National Institute for Environmental Studies, Japan

IPCP International Panel on Chemical Pollution

Universidade Federal do Rio de Janeiro

## IPCP Webinar Series: POPs in plastic and monitoring approaches

# Monitoring chlorinated paraffins in plastic products

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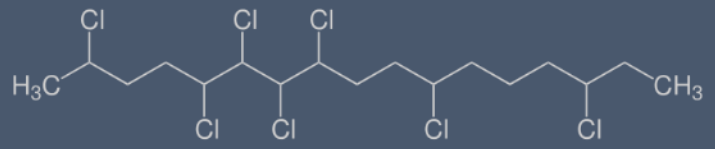
*April 2023*

# Chlorinated Paraffins (CPs)




- *Chemical additives produced since the 1930's ($C_xH_{2x+2-y}Cl_y$).*
- *Multipurpose applications.*
- *SCCPs ($C_{10}$–$C_{13}$) — MCCPs ($C_{14}$–$C_{17}$) — LCCPs ($C_{18}$–$C_{30}$).*



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# Global Historical Production, Use, In-Use Stocks, and Emissions of Short-, Medium-, and Long-Chain Chlorinated Paraffins

Chengkang Chen, Anna Chen, Faqiang Zhan, Frank Wania, Shaoxuan Zhang, Li Li,* and Jianguo Liu*

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- *A total of ~33 million metric tonnes of CPs have been produced and used globally,* **~40% of which still resided in in-use products by 2020** *and is available for long-term emissions in the next decades.*

- *Global* **cumulative emissions of CPs have increased to ~5.2 million metric tonnes by 2020**, *with SCCPs, MCCPs, and LCCPs accounting for ~30, 40, and 30%, respectively.*

- *While the* **production, use, and emissions of CPs** *started declining in regions such as Western Europe, they* **remain high in China.**



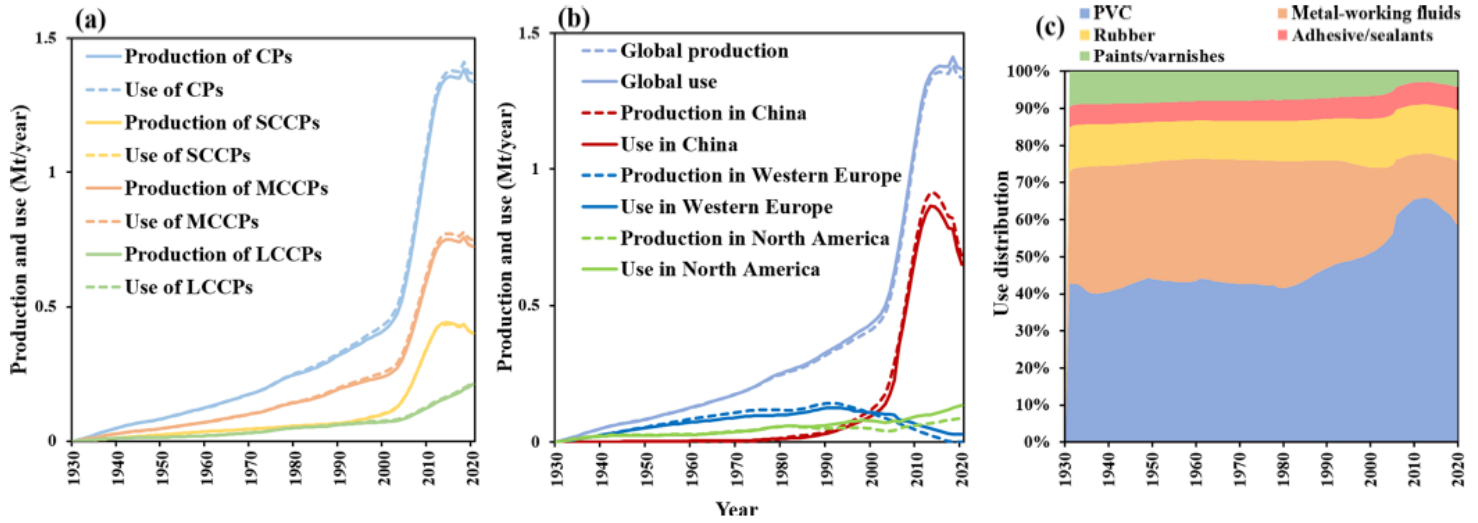


Figure 2. Temporal trends of the global annual production and use of CPs, SCCPs, MCCPs, and LCCPs (a), distribution of production and use of CPs globally and in three selected regions (b), and distribution of CP use among five major end-use applications (c) during 1930−2020.

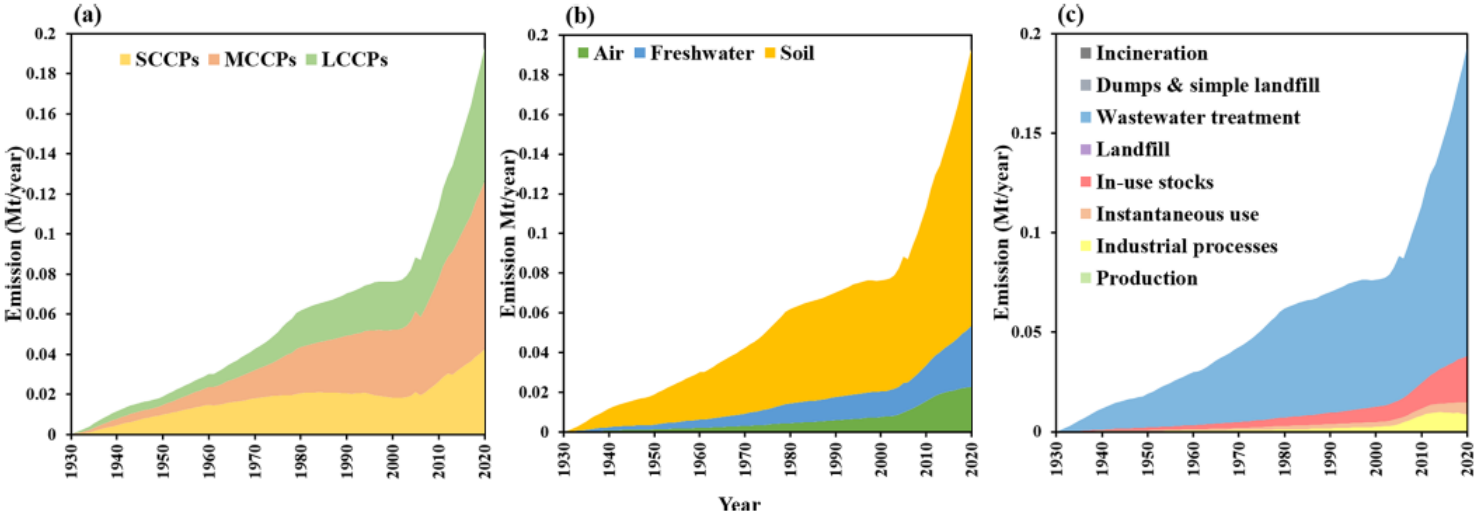


Figure 4. Temporal evolutions of global emissions of CPs (a) for SCCPs, MCCPs, and LCCPs; (b) to different receiving environments; and (c) from various emission sources.

https://doi.org/10.1021/acs.est.2c00264

# Restrictions and phase-out

- *In 2017, SCCPs were listed under the Stockholm Convention on Persistent Organic Pollutants (POPs) with specific exemptions.*
- *In 2021, MCCPs were proposed for listing as POPs and were recommended to be added to the EU RoHS directive.*
- *SCCPs are currently listed under Basel and Rotterdam Conventions.*
- *Two tentative Low POP Content (LPC) limits (100 and 10,000 mg $kg^{-1}$) have been proposed under the Basel Convention.*

BASEL CONVENTION
the world environmental agreement on wastes

ROTTERDAM CONVENTION

STOCKHOLM CONVENTION

# National implementation of the Conventions

- **For the through implementation of the Stockholm Convention, a Country-Party must:**

- *Develop POP inventories to define proper chemical management within the country context.*

- *Assure that SCCPs are only used for the specific exemptions defined in the listing decision and that other CPs traded as MCCPs or LCCPs do not contain SCCPs >1% (w/w).*

- *Promote environmentally sound management of end-of-life products containing SCCPs and SCCP waste (also under Basel Convention).*

BASEL CONVENTION
*the world environmental agreement on wastes*

ROTTERDAM CONVENTION

STOCKHOLM CONVENTION

# Challenges in the implementation of the Conventions

- *CPs are produced and traded based on the chlorine content.*
- *Several studies have reported commercial CP mixtures containing >1% SCCPs.*
- *China is the largest global producer of CPs (~1.5 million tonnes) and a very relevant commercial partner of many countries.*
- *Most of the Chinese CP production (88% SCCPs and 74% MCCPs) has been used in PVC manufacturing.*
- *Products containing CPs are not labelled and, both commercial CP mixtures and products containing CPs, do not contain specific codes to track their foreign trade data.*

# Chlorinated paraffins in products

Emerging Contaminants 6 (2020) 143–154

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Emerging Contaminants

journal homepage: http://www.keaipublishing.com/en/journals/emerging-contaminants/


## Chlorinated paraffins in the technosphere: A review of available information and data gaps demonstrating the need to support the Stockholm Convention implementation

Yago Guida [a,*], Raquel Capella [a], Roland Weber [b]

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**Table 3**
CP concentrations in consumer goods. Mean (minimum–maximum) values in mg $kg^{-1}$.

| Ref. | Product (sample) | SCCP | MCCP | LCCP |
|---|---|---|---|---|
| [86] | PVC (12) | 78 (30–35,000) | – | – |
| [17] | Cables & Cords (15) | 13,611 (1100–45,700) | – | – |
| | Covers & Packing (8) | 15,737 (2600–60,000) | – | – |
| | Leather (artificial) (13) | 3954 (1100–14,000) | – | – |
| | Sports equipment (18) | 19,056 (1800–90,000) | – | – |
| | Stickers (5) | 11,600 (2000–18,000) | – | – |
| | Toys (20) | 26,893 (1900–100,000) | – | – |
| | Domestic products (19) | 11,032 (700–47,000) | – | – |
| [83] | PVC (21) | 40,770 (nd–190,896) | 28,116 (nd–144,751) | – |
| | rubber (25) | 614 (nd–13,144) | 1329 (nd–22,774) | – |
| | PET (19) | 0.2 (nd–3) | 0.04 (nd–0.1) | – |
| | PE (5) | 0.1 (0.02–0.3) | 0.02 (nd–0.2) | – |
| | PP (18) | 4 (nd–69) | 2 (nd–36) | – |
| | Food packing I[a] (20) | 2 (0.01–8.3) | 1 (nd–10) | – |
| [84] | Food packing II (6) | 3 (1–5) | 2 (0.5–4) | – |
| [85] | Rubber track products (15) | 3639 (14–12,800) | 41,368 (9–160,000) | – |
| | Adhesives (5) | 3344 (62–7140) | 41,523 (43–202,000) | – |
| | Rubber granulate (10) | 3 (nd–24) | 2.5 (0.1–24) | – |
| [70] | Rubber granulate (9) | 5 (2–9) | 24 (9–54) | 3 (1–5) |
| | Playground tiles (6) | 8 (2–25) | 22 (10–51) | 6 (1–24) |
| | Car tires (10) | 1 (nd–2) | 9 (1–60) | 1 (nd–5) |

[a] Made of biaxially oriented polypropylene (BOPP) and vacuum metalized PET (VMPET). PVC - polyvinyl chloride. PET - polyethylene terephthalate. PE - polyethylene. PP – polypropylene.

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# Widespread presence of chlorinated paraffins in consumer products†

Steven Kutarna,[a] Xuan Du,[a] Miriam L. Diamond,[bc] Arlene Blum[de] and Hui Peng[*ac]

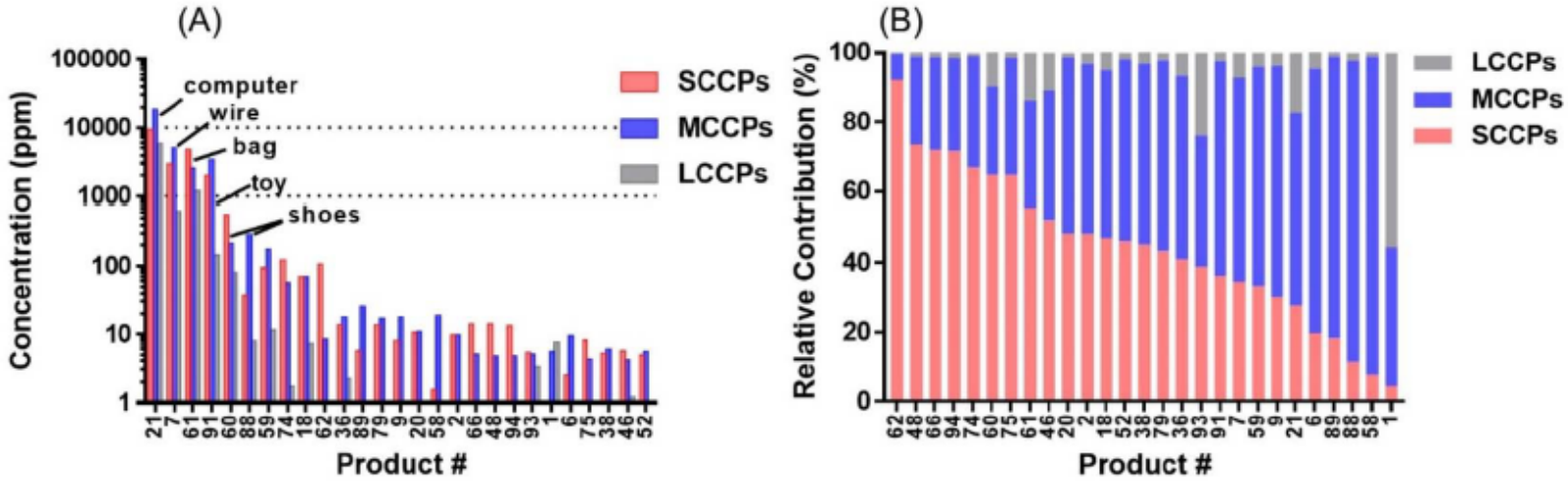


Fig. 3 Concentrations and profiles of chlorinated paraffins in 27 indoor products with ΣCPs > 10 ppm. (A) Concentrations of CPs detected in products. The top 6 products are highlighted. (B) Relative contributions of SCCPs, MCCPs and LCCPs to ΣCPs in different products.

Environmental Science & Technology
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# Distribution and Emission Estimation of Short- and Medium-Chain Chlorinated Paraffins in Chinese Products through Detection-Based Mass Balancing

Chengkang Chen, Anna Chen, Li Li, Wangyuan Peng, Roland Weber, and Jianguo Liu*

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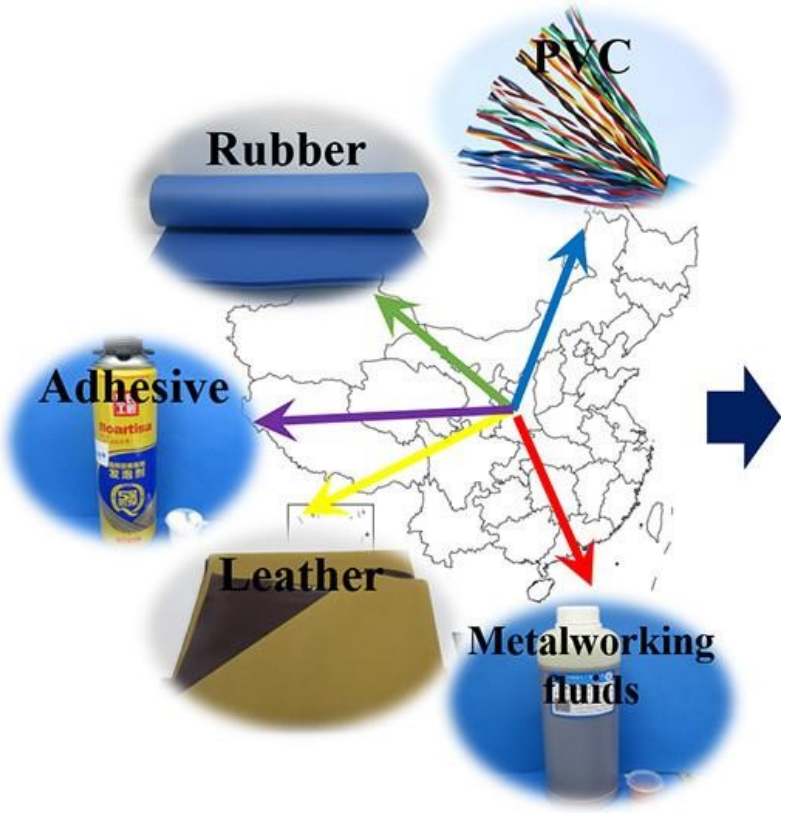


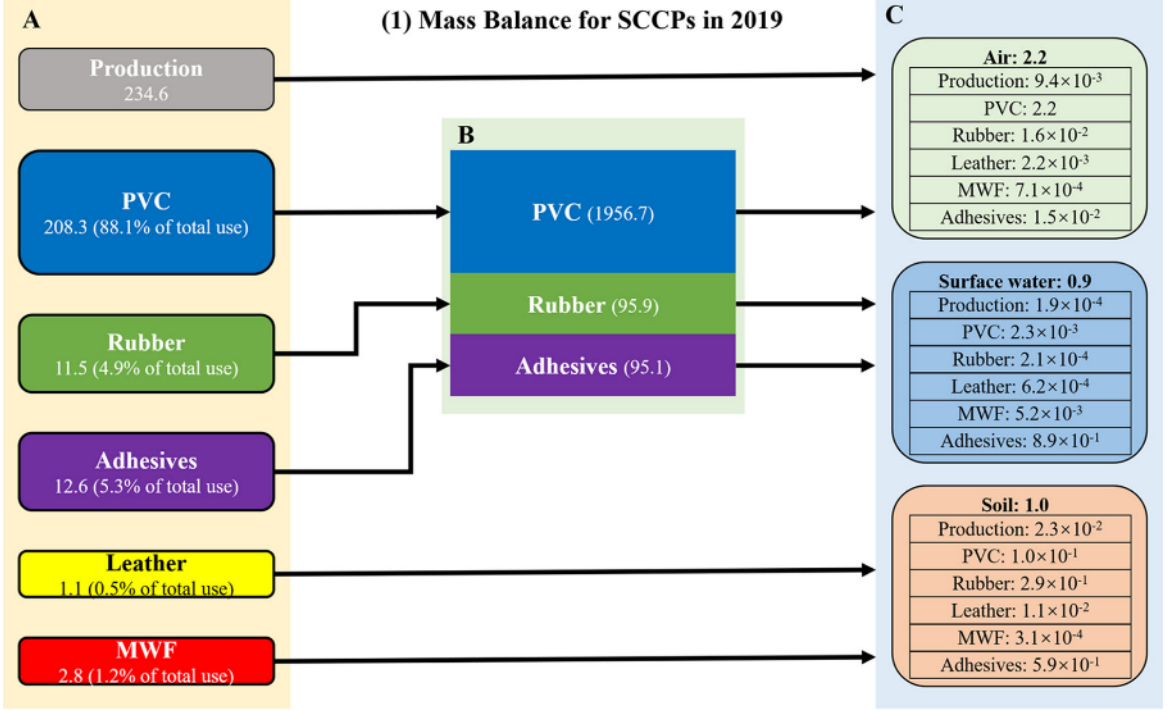


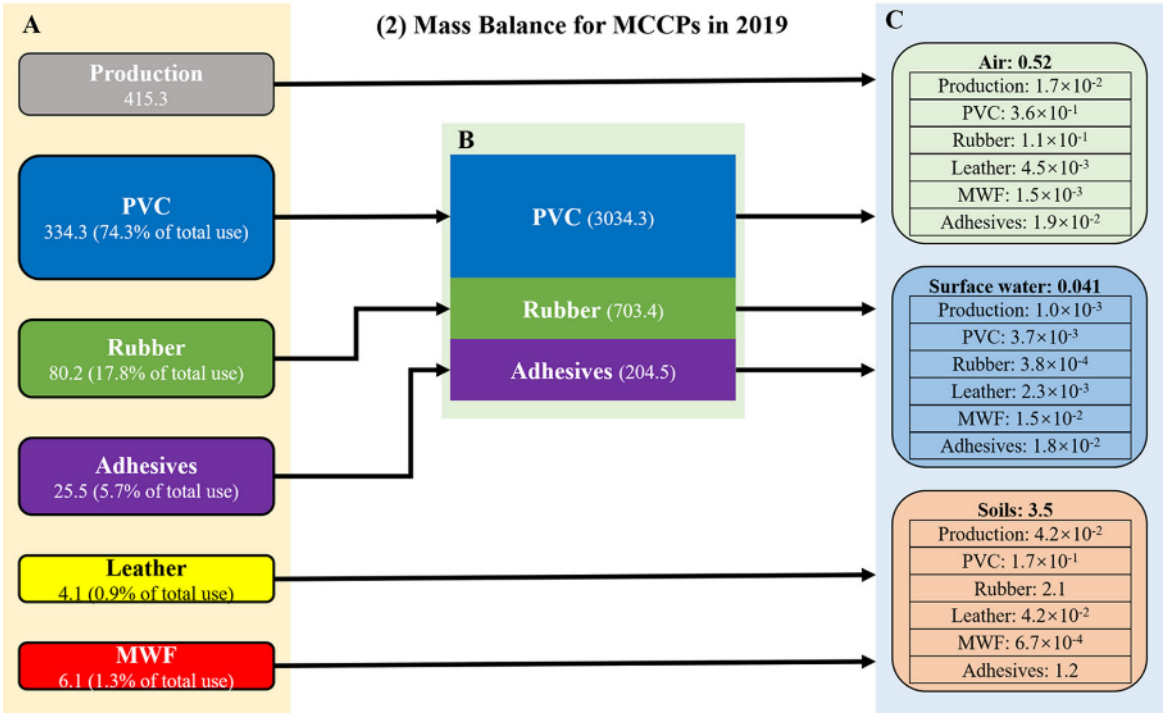


https://doi.org/10.1021/acs.est.0c07058

Ramungul *et al. J Environ Expo Assess* 2023;2:2
**DOI:** 10.20517/jeea.2022.081601

Journal of Environmental Exposure Assessment

Research Article

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# Circular economy without chemicals controls? Evidence of recirculated toxic plasticizers in flexible PVC products

**Nudjarin Ramungul[1], Yot Boontongkong[1], Pavares Viwatthanasittiphong[1], Nuengruthai Chuayrueng[1], Yaowadee Temtanapat[2], Saisamorn Koonhorm[1], Arjaree Ausavanonkulporn[1]**

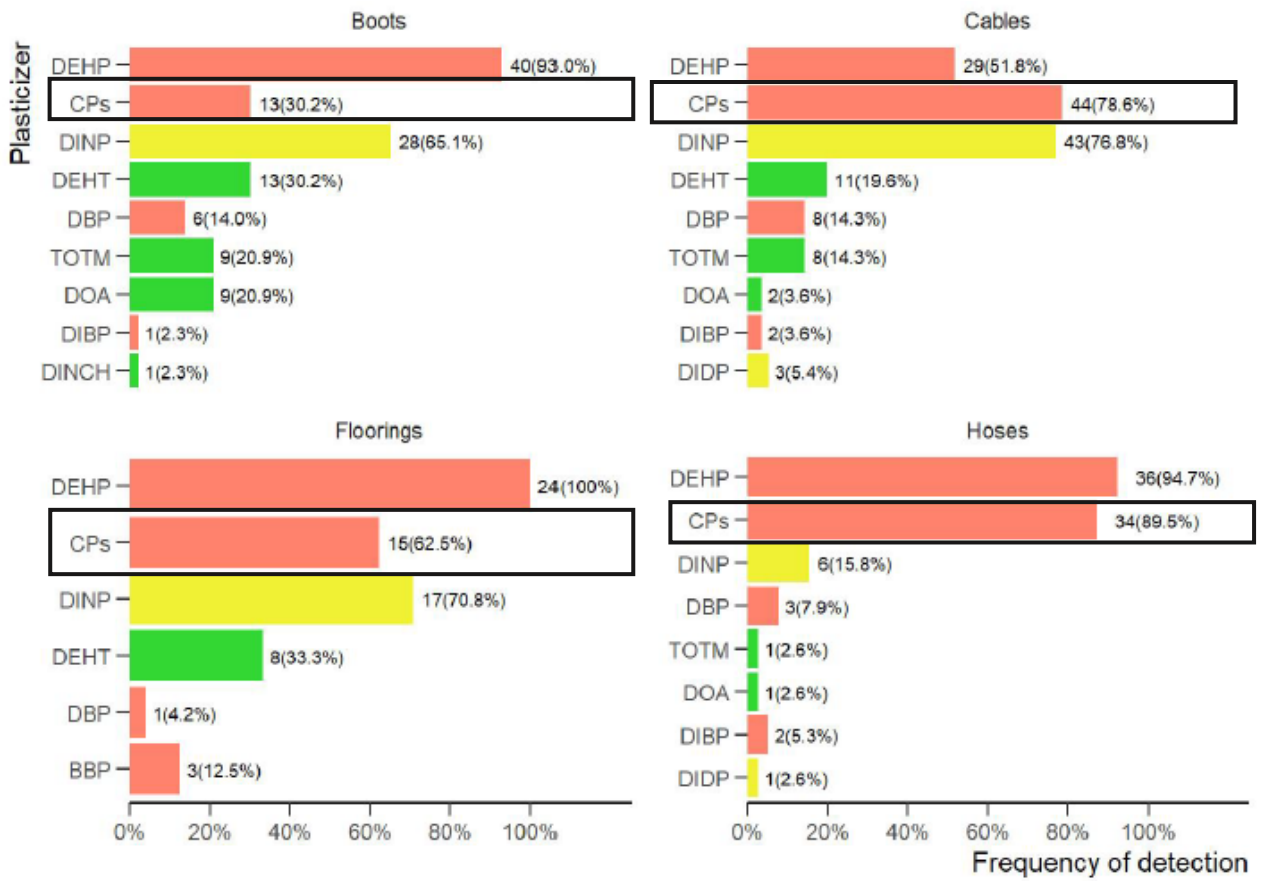


**Figure 5.** Frequency of each plasticizer detected by Py/TD-GC-MS. The mixture of DEHP and CPs is the most common popular plasticizer combination, except for cable sheaths where DEHP has been replaced by DINP. Red bars: restricted plasticizers; Yellow bars: yet to be widely restricted PAEs; Green bars: non-PAEs alternatives.

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# Short- and medium-chain chlorinated paraffins in polyvinyl chloride consumer goods available in the Japanese market

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**Objective: to assess SCCP and MCCP homolog contents of PVC consumer goods available in the Japanese market.**





# Material and Methods [18,19]

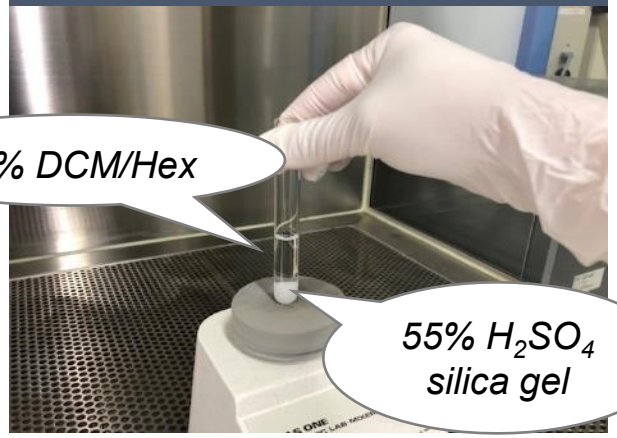
*Consumer goods*
*2017–2019*
*100-yen store; do-it-yourself store; furniture shop in Tsukuba, Ibaraki*

*87 PVC-based products:*
*38 electrical and electronic cable sheaths*
*10 house interior products*
*39 children's products*

## Powdered


*Freezer mill after cutting*

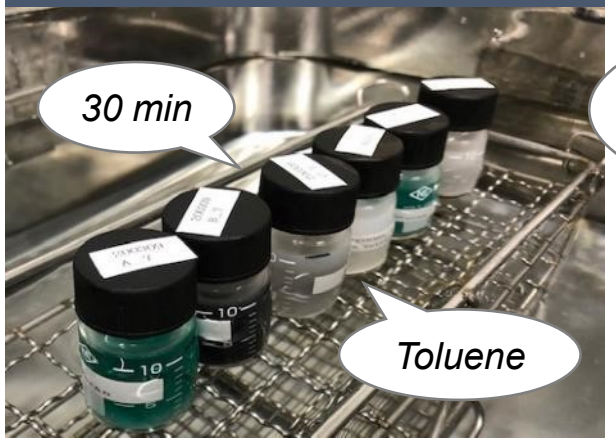
## Clean-up



*10% DCM/Hex*

*55% $H_2SO_4$ silica gel*

## Ultrasonic extraction



*30 min*

*Toluene*

## LC-MS/MS

*5 mM $CH_3COONH_4$ aq /MeOH*

*CN column*

*$ESI^-$*

# Results & Discussion

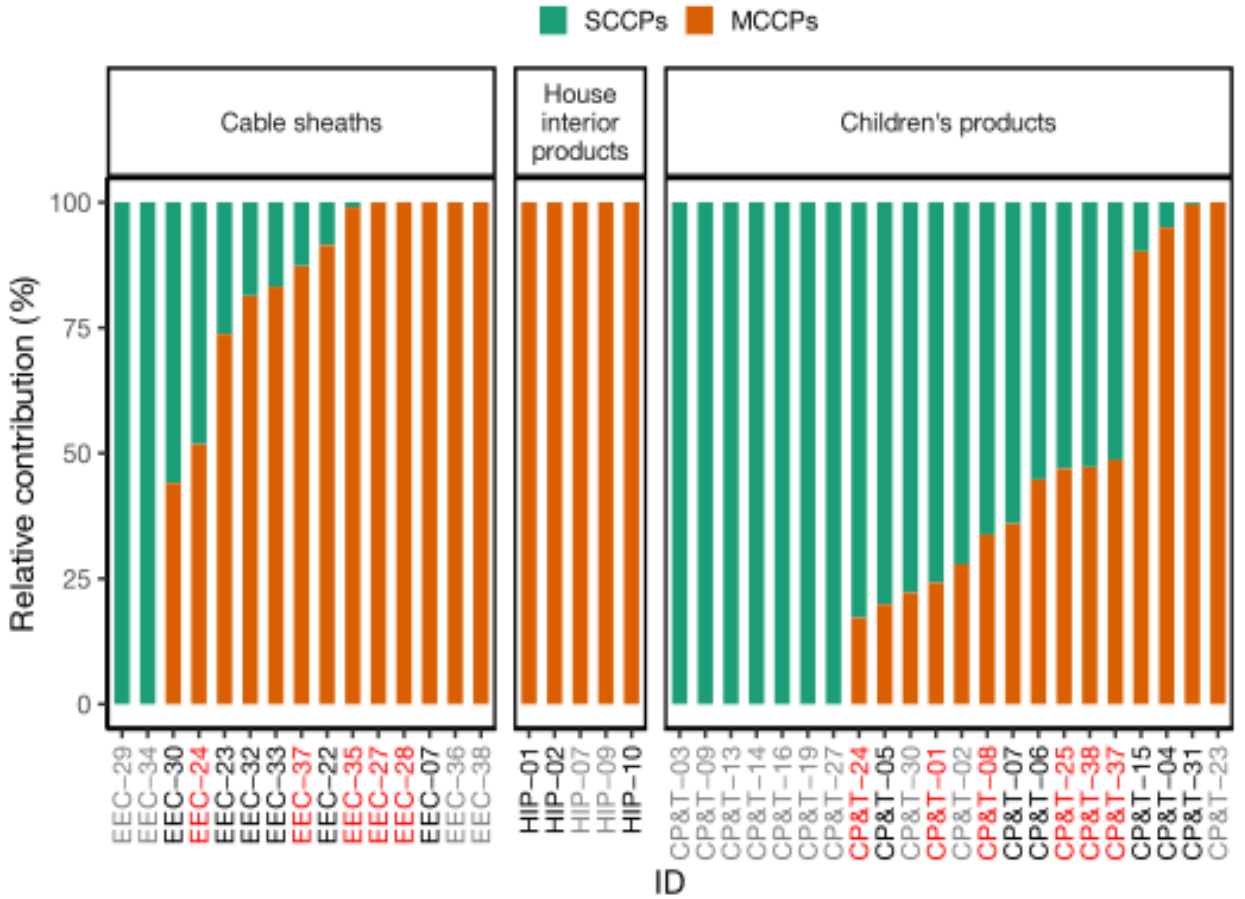
- *CPs were detected in 42 out of 87 samples.*

| Products | SCCPs (mg $kg^{-1}$) | SCCP DF | MCCPs (mg $kg^{-1}$) | MCCP DF |
|---|---|---|---|---|
| Cable sheaths | 1.3–8500 (79) | 12/38 | 1.2–59,000 (1200) | 13/38 |
| House interior products | <LOQ | 0/10 | 3.5–550 (120) | 5/10 |
| Children's products | 2.0–120,000 (75) | 21/39 | 1.6–25,000 (2200) | 15/39 |

- *Most of the PVC consumer goods purchased in Japan were manufactured in China. However, all products not made in China had a total CP content <0.1% (w/w).*
- *The highest concentrations were detected in children's products, but besides the most contaminated sample (children's flipflop) only 3 other samples had SCCP contents >1% (w/w).*

# Results & Discussion

- *In total 11 products had CP contents >1% (w/w)*
- *Therefore, intentional CP applications as plasticizer or flame retardant cannot be assumed for most products*
- *Children's products were more impacted by SCCPs whereas cable sheaths and house interior products were more affected by MCCPs*
- *SCCP/MCCP ratios show that although it is possible to have single chain-length groups, several products are still impacted by CPs containing SCCPs >1%*

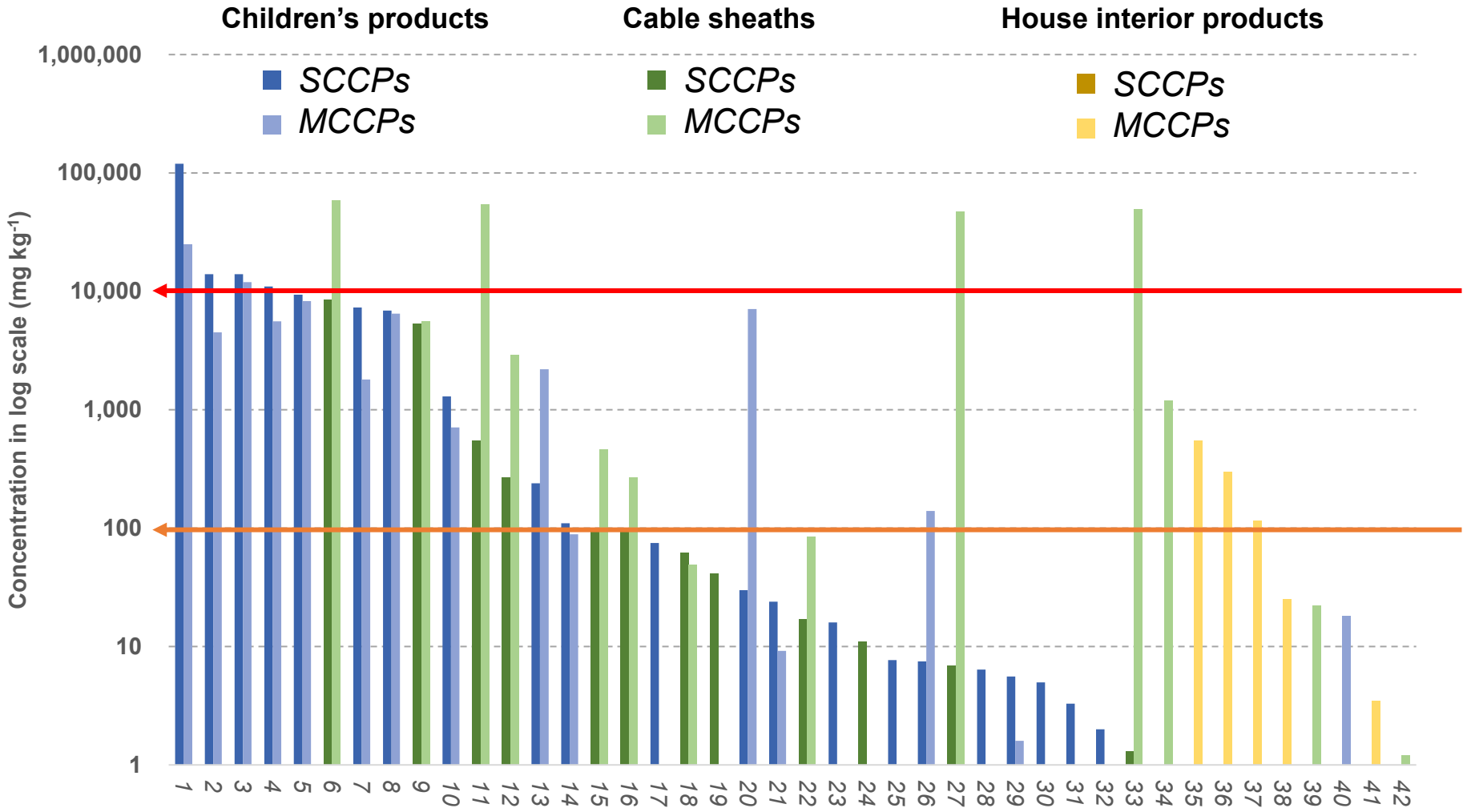



*Relative contribution of SCCP and MCCP mass fractions to total CP contents in PVC products. Colored labels indicate CP content range: gray < 100 mg kg$^{-1}$, black ≥ 100 mg kg$^{-1}$ and red ≥ 10,000 mg kg$^{-1}$*

# Results & Discussion

| Product (n) | Region | Sampling year | SCCPs (mg kg$^{-1}$) | MCCPs (mg kg$^{-1}$) | >DF (%) | Reference |
|---|---|---|---|---|---|---|
| **Cable sheaths (38)** | **Japan** | **2017–2019** | **1.3–8500 (79)** | **1.2–59,000 (1200)** | **34%** | **This Study** |
| Cable sheaths (2) | Belgium | 2019 | 1.4–1.5 (1.5) | <LOQ | 100% | McGrath et al., 2021 |
| Cable sheaths (13) | China | 2018–2019 | 150–52,000 (11,000) | 100–94,000 (43,000) | 100% | Chen et al., 2021 |
| Cable sheaths (11) | China | na | 56–190,000 (68,000) | 15–140,000 (58,000) | 100% | Wang et al., 2018 |
| **House interior products (10)** | **Japan** | **2017–2019** | **<LOQ** | **3.5–550 (120)** | **50%** | **This Study** |
| Hosepipes for plumbing (10) | China | 2018–2019 | 5200–130,000 (55,000) | 5900–190,000 (97,000) | 90% | Chen et al., 2021 |
| Floorings (6) | China | 2018–2019 | 2000–12,000 (6200) | 3100–58,000 (8500) | 50% | Chen et al., 2021 |
| Plastic films (4) | China | 2018–2019 | 100 [a] | 70–1600 (800) | 75% | Chen et al., 2021 |
| Soft plastic curtains (14) | China | 2018–2019 | 64,000–320,000 (180,000) | 37,000–280,000 (100,000) | 100% | Chen et al., 2021 |
| Floorings (4) | China | na | 1300–3200 (3100) | 590–3200 (1500) | 75% | Wang et al., 2018 |
| **Children's products & toys (39)** | **Japan** | **2017–2019** | **2.0–120,000 (75)** | **1.6–25,000 (2200)** | **54%** | **This Study** |
| Children's products & toys (60) | Global | na | 8.4–20,000 (300) | na | 45% | Miller and DiGangi, 2017 |

# Results & Discussion




*Upper Basel LPC limit for SCCPs in waste*

*Lower Basel LPC limit for SCCPs in waste*

# Conclusions

- *SCCPs are still often present in PVC consumer goods currently available in the Japanese market.*
- *Some manufacturers may use technical CP mixtures in PVC products with less than 1% w/w SCCP content, but many other products still contain larger fractions of SCCPs.*
- *In most cases, CP contents were below the contents reported for intentional use in PVC manufacturing.*
- *Potential intentional SCCP application in children's products.*
- *CPs were predominant in products made in China, highlighting the need to establish wide monitoring of imported PVC products.*
- *Considering the LPC limits proposed under the Basel Convention, waste and recycling streams also need to be monitored*

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