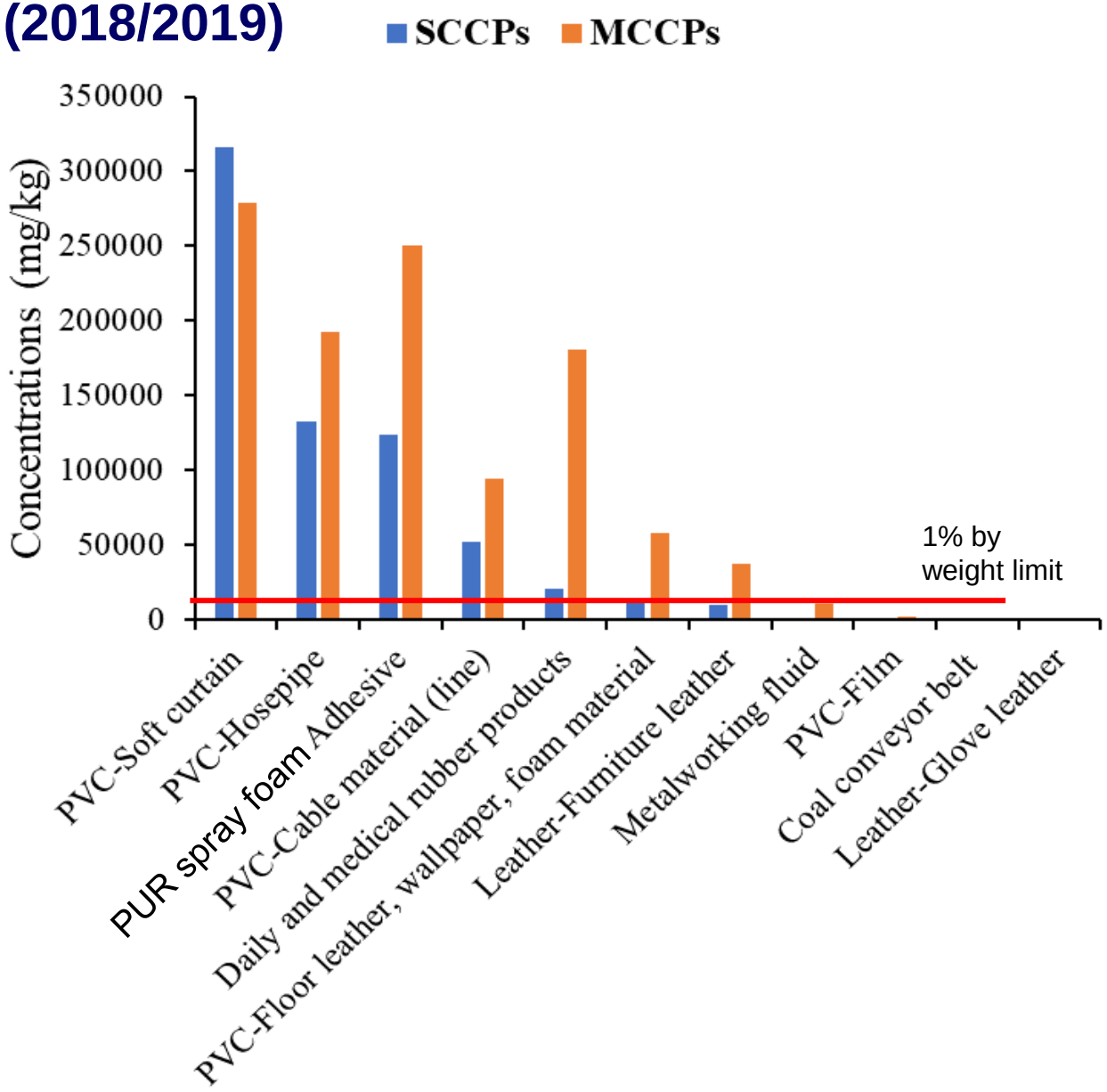
- 5.1.1. **Additive in PVC production and assessment**
- 5.1.2. **Rubber production and rubber products**
- 5.1.3 **Paints including waterproofing and fire-retardant paints**
- 5.1.4 Leather production (fatliquoring) and products
- 5.1.5. **Adhesives and sealants**
- 5.1.6. Production of textiles

- All the sectors where SCCPs are possibly used in the manufacturing of products should be assessed for the current and past use of SCCPs in these productions. For this assessment industries and productions possibly using SCCPs in the country need some analysis.
- For China monitoring data on SCCPs/MCCPs in products (Chen et al. (2021) ES&T. 55, 7335–7343). story

Use of SCCPs and MCCPs in China (>50% of global use)

Concentrations of SCCPs & MCCPs in products (impacts/determine global use/presence)

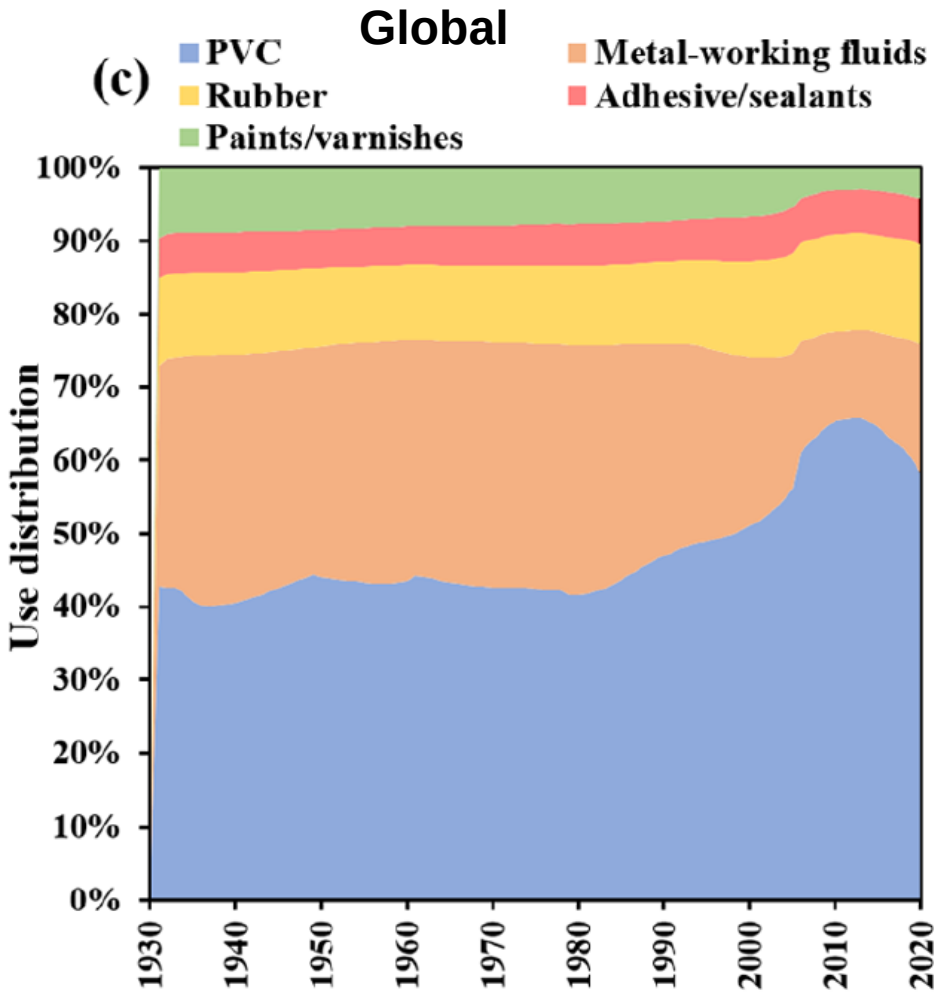
- **124 product samples from markets in China (2018/2019)**
- **High share PVC, rubber & PUR spay foam;**
- Low in metal working fluids; conveyor belt.

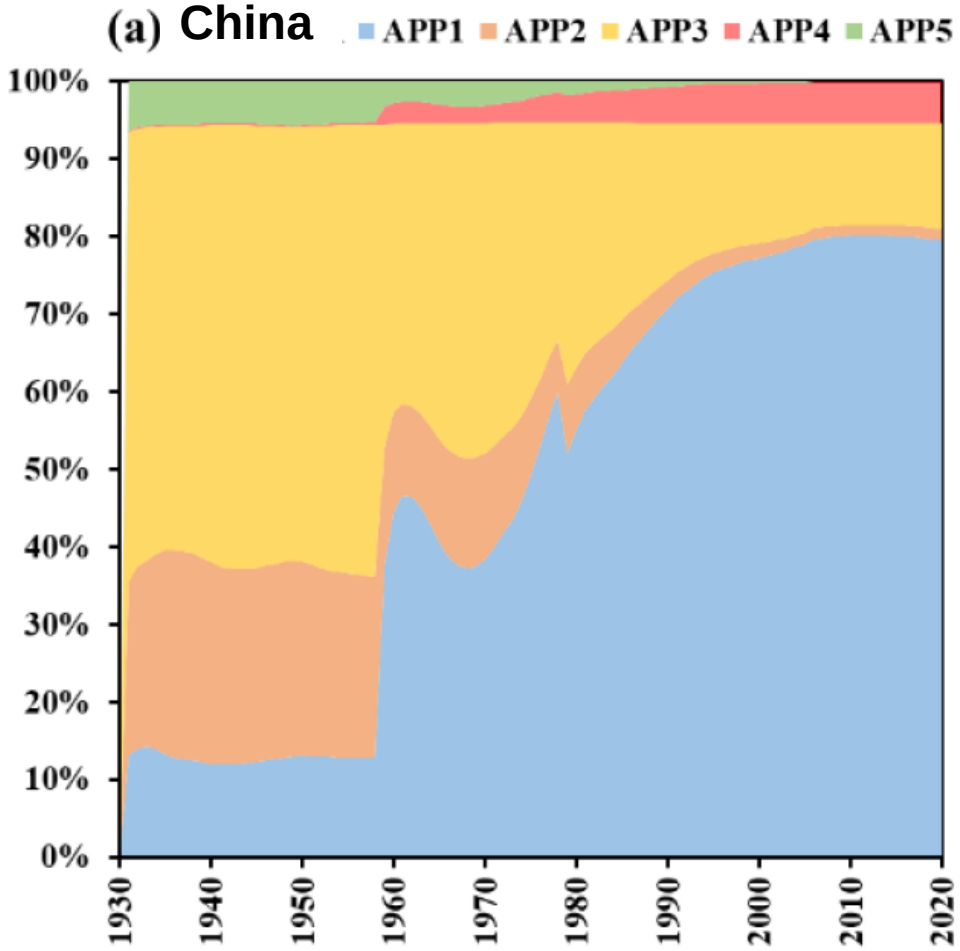


Chen et al. (2021) Environ. Sci. Technol. 55, 7335–7343.
https://doi.org/10.1021/acs.est.0c07058

Estimated former and current use share of CPs globally in China

- Major overall use of CPs is in PVC followed by rubber.
- The study likely underestimate uses in leather and paints **(limited use data from India).**

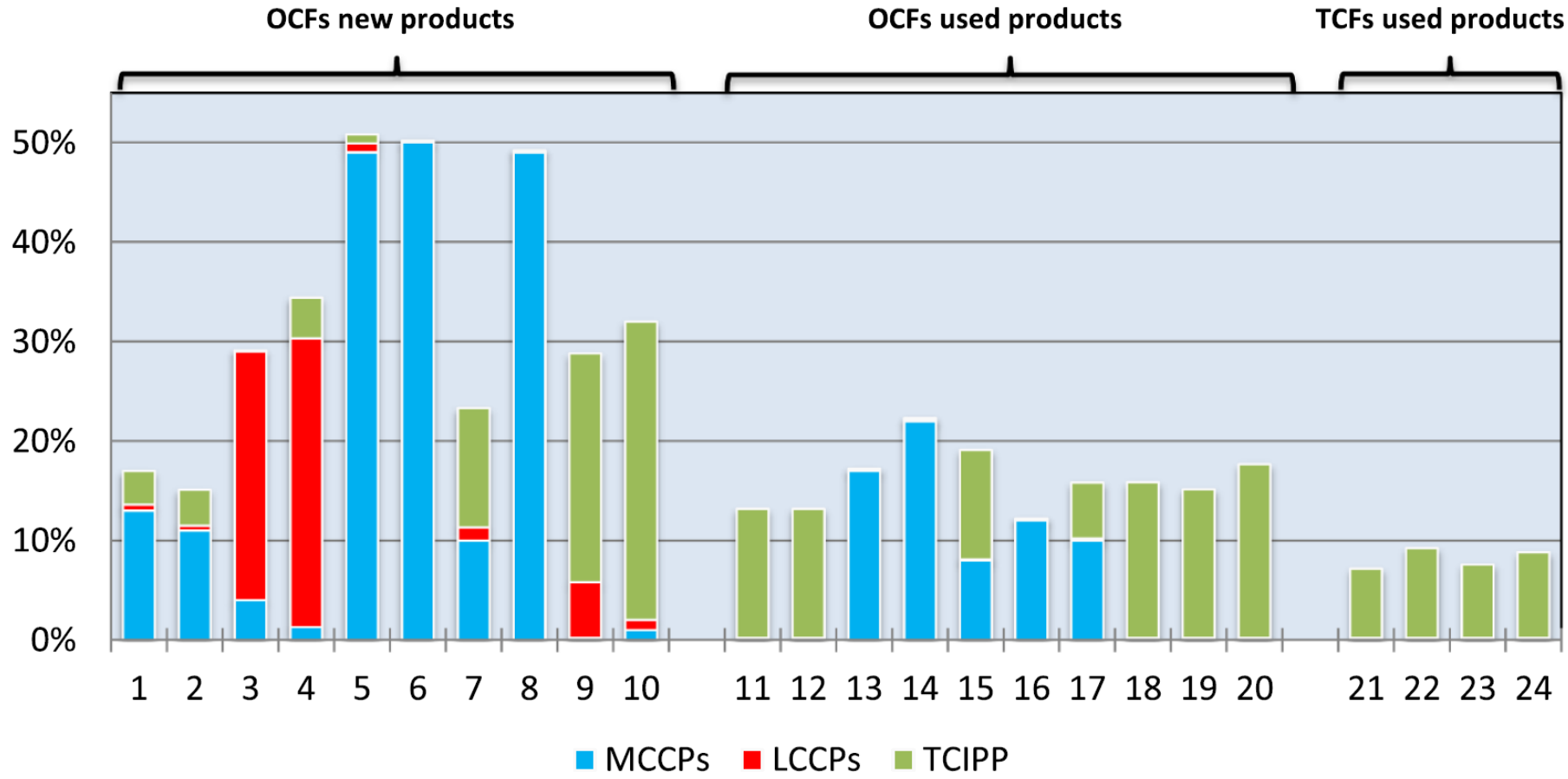




Chen et al. (2022) ES&T https://doi.org/10.1021/acs.est.2c00264

High CP and PFR used in EU & release from PUR foam

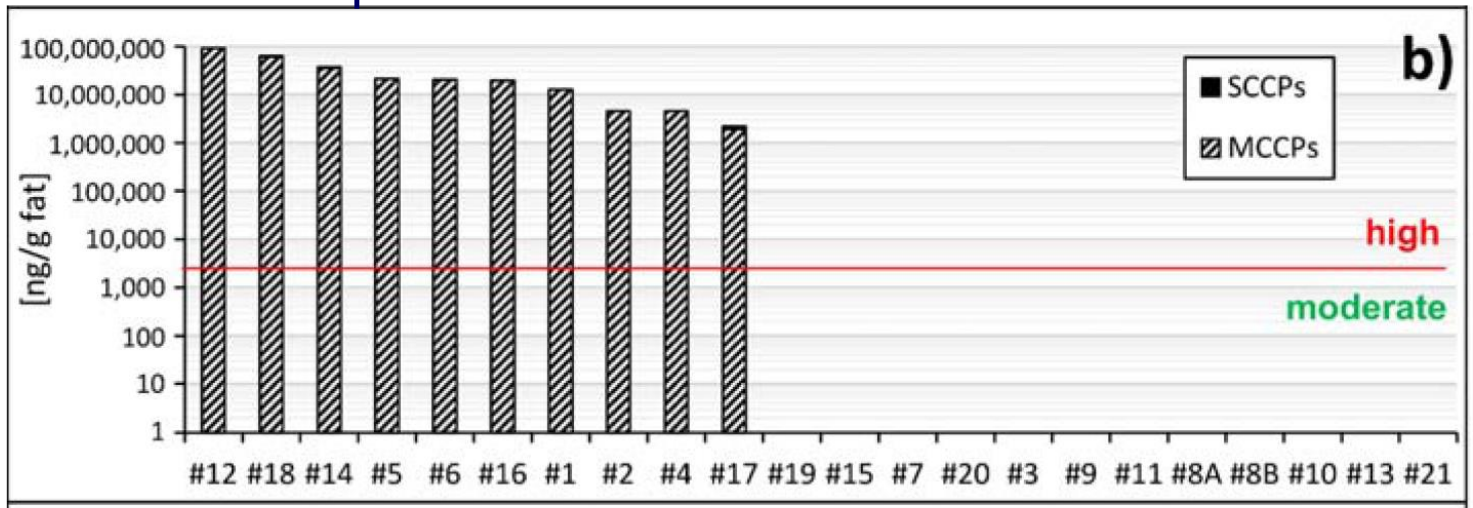
- **Up to 50% FRs (particular CPs) in one- and two-component spray polyurethane foams** (OCF; TCF) with major use of CPs **(MCCP & LCCP) and phosphorus flame retardants (PFRs).**
- Lower levels of CPs and PFRs in PUR foam in use indicate that a share of FRs were released during lifetime.
- High PFR and CP levels in indoor air/dust also indicate relevant releases from products (~1%/a).

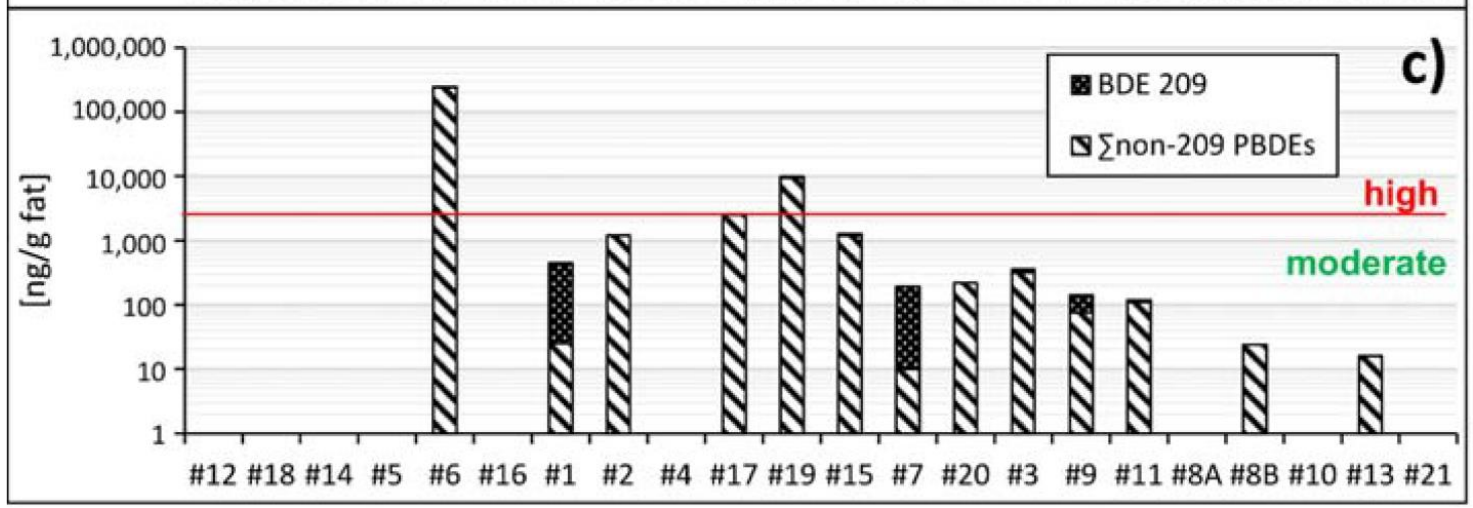


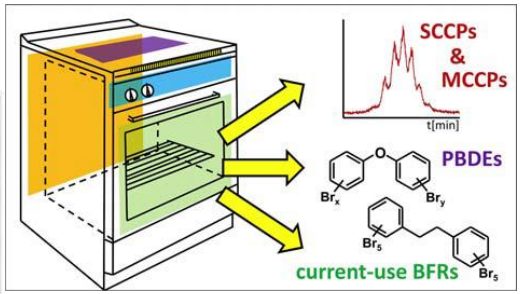
Brandsma et al. (2021) Journal of Hazardous Materials 416 (2021) 125758

SCCPs/MCCPs in Products – Baking Ovens

- High level SCCPs/**MCCPs** (mg/g) inside of 50% of German backing ovens.
- Source from cables/plastic additive evaporating when the oven is heated. PVC cables can contain 10 to 30% CPs. PBDE levels lower.
- Direct exposure source to food and humans.







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https://doi.org/10.1016/j.scitotenv.2017.09.112

High levels of medium-chain chlorinated paraffins and polybrominated diphenyl ethers on the inside of several household baking oven doors☆

Christoph Gallistl, Jannik Sprengel, Walter Vetter *

Contents lists available at ScienceDirect

Food Chemistry: X

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https://doi.org/10.1016/j.fochx.2021.100122

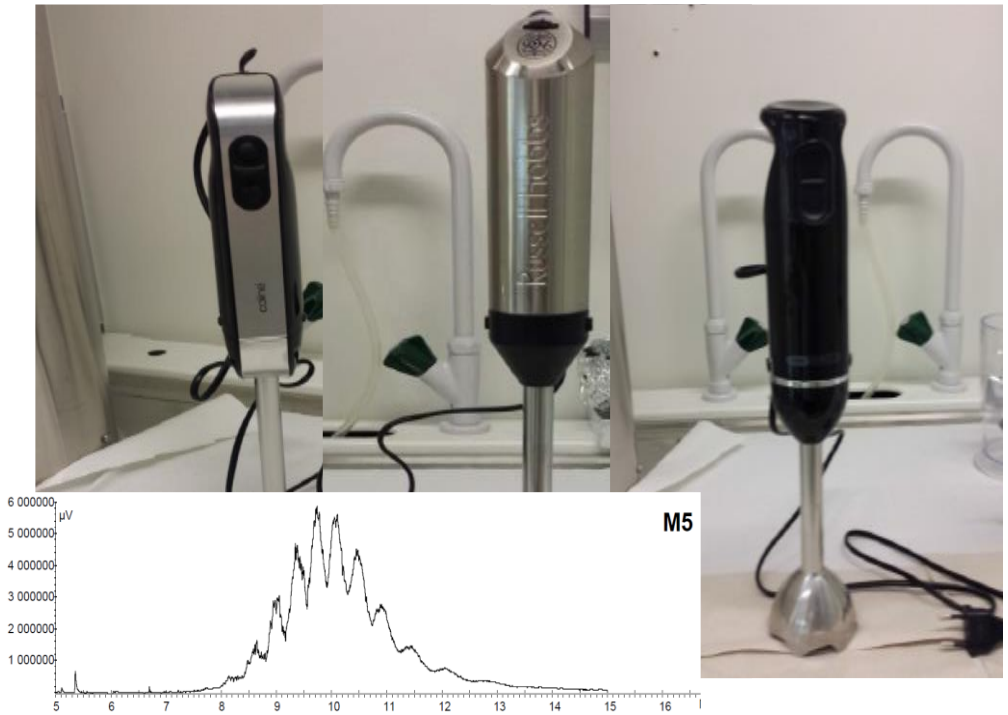
Transport of chlorinated paraffins (CPs) from baking oven doors into the food

Jannik Sprengel [a], Stefanie Rixen [a], Oliver Kappenstein [b], Walter Vetter [a,*]

Gallistl et al. (2017) Science of the Total Environment 615 (2018) 1019–1027

SCCPs/MCCPs in Products – Food Blenders

- **8 of 12 food blenders tested leach SCCPs/MCCPs (µg/g) into blended food under normal use with 5 food blenders at high levels (long term release).**
- The test of **repeated use** of a blender **did not lead to reduced release**.
- Source: either from plastic/PVC parts or from lubricants (embedded in metal structure).
- **Direct high exposure source to food and humans.**



Share of SCCPs/MCCPs/LCCP leaking from food blender (Yuan et al. 2017)

Product	Bought (year)	SCCP (%)	MCCP (%)	LCCP(%)	Chlorine (%)
Hand blender	2014	9	91		54
Hand blender	2014	19	81		55
Hand blender	2014	33	67		55
Hand blender	2016	59	35	6	57
Hand blender	2016	12	88		52
Hand blender	2016	33	67		56

Strid A et al. (2015) Hand blenders available on the Swedish market may contaminate food with chlorinated paraffins. Report Stockholm University.and Swedish Toxicology Sciences Research Center (Swetox);
Yuan et al. (2017) Chlorinated paraffins leaking from hand blenders can lead to significant human exposures Environment International 109, 73–80.

Inventory of SCCPs/MCCPs in PVC imports

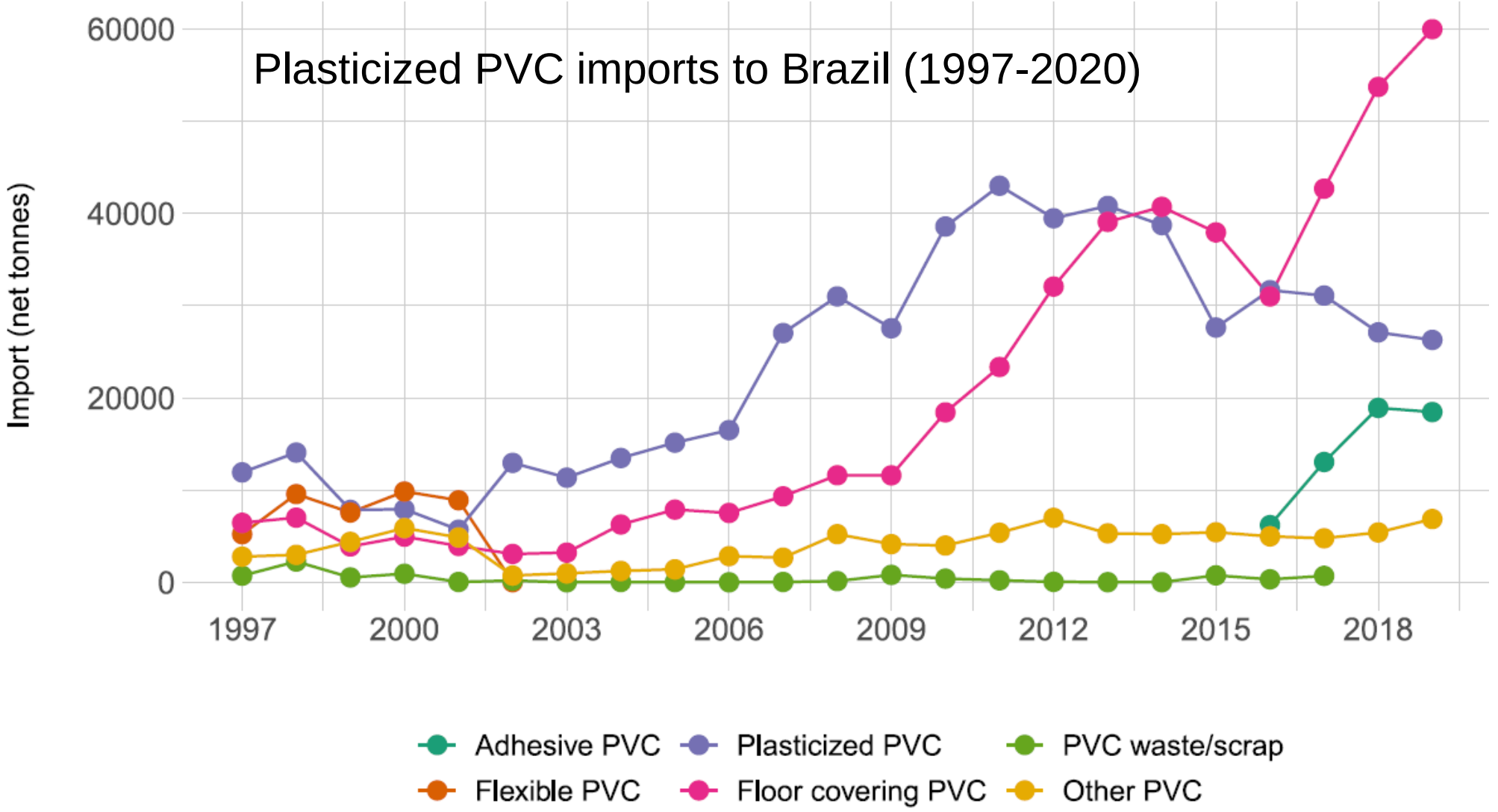
- **Assessment of PVC imports** to a country **using UN Comtrade Database**. In particular the **HS codes** of **PVC** which contain **additives**.

HS Codes	Description
(3904)	(Polymers of vinyl chloride or of other halogenated olefins, in primary forms)
390422	Vinyl chloride, other halogenated olefin polymers; **plasticised** poly(vinyl chloride), in primary forms, mixed with other substances
391530	Vinyl chloride polymers; waste, parings and scrap
391810	**Floor, wall or ceiling coverings**; of polymers of vinyl chloride, whether or not self-adhesive, in rolls or in the form of tiles
392043	Plastics; polymers of vinyl chloride, containing by weight **not less than 6% of plasticisers**; plates, sheets, film, foil & strip (not self-adhesive), non-cellular & not reinforced, laminated, supported or similarly combined with materials
392049	Plastics; polymers of vinyl chloride, containing by weight, **less than 6% of plasticiser**; plates, sheets, film, foil and strip (not self-adhesive), non-cellular and not reinforced, laminated, supported or similarly combined with materials
392112	Plastics; plates, sheets, film, foil & strip, of polymers of vinyl chloride, cellular

Source: https://www.foreign-trade.com/reference/hscode.htm?code=3904

Inventory of SCCPs/MCCPs in imports in products: PVC

- **Large imports of PVC** to South America under **HS codes** which contain **additives**.



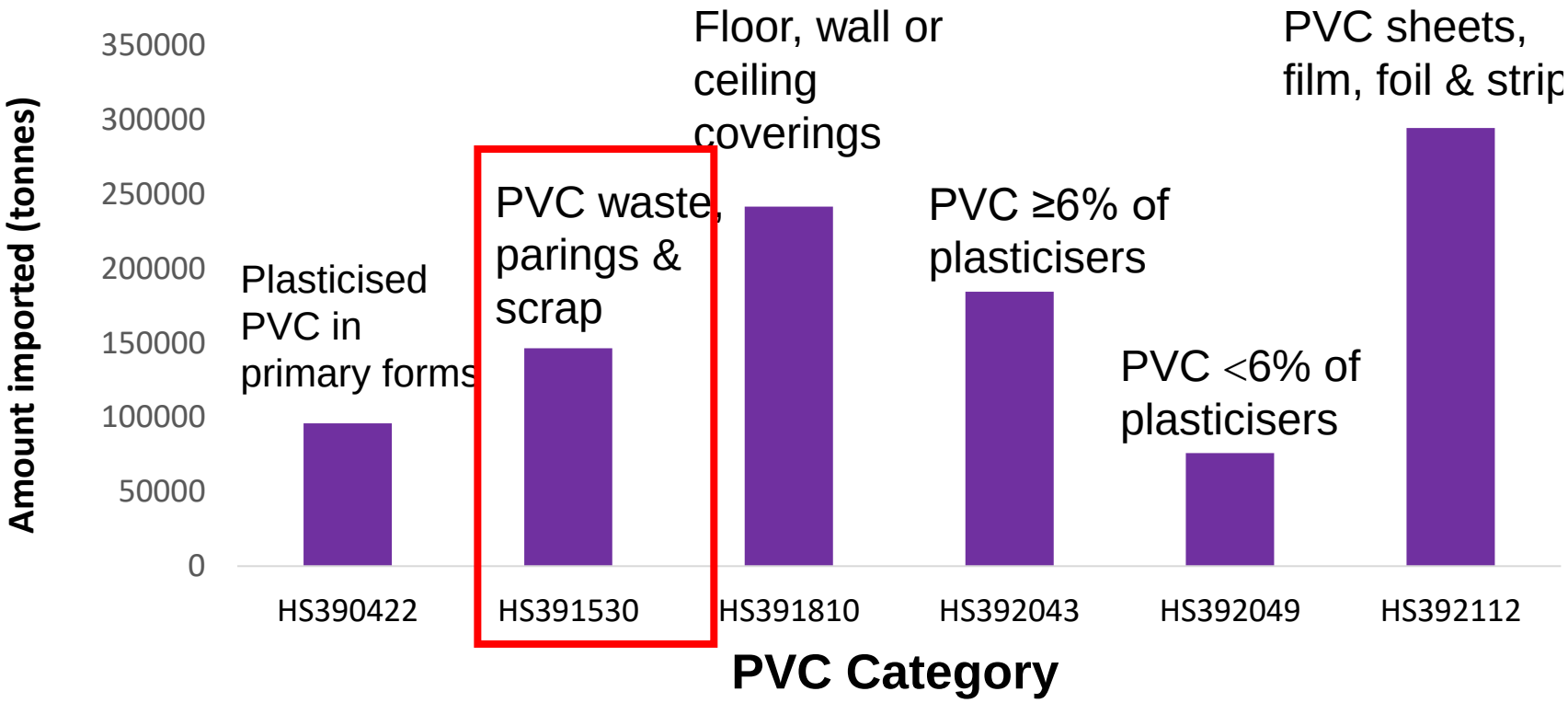
Source: Guida et al. Chemosphere 287, 132344. https://doi.org/10.1016/j.chemosphere.2021.132344

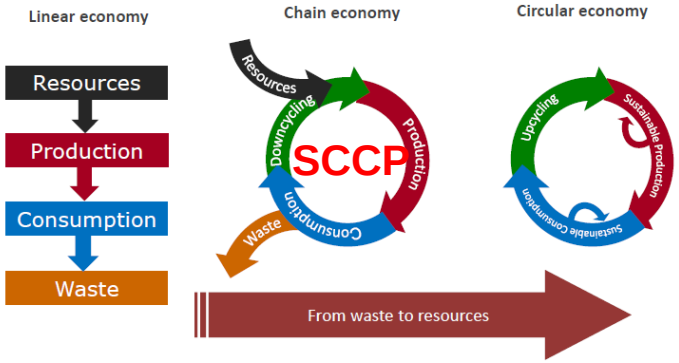
Inventory SCCPs: Plasticized PVC imports (Nigeria)

Assessment of plasticized PVC imports to country using UN **Comtrade Database**

- Individual HS codes can be assessed for total imports (not CP specific)
- We know the SCCP/MCCP use in products in China. For these possible to make an estimate.
- **Next step**: **monitoring of products** and of **PVC recycling**.

Plasticized PVC Imports to Nigeria (1996 to 2018)





Babayemi, Nnorom, Weber (2022) Emerging Contaminants https://doi.org/10.1016/j.emcon.2022.07.004

Inventory of SCCPs (PCBs/PCNs) in Open Application:
Import of rubber and rubber products

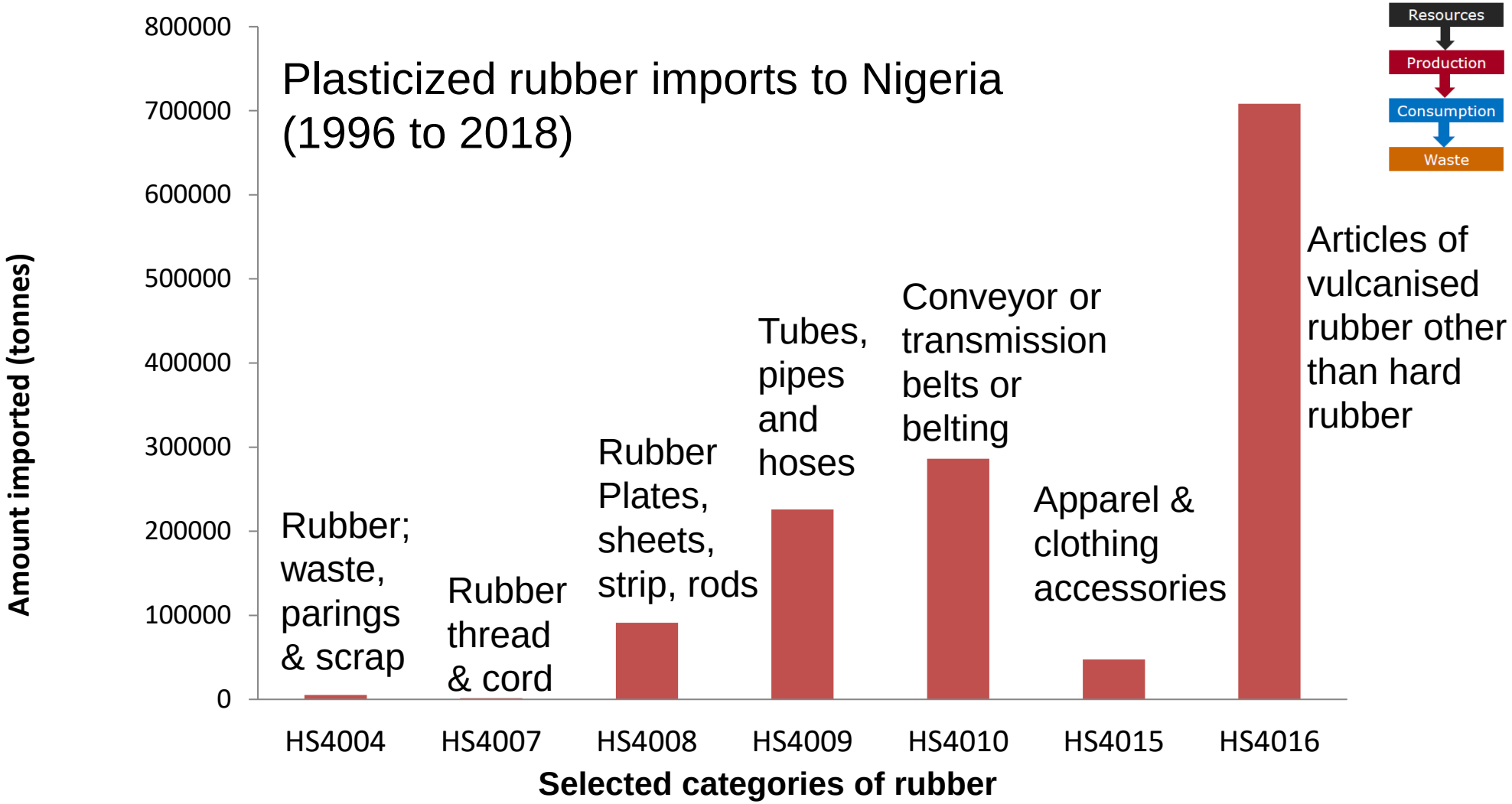
- A wide range of rubber types and products potentially containing plasticizers including SCCPs are traded and might be imported.

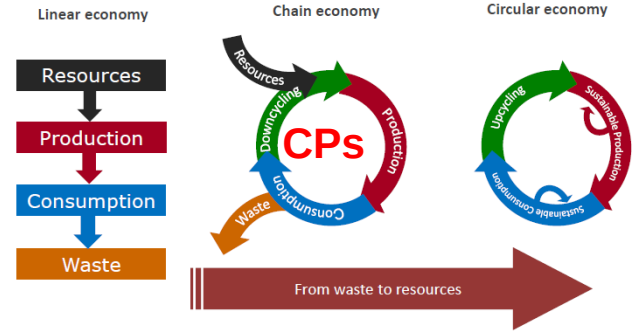
HS Code	Description
400239	Rubber; synthetic, halo-isobutene-isoprene rubber (CIIR or BIIR), in primary forms or in plates, sheets or strip
400241	Rubber; synthetic, chloroprene (chlorobutadiene) rubber (CR), latex, in primary forms or in plates, sheets or strip
400249	Rubber; synthetic, chloroprene (chlorobutadiene) rubber (CR), (other than latex), in primary forms or in plates, sheets or strip
400300	Rubber; reclaimed rubber, in primary forms or in plates, sheets or strip
400400	Rubber; waste, parings and scrap of rubber (other than hard rubber) and powders and granules obtained therefrom
4007	Vulcanised rubber thread and cord
4008	Plates, sheets, strip, rods & profiles, of vulcanised rubber other than hard rubber
4009	Tubes, pipes and hoses, of vulcanised rubber (other than hard rubber), with or without their fittings (e.g. joints, elbows, flanges)
4010	Conveyor or transmission belts or belting, of vulcanised rubber
4015	Articles of apparel and clothing accessories (including gloves, mittens and mitts), for all purposes, of vulcanised rubber other than hard rubber
4016	Articles of vulcanised rubber other than hard rubber

Inventory of SCCPs: Import of plasticized rubber products

Assessment of rubber imports using the **UN Comtrade Database.**

Conveyor belts are a major rubber application require addition of FRs for uses with flammability standards (ISO 340:2013).





Babayemi, Nnorom, Weber (2022) Emerging Contaminants https://doi.org/10.1016/j.emcon.2022.07.004

SCCPs and MCCP imports in products to Nigeria

Based on average SCCP & MCCP in PVC and rubber products and PUR foam in China (Chen et al. 2021) the amount of imported SCCPs and MCCPs in PVC, rubber and PUR spray foams was estimated.

Import categories (1996 to 2018)	From China (tonnes)	SCCP (mg/g) (Base on Chen et al 2021)	Amount of SCCP imported (tonnes)	MCCP (mg/g) Base on Chen et al 2021)	Amount of MCCP imported (tonnes)
PVC					
HS390422	57,033	0.8 (0.08%)	46	0.1 (0.01%)	6
HS391530	87,035	54.9 (5.49%)	4,778	97.4 (9.74%)	8,477
HS391810	143,500	6.2 (0.62%)	890	8.5 (0.85%)	1,220
HS392043	109,620	180 (18%)	19,732	102.6 (10.26%)	11,247
HS392049	45,147	180 (18%)	8,126	102.6 (10.26%)	4,632
HS392112	174,887	0.8 (0.08%)	140	0.1 (0.01%)	17
Total	**617,222**		**33,712**		**25,599**
Rubber					
HS4004	184,545	0.2 (0.02%)	0.4	0.1 (0.01%)	0.2
HS4007	76,005	0.2 (0.02%)	0.1	0.1 (0.01%)	0.05
HS4008	294,422	16.2 (1.62%)	502	60.9 (6.09%)	1,888
HS4009	76,808	0.2 (0.02%)	15	0.1 (0.01%)	8
HS4010	97,333	0.2 (0.02%)	19	0.1 (0.01%)	8
HS4015	16,159	10.8 (1.08%)	175	57.8 (5.78%)	934
HS4016	240,838	2.8 (0.28%)	674	122.4 (12.24%)	29,479
Total	**986,110**		**1,386**		**32,317**
Adhesive/PUR spray	28,289	82.4 (8.24%)	2,331	71.4 (7.14%)	2,020
Grand Total			**37,429**		**59,936**

Babayemi, Nnorom, Weber (2022) Emerging Contaminants https://doi.org/10.1016/j.emcon.2022.07.004

SCCPs in consumer products in the European Union

Consumer products which have been found contaminated with SCCPs above the regulatory limit of 1500 mg/kg in the European market (RAPEX 2017), include:

- **Toys** like **plastic doll**, **toy doctor set** (stethoscope), **bouncy toy**, stickers for children, rubber knife, **toilet seat for children**;
- **Sports equipment**: **Beach ball, baseball glove, Fitness gloves**, Abs trainer, **Yoga mats, all-purpose mat;**
- Artificial leather (PVC) wallet, handbags, mobile phone bag, brush case black, toiletry bag, wallet case for smartphones;
- Cables in motor vehicle sidelight, USB-cord, digital thermometer cable, extension lead, kettle cable, game controller (cable), electric kettle (cord), lighting chain (cord);
- Baking ovens and kitchen blenders;
- Other plastic/polymers like steering wheel cover, selfie stick, mobile phone case, rain cover for pushchair, cloche cover, garden equipment;
- **Other products (see Annex 1 SC SCCP inventory guidance).**

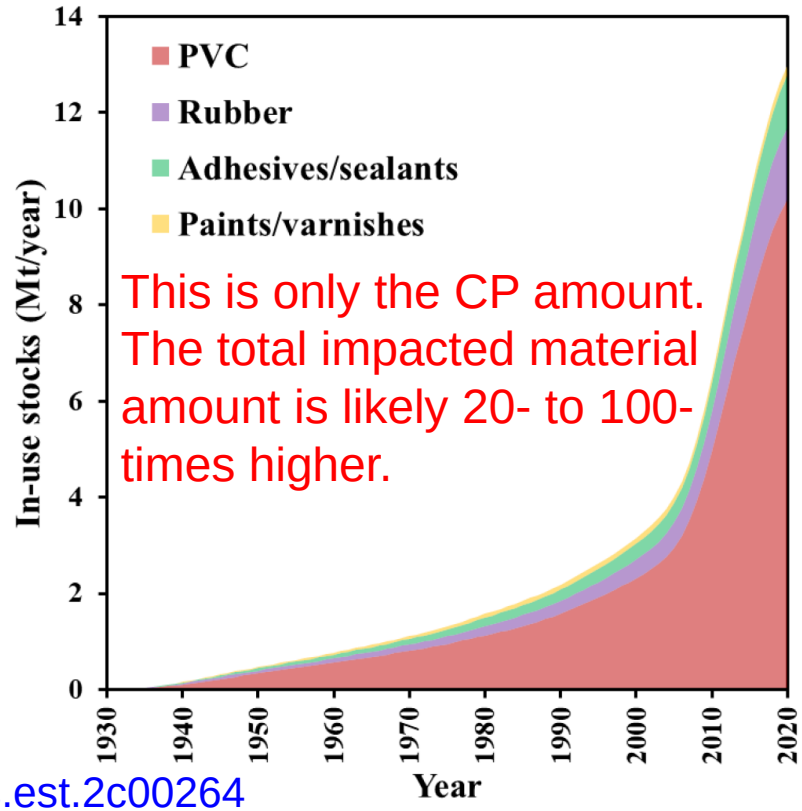
Product (2017 survey)	SCCP content mg/kg
Sports equipment: Boxing gloves	4400
Sports equipment: Gym ball	8500
Sports equipment: Yoga mats	8 000 – 69,000
Bathtub pillow	17 000
Electric shaver (cable)	9800
Hobby/sports equipment: Hot pack	4000
Exercise/sports equipment: tube (handle)	90 000
Speaker (cord)	10 000
Selfie stick (cord)	45 700
USB (cable)	16 000
In-ear headphones (USB cord)	3000
LED candle (cord)	13 000
Power cord/cable	26 000
Toy pistol (plastic cord)	7000
Radio controlled car (tyres)	17 000
Bath toy	13 400
Game controller	43 000
Plastic doll	8 600
Babies' sleeping bag (anti-slip knobs)	18 000
Breastfeeding pillow (packaging)	60 000
Handle (cycle parts)	3 500
Hammer (handle)	2 800
Claw hammer (handle)	7000

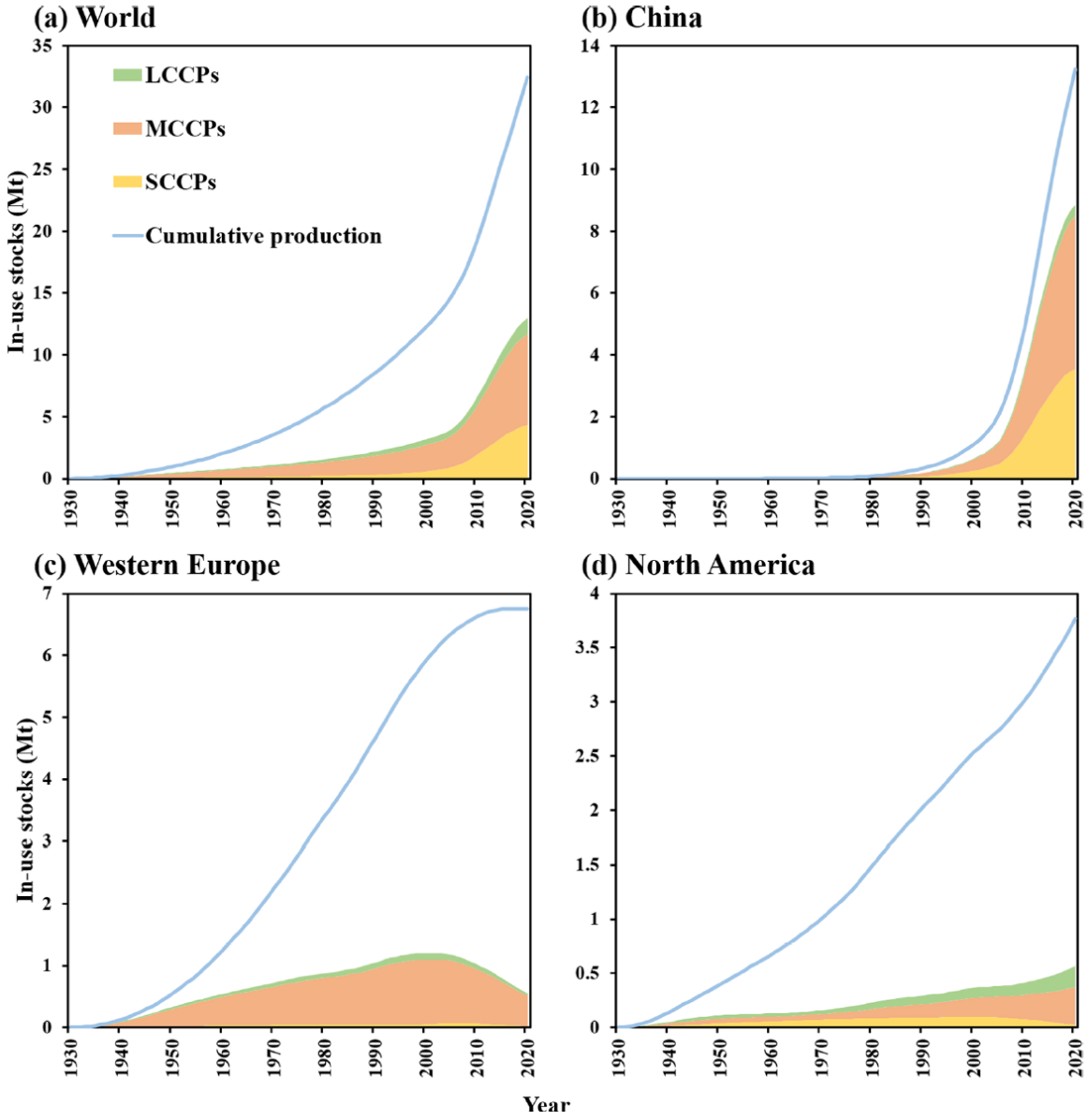
UNEP (2019) Guidance on preparing inventories of short- chain chlorinated paraffins (SCCPs) - Detailed guidance.

Estimated global stock of CPs

- Recent study estimated the global historic and current in use of SCCPs, MCCPs and LCCPs.

- Estimated that 33 Mt have been produced and 13 Mt are still in use with more than 8 Mt in use in China.
- **Major stocks in PVC, less in rubber and sealants/** PUR. Leather and paints likely underestimated.





Chen et al. (2022) ES&T
https://doi.org/10.1021/acs.est.2c00264

Total amounts and management needs of plastics containing SCCP/MCCPs much larger than PCB open application

- **13 million tonnes of CPs in likely ~200 Mt impacted PVC, rubber and PUR products**.
- **Additional 1 Mt CP mixtures containing SCCP/MCCPs** still (Guida et al. 2022; Xia et al. 2021) produced/yr mainly in China and India as additives in ~10 Mt PVC, PUR foam and rubber as plasticizer and flame retardant (Chen et al. 2021). Considering average of 10% additive content they result in ca. **10 Mt of POPs containing polymers/yr newly produced.**
- The **entire product categories (pl-PVC,** rubber?, rigid PUR) might exceed Basel Convention low POP content (**100 or 10000** mg/kg) and need to be managed in future **(likely billion tonnes scale)**

- The SCCP (and MCCP) containing products and wastes are considerable more than the PCB containing wastes. They are currently used and the products increase 10 million t/year. They have been used since more than 70 years in the same applications as PCBs. Therefore the inventory for PCBs in open application is best conducted together with the SCCP (and PCN) inventory.

Thank you for your attention !

More Information

SCCP Stockholm Inventory Guidance: ##

Review production & use CPs: Li et al (2022) ##

SCCP in the technosphere: Guida et al. https://doi.org/10.1016/j.emcon.2020.03.003

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/