Short-Chain Chlorinated Paraffins (SCCPs), a Toxic Industrial Chemical Included for Global Prohibition, Contaminate Children's Toys

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Introduction

Short-chain chlorinated paraffins (SCCPs) are widely used as industrial lubricants and coolants in metalworking applications. However, they are also present in consumer products when used as plasticizers and flame retardants, especially in polyvinyl chloride (PVC) plastic, as well as in rubber, textiles, and polymers. Additionally, they are used as plasticizers in such applications as sealants, adhesives, and paints [1]. According to a recent scientific study *"no other persistent anthropogenic chemical has been produced in such quantities* [as chlorinated paraffins]" [2] Production and use of SCCPs is increasing [3]. In 2016, a Stockholm Convention expert committee recommended listing SCCPs in the treaty for global elimination [4]. The expert committee noted that SCCPs are ubiquitous in the global environment, wildlife, and humans [5]. They also fulfill key treaty characteristics as they are persistent, bioaccumulative, and transported long distances to remote locations, including the Arctic and Antarctic. SCCPs were listed under provisions of the Stockholm Convention for global elimination with the allowance of time-limited exemptions for certain industrial uses at the 8th Conference of the Parties in April 2017 [6]. SCCPs are toxic to aquatic organisms at low concentrations; adversely affect the kidney, liver, and thyroid; and disrupt endocrine function [7, 8, 9]. SCCPs are classified in the 13th Edition of the Report on Carcinogens by the U.S. National Toxicology Program as *"reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity from studies in experimental animals* [10]*."* SCCPs are found in fish, seals, walrus, and whales of the Arctic that serve as traditional foods of Indigenous peoples [11, 12, 13]. SCCPs are also found in the breast milk of Arctic Inuit women [14]. The Stockholm Convention review of SCCPs found reports of contamination in consumer products – including children's products and food contact materials. This study investigated the levels of SCCPs in children's toys purchased in 10 countries and in hand blenders used to make baby food because we hypothesized that they are ubiquitous in a range of consumer products, including toys.

Materials and methods

One gram of sample (cryogenically milled) was extracted by shaking with the solvent mixture *n*-hexane:dichloromethane (4:1; v/v) for 3 h. The crude extract was purified using gel permeation chromatography in the Bio-Beads S-X3 column with the mixture cyclohexane-ethylacetate (1:1, *v/v*). The fraction corresponding to elution of SCCPs was evaporated, residues were dissolved in cyclohexane and transferred into the vial for final instrumental analysis. The instrumental measurement was performed on an Agilent 7890B gas chromatograph coupled with a 7200 QTOF mass spectrometer (both Agilent Technologies, USA) in negative chemical ionization

(NCI). A capillary column DB-5MS (30 m x 0.25 mm x 0.25 μm, Agilent Technologies, USA) was used for separation of target compounds. The following instrumental settings were applied: He flow (carrier gas) - 1 ml/min; Inlet temperature - 280°C; Injection - 1 μl pulse splitless (206.7 kPa, 30 psi); Temperature program - 140°C (held 1 min) - 30°C / min to 310°C - 2°C / min to 325°C (held for 2 min), total analysis time 16.2 min; Transferline temperature - 280°C; Reaction gas – methane; Ion source temperature - 150°C; Acquisition rate - 5 spectra/s; HRMS - 12,500 FWHM . The quantification method is based on the calculation of the chlorine content within the SCCPs fraction. Six standard mixture (technical mixtures) of the same concentration (10 μg/ml), but with different average chlorine contents, were measured. 48 masses (24 quantification and 24 confirmation ions) corresponding to [M Cl] - ions representing individual congener groups (each characterized by the compound formula) were monitored. A total response factor (TRF) was calculated. This quantification method is based on a study by Xia et al. 2016 [15].

Results and discussion

Laboratory analyses of 60 toys and other children's articles from 10 countries (Brazil, Canada, China, Czech Republic, India, Japan, Kenya, Netherlands, Russia, and United States) found that 45% (27) of the samples contained SCCPs at concentrations ranging from 8.4 to 19,808 parts per million (ppm). Toys and children's articles analyzed in this survey included plastic animals, jump ropes, sandals, rain boots, plastic balls, pendants, and swim gear. A majority of the labeled products containing SCCPs were manufactured in China. SCCPs are pervasive in a broad range of household products that may contribute to human exposure. Children are more vulnerable because their physiology and behavior may cause higher exposures through skin absorption, inhalation, and ingestion. This study found a hand blender which contained SCCP contamination, with a level measured in leachate of 3.3 ppb. This product can contaminate prepared foods and is commonly used to prepare baby food. None of the product labeling indicated that they contained substances of current global concern.

The levels of SCCPs found in this study were similar to those observed in previous studies. SCCPs exceeded permitted levels in children's products tested in Norway, with concentrations ranging from 1,600 – 107,000 ppm (0.16-10.7%) [16]. When conducting tests on household articles, the Swedish Chemicals Agency found that of 62 articles tested, 16 contained SCCPs in high concentrations; and 11 of the articles contained lower concentrations of SCCPs that were thought to have resulted from contamination in the manufacturing or delivery process [17]. In Germany, 19 of 84 plastic products contained SCCPs, with concentrations ranging from 440-50,000 ppm [18]. Levels of SCCPs ranging from 4,000 – 69,000 ppm (0.4-6.9%) were found in mats tested in Austria [19]. In Sweden, a recent study demonstrated that hand blenders used in food preparation for babies and infants are unexpected and serious sources of exposure to SCCPs. Eight out of twelve hand blenders leaked SCCPs into prepared food. The scientists concluded: *"the presence of chlorinated paraffins in household appliances that contaminate food during preparation is unacceptable and actions have to be taken immediately* [20]*."*

In 2015, the European Commission set a weak regulatory limit of 0.15% by weight (1,500 parts per million) for SCCPs in articles [21]. Six of the toys in this study (10%) significantly exceeded this standard with levels of 4,376 ppm (a baby bib purchased in India), 4,866 ppm (a baby bib purchased in Kenya), 6,918 (beach ball purchased in Kenya), 9,715 ppm (a gym ball purchased in the Czech Republic), 13,973 ppm (a plastic duck purchased in Brazil), and 19,808 ppm (a jump rope purchased in Japan). Several countries where SCCPs are banned (including Austria, Germany, Norway, and Sweden) have taken enforcement actions when inspections revealed that SCCPs exceeded permitted levels in household products.

The Stockholm Convention expert committee (known as the POPs Review Committee or POPRC) recommended listing SCCPs in Annex A of the treaty for global elimination. The Conference of the Parties of the Stockholm Convention listed SCCPs in Annex A of the Convention in April 2017 with specific time-limited exemptions [22]. Listing SCCPs in Annex A of the treaty prohibits production, use, import, and export of SCCPs, except for purposes of environmentally sound disposal in accordance with Convention provisions. The Stockholm Convention also includes measures to address releases from stockpiles and wastes in Article 6. This includes establishment of hazardous waste limits known as low POP content levels (LPCLs). These limits define the value at which wastes are considered to be POPs wastes and therefore must be *"Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed" (*Stockholm Convention Article 6.1 d ii.) Thus, LPCLs are crucial for defining which wastes are hazardous according their POPs content. The provisional LPCLs for most POPs listed in the treaty have been set at 50 ppm. However, lower limits have been proposed for some substances [23]. For example, PCBs have had a provisional LPCL of 50 ppm, but a limit of 10 ppm has been proposed. If SCCPs are listed in the Convention, then an expert group will study the matter and make a proposal for LPCL for consideration at the Conference of the Parties in 2019. Using 50 ppm as a "typical" LPCL for comparison reveals that a significant proportion of the products in this study would be considered hazardous waste. Eighteen toys (67%) exceeded 50 ppm SCCPs. If a lower LPCL of 10 ppm is used for comparison, then 96% of the samples (26 of 27) exceeded this limit and would be classified as hazardous waste and subject to treaty waste provisions.

SCCPs are substances of global concern and now included for world-wide elimination under the Stockholm Convention. Surprisingly, SCCPs are widely present in children's toys made of plastic. Ninety-six percent of the toys with measureable concentrations of SCCPs contained levels of 10 ppm or greater. These results compare with other studies that found SCCPs in consumer products, even though they are banned—often in high concentrations and above permitted levels. Products containing SCCPs are likely to be a significant pathway for human exposure and particularly harmful for infants and children. It will be important to monitor levels of SCCPs in consumer products as a measure of the effectiveness of the Stockholm Convention.

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References
[1] Persistent Organic Pollutants Committee (POPRC) (2016) Risk Management Evaluation on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC12/11/Add.3.
[2] van Mourik, L. et al. (2016) Chemosphere, **155** 415-428.
[3] Glüge, J. et al. (2016) Science of the Total Environment, **573** 1132-1146.
[4] Persistent Organic Pollutants Committee (2015) Risk Profile on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC.11/10/Add.2.
[5] Persistent Organic Pollutants Committee (2015) Risk Profile on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC.11/10/Add.2.

[6] Allan J. et al. (2017) Earth Negotiations Bulletin—A Reporting Service for Environment and Development Negotiations, Volume 15 Number 252: http://enb.iisd.org/chemical/cops/2017/
[7] U.S. Environmental Protection Agency Short-Chain Chlorinated and Other Chlorinated Paraffins Action Plan (2009) http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/sccps_ap_2009_1230_final.pdf.
[8] Persistent Organic Pollutants Committee (2015) Risk Profile on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC.11/10/Add.2
[9] Zhang, Q et al. (2016) Environment International, **94** 43-50.
[10] U.S. National Toxicology Program Report on Carcinogens, Fourteenth Edition, Chlorinated Paraffins (2016) http://ntp.niehs.nih.gov/ntp/roc/content/profiles/chlorinatedparaffins.pdf
[11] Vorkamp, K. et al. (2014) Chemosphere, **111** 379-395.
[12] Tomy, GT et al. (2000) Environ. Sci. Technol., **34** 1615-1619.
[13] Reth, M. et al. (2006) Sci. Total Environ., **367** 252-260.
[14] Tomy, GT. (1997) Thesis, University of Manitoba, Winnipeg, Manitoba.
[15] Xia, D., et al., (2016) Environmental Sci. Technol., **50(14**) 7601-7609.
[16] Persistent Organic Pollutants Committee (POPRC) (2016) Risk Management Evaluation on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC12/11/Add.3.
[17]A Report of the Swedish Chemicals Agency: Analyses by the Swedish Chemicals Agency in connection with enforcement 2008-2013. And summarized in the Risk Management Evaluation on Short-Chain Chlorinated Paraffins. 2016. Persistent Organic Pollutants Committee (POPRC) Annex F Submission by Sweden. UNEP/POPS/POPRC12/11/Add.3.
[18] Persistent Organic Pollutants Committee (POPRC) (2016) Risk Management Evaluation on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC12/11/Add.3.
[19] Persistent Organic Pollutants Committee (POPRC) (2016) Risk Management Evaluation on Short-Chain Chlorinated Paraffins, UNEP/POPS/POPRC12/11/Add.3. (Annex F Submission by Austria), UNEP/POPS/POPRC12/11/Add.3).
[20] Strid, A. et al. (2014) A Report of the Swedish Toxicology Sciences Research Center and the Department of Materials and Environmental Chemistry, Stockholm University.
[21] Official Journal of the European Commission (2015), amending Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annex I: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32015R2030&qid=1492294902869&from=EN.
[22] Allan J. et al. (2017) Earth Negotiations Bulletin—A Reporting Service for Environment and Development Negotiations, Volume 15 Number 252: http://enb.iisd.org/chemical/cops/2017/
[23] Conference of the Parties to the Basel Convention (2017), Supporting information on the concentration levels to define the low persistent organic pollutant content values for persistent organic pollutants listed in Annexes A, B and C to the Stockholm Convention, UNEP-CHW.13-INF-66.