Optimising analytical methods for chlorinated paraffins to evaluate their levels in Australia

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Chapter 9

Final discussion and outlook

9.1 Key findings

The general aim of this PhD study was to advance analytical capabilities for chlorinated paraffins (CPs) to allow for the first time a preliminary evaluation of their levels in Australia.

Two literature reviews were conducted covering what was known about the environmental occurrence of these compounds (Chapter 2), as well as what the contemporary analytical capabilities were at that time (2014) and challenges arising from shortcomings with these (Chapter 3). The key findings of Chapter 2 confirmed the rising concerns about CPs, but also that a lot is still unknown about these compounds. CPs are high production volume chemicals (>1 million tonnes/yr in China alone) and the majority show resistance to environmental degradation (i.e. persistence, P). At least some CPs are globally distributed around the world (i.e. long-range transport potential), including remote areas, and are also suspected of bioaccumulation (B) and toxicity (T) potential. For example, SCCPs were classified as persistent organic pollutants (POP) under the Stockholm Convention in 2017 [1], while MCCPs are under evaluation by regulations such as REACH.

MCCPs and LCCPs have received little attention in the past, but as replacement chemicals for SCCPs, they are the focus of an increasing number of studies since 2014. Major knowledge gaps include information on the production from other countries suspected of relevant CP production volumes (i.e. India and Brazil), the environmental levels and hazard potential of MCCPs and LCCPs in general, as well as the evidence on which congener groups (including those of SCCPs) show PBT characteristics.

Their complexity and the challenges that arise with their chemical analysis, including quantification, make it difficult to address these gaps. Chapter 3 presented the key challenges, which are their response on most detection systems and their separation, by gas or liquid chromatography (GC or LC, respectively) and mass spectrometry (MS). Their response (i.e. signal on a detector for a given mass of CPs injected into an instrument) is low compared to other organohalogen compounds and, on most detectors, chlorine-dependant. Separation is problematic, as single GC and low resolution MS (GC-LRMS, resolution of 1,000) is unable to differentiate between CPs as well as distinguish them from other organohalogen compounds. In addition, suitable individual standards for congener specific analysis and certified reference materials (CRMs) for method validation are commercially unavailable. In the absence of individual standards, analysis relies on using mixtures for quantification. Because of the chlorine-dependant response of CPs, the compositions (i.e. relative abundance of the congener groups) of these mixtures must resemble as much as possible those found in samples to prevent quantification errors. This is difficult in case of environmental matrices, particularly for biota, in which the composition might differ because of 'weathering' effects by environmental and biological processes. The current available quantification mixtures cannot individually provide a quantification reference for the mixtures found in such samples.

Chapters 3 and 4 presented the different analytical methods developed over the years,

all with varying success. As a result, large differences in results are found between laboratories, as shown in Chapter 4. This review found that biota samples appeared to be most challenging matrices, with up to 137% 'between-lab' coefficient of variation (CV). Over recent years, the difference has gradually decreased however, resulting in between-lab CVs in the 2016 interlaboratory comparison of ca. 50% (standard solution), 47% (soil), 72% (dust) and 50% (biota), suggesting improvement.

With Chapter 3 a novel promising method, the chlorine-enhanced atmospheric pressure chemical ionisation time-of-flight MS, APCI-ToF-HRMS [2], was identified due to the high resolution (10,000) and fast acquisition time (<2 min acquisition time), while two-dimensional GC (GC×GC) could also be a promising tool to be further explored. Hence, in Chapter 5 we tried to improve these capabilities by developing and/or adapting two determination methods and evaluating these two techniques, along with existing techniques, to identify the most suitable one for the purposes of this study. A GC×GC coupled to a micro-electron capture detector (GC×GC-μECD) technique was developed and combined with a chlorine response correction method for quantification. Even with GC×GC though, separation between congeners remains largely incomplete, but the technique can detect and separate at least some lower chlorinated congeners (CPs with $Cl_{<5}$). The APCI-ToF-HRMS method was also adapted by increasing the resolution (21,000) and sensitivity for lower chlorinated CPs, and by combining it for the first time with the same chlorine response correction method as GC×GC. To identify the most suitable technique for this study, the performance of these two novel methods as well as two existing methods was evaluated. The APCI-ToF-HRMS was found most suitable, as it is relatively fast, able to detect all CPs (including CPs with Cl_{3-4}) and achieves the required MS resolution needed for differentiation between congener groups as well as other compounds such as polychlorinated alkenes. This method also produced satisfactory results (z scores <2) in the latest interlaboratory study rounds (Chapter 4) and in the interlaboratory study organised by EU-RL [3]. We also aimed to advance analytical capabilities by identifying suitable SCCP levels in the three candidate CRMs by four different instrumental methods. The agreement in the quantification between most of the instruments provide a good basis for the possible certification of one of these materials.

Using the APCI-ToF-HRMS technique, Chapters 6-8 allowed a quantification and evaluation of CPs levels in Australia. For this we choose samples with potentially increasing complexity that were available through systematic sampling and archiving programs at QAEHS. Specifically, we analysed CPs in sewage sludge from 15 waste water treatment plants, extracts of passive air samplers deployed for one year at 15 sites covering different land-use, and stratified pooled serum samples from the Australian Human Biomonitoring Program covering different collection period and age groups.

The APCI-ToF-HRMS method was very efficient in measuring CPs in sewage sludge (Chapter 6) due to the high concentrations of these chemicals and the close resemblance of the composition in the quantification mixtures and the actual samples. Hence, the

deconvolution method of Bogdal et al. [2] was sufficient for quantification. MCCPs dominated over SCCPs, with concentrations ranging from below method detection limit (<MDL) to1,400 and 540-3,600 ng/g dry weight for SCCPs and MCCPs, respectively. These levels were similar to those reported elsewhere (apart from China). CP levels were high and sample amount extracted were large, and maybe because of this also LCCPs were detected (<MDL-960 ng/g dry weight).

The APCI-ToF-HRMS method also allowed quantification of CPs in air (Chapter 7). The CP composition in air can differ from the quantification mixtures used in this study. To overcome this, the chlorine correction quantification method was successfully applied. MCCPs were only found above the limit of quantification at two sites, while SCCPs were found at ten. Estimated annual mean concentrations ranged from <MDL to 1.3 and <MDL to 1.8 ng/m^3 for SCCPs and MCCPs, respectively, with a significant decreasing trend in levels from densely populated areas to less dense ones. These atmospheric concentrations from all sites, representing mostly remote and rural sites, were in the lower range of levels reported globally, which have been predominantly urban and industrial sites. They were still higher (30-fold) than extremely remote sites (i.e. polar regions).

We further explored the same technique used in Chapter 7 to assess the occurrence and accumulation of CPs in the general Australian population by using pooled human serum (Chapter 8). SCCPs concentrations ranged from <MDL to 360 ng/g lipid weight and those for MCCPs from <MDL to 910 ng/g lipid weight. In terms of time trends, ΣSCCPs levels were below the MDL in serum collected between 2002 and 2011 with levels above the MDL in the latter collection periods (i.e. 2012–2015). We further found that ΣMCCPs levels showed an increasing trend since 2008, suggesting an increasing exposure to humans. While no significant trend with age groups was identified, highest levels were found in the oldest (46-60 years) and youngest cohorts (<4 years). Considering their current principal applications in Australia (e.g. plasticisers, lubricants and flame retardants in indoor materials), indoor exposure might be likely.

Throughout this thesis, CP levels were sometimes compared with that of a typical persistent, bioaccumulative and toxic compound, i.e. a legacy POP, polychlorinated biphenyls (PCBs). An example is their estimated cumulative production [10], ca. 10-fold higher than PCBs [29]. For some of the same air sampling sites and serum samples analysed in this PhD study, PCB levels were also analysed. SCCPs and MCCPs surpassed the PCB concentrations at the same air sites by 28 and 47 times, respectively, and by 13 and 26 times in the same serum samples confirming that CPs have the potential to accumulate in humans. Others also found CPs in substantial amounts in (mainly aquatic [14]) biota, as well as in human breast milk in levels associated with health risks [30]. Considering this and their still increasing annual production volumes, more attention to these compounds is warranted to investigate whether control measures are needed and for which type of CPs.

9.2 Discussion and future perspectives

Review and analysis of literature in this thesis showed that CPs are produced in large amounts, distributed across the globe and there is a need for systematic studies. While the thesis focused on contributing to the improvement of the analysis of CPs to provide much needed information on their contemporary levels, it is apparent that still more work is required on improving the analysis. In regard to future perspectives and areas for improvement, two aspects in particular, viz. chemical analysis and hazard potential assessments, are discussed in order to better assess potential risks associated with the former and current use of CPs, and to ultimately allow accurate risk assessments and the establishment of effective regulation to prevent harm and control risks.

9.2.1 Chemical analysis

Currently, a standardised method for CP analysis is still unavailable. Current rapid developments in instrumental techniques (e.g. HRMS Orbitrap and ToF, possibly in combination with GC×GC etc.) bring a satisfactory method within reach, and more improvements are expected. For example, in reporting information per congener group, or even congener-specific analysis by using the GC×GC developed in this study, may be possible in the near future.

Due to the recently acquired POP status of SCCPs, accurate analytical techniques should be able to at least differentiate between SCCPs and MCCPs. MCCPs are currently often found in higher levels than SCCPs [9, 12-14], which is a reason to analyse MCCPs as well. In general, reporting total SCCPs, MCCPs or LCCPs, let alone total CPs, is unlikely to be very meaningful from a fate, toxicological and hazard potential context. The uptake, and biological persistence and potential health effects of CPs are all likely structure-dependant. Different alternatives are considered and discussed below. These include congener-specific analysis, congener group-specific analysis (e.g. $C_{10}Cl_5$, $C_{10}Cl_6$), and analysis per carbon chain length and different chlorination degrees (e.g. C10 50% Cl).

The GC×GC technique developed in this study and the increasing number of individual CP standards that are becoming available (Chiron, Norway) enables congener specific analysis, although it is recommended to use HRMS ToF instead of μECD. One of the drawbacks of congener-specific analysis is that it would need a lot of reference standards, which are still unavailable [15]. It would also lead to enormous datasets, for which integration and quantification procedures will be tedious and time consuming for routine monitoring [15]. Data reduction (i.e. marker congeners) may help in focussing on the relevant information. Suggested future studies would start with evaluating the available individual standards on their 'CP marker' potential, i.e. CPs with high toxicity potential, found at higher concentrations in the environment, in food, or in human fluids/tissues, as well as options for separation.

At the moment the APCI-qToF-HRMS is a very promising method as it can determine

both SCCPs and MCCPs (also LCCPs), differentiate between them and has the potential for congener group specific analysis. For quantification, the method that corrects for chlorine response, applied in this PhD study, as well as the deconvolution quantification method [2] can be applied,. The first one has the potential for carbon chain specific analysis and the second one has the ability for congener group-specific analysis for at least SCCPs [2]. The recently commercially available individual carbon chain lengths mixtures (i.e. C_{10} instead of $C_{10\text{-}13}$, $C_{14\text{-}17}$ or $C_{18\text{-}20}$) with different chlorination degrees (LGC limited, United Kingdom) further facilitate this type of analysis. More mixtures with a composition pattern other than the current commercial standards (LGC) and more like those of Cereclor, Witachlor and Hüls [16] are still needed.

Since the publication of the review on CP analysis in 2015 (Chapter 3), other promising novel methods have been developed. For example, Yuan et al. [17] also applied successfully the SCCP congener group-specific deconvolution method on data obtained by GC-ECNI-HRMS and GC-ECNI-Q-Orbitrap-HRMS. The congener group levels obtained by these three instruments agreed well with each other ($R^2 > 0.90$) [17] and all instruments have the required resolution to differentiate between CPs and other compounds. Xia et al. [18] developed a method using GC×GC-ECNI-ToF-MS, although this method still only accounts for CPs with $Cl_{5\text{-}10.}$

Partly because of these developments, the use of the most commonly applied techniques at the start of this PhD study (GC coupled to a LRMS in electron capture negative ionisation mode, GC-ECNI-LRMS [19]) is gradually decreasing. The results of Chapter 4 show that the results obtained by this technique are often unsatisfactory (z-scores > 3), typically resulting in an underestimation (see Chapter 5). It may be time to completely move away from GC-ECNI-LRMS and caution should be taken when interpreting data obtained with this technique.

Probably because the lack of a standardised method, including quality assurance and quality control (QA/QC) practices, information on QA/QC reported in studies focusing on determining CPs in the environment is limited in many studies. For example, information about blank level values, established MDLs (including how they are established), relative standard error values for the quantification methods used, calculated chlorine content of the mixtures (when using a chlorine response correction factor) and relative abundance of the CP congener groups, all essential for the quality of the results, are often missing in reports and publications.

Blank levels (range) in particular should be reported. The relatively high CP levels in dust [20] could be a major contamination problem for CP analysis, especially in typically low level matrices such as biota, air, and humans. SCCPs, MCCPs and LCCPs are found in μg/g levels in dust (dry weight) and measures should be taken to prevent inadvertent contamination when doing extractions. Examples are working in a clean room with low particle density and covering everything with aluminium foil. It is also crucial to take multiple (e.g. *n*=1-2 per batch of 6-8 samples) procedural blanks through the extraction procedure, to investigate blank levels, including the consistency between blanks.

The experience from this thesis suggests that QA/QC pose many challenges to the analysis of CPs. Transparent reporting of QA/QC parameters including those of blanks etc. are essential for the interpretation of data. It is recommended QA/QC practices be specified as a matter of routine for CP analysis. Certifying some of the candidate CRMs will assist in that. Continuing to monitor laboratory agreements, such as that by EU-RL for dioxins and PCBs (Freiburg, Germany) might assist in standardising the analysis that hopefully include QA/QC practices as well.
In summary, given the current developments, it is now prudent to start focusing more on the analysis of congener groups, or at least carbon chain lengths with different chlorination degrees, rather than the groups (i.e. ΣSCCPs, ΣMCCP, ΣLCCPs) to better understand their hazard potential.

9.2.2 Hazard potential assessments

Assessing the hazard potential of CPs includes investigating their global distribution as well as determining accurate levels and their PBT potential. For assessing their global distribution, identifying 'hot-spots' (i.e. countries and/or environments in which the levels are high) and their accumulation potential, data from different studies are usually compared. Comparing CP results obtained by studies with different instrumental techniques is difficult, because of the large differences found in results for the same samples between them (i.e. between-lab CVs, Chapter 4). When comparing data obtained by different techniques, data from a given instrument could be reported by taking the average along with an average error percentage from that instrument, which can be determined by the results of interlaboratory studies. This will facilitate a general comparison and is another reason to continue monitoring the instrumental agreement in results by interlaboratory studies, not only for SCCPs but also for MCCPs.
While congener-specific assessments of PBT potential are still difficult due to separation issues, assessing the PBT potential per carbon chain length with different chlorinated degrees is possible and preferred over assessments based on groups. This is because the potential is dependent on the carbon chain length, the chlorine content, or both. For example, in terms of environmental persistence, Gawor et al. [21] modelled the half-lives of CPs in air and found them to be more dependent on the chlorine content than carbon chain length, i.e. CPs with a higher chlorine content have relatively longer half lives in the environment. The metabolism potential is also dependent on the carbon chain length, i.e. CPs with shorter carbon chain lengths have a higher metabolism potential. Low chlorinated C14 MCCPs might be in turn more degradable than high chlorinated SCCPs. A key question in degradation potential is which compounds CPs degrade (or metabolize) more easily and how. Do they degrade down to other CPs with shorter chain lengths and fewer chlorine atoms?
In terms of identifying environments containing high levels of CPs, limited data shows that CPs can be found in extremely high, though varying amounts in indoor materials such as glass surface films [23], domestic products[24], ovens [25], hand blenders [26]

and in dish cloths [27]. Therefore, more indoor exposure assessments are recommended, including investigating indoor compartments suspected to contain CPs, (i.e. indoor air, dust and food), but especially potentially high risk exposure groups (i.e. toddlers and pets). As CPs accumulate in dust, exposure of toddlers, due to their relatively large dust intake (ca. 15% [28]), and pets, due to living habits low to the ground, should be investigated. This also includes assessing CP levels in different brands/types of the same product/object (which has been done for example for ovens [25] and hand blenders [26]) to identify those with extremely high levels, as these varies between brands.
Clearly, more studies are necessary to investigate their PBT potential as well as current exposure to humans. Some analytical capabilities (i.e. SCCP congener group analysis [17] or carbon chain length with different chlorine content with APCI-ToF-MS) are available or within close reach to enable the commencement of such studies on uptake, distribution, degradation and elimination potential.

9.3 Final thoughts on terminology

The term 'chlorinated paraffin' and current sub-categorisation (i.e. SCCPs, MCCPs and LCCP) raises some uncertainties. First, there is variation in what defines a polychlorinated *n*-alkane as a 'chlorinated paraffin'. The term 'chlorinated paraffin' was first mentioned in a peer reviewed article from 1916 [4]. As it is a technical preparation and a term used for industrial mixtures, it might also include other compounds. Their first known categorisation as such was in 1933 and based on their chlorine content, expressed in percentage terms and on a weight basis [5]. In 1974, Zitko et al. [6] defined CPs as a 'technical preparation' of $C_{10\text{-}30}$ paraffins with a chlorine content 20-70%. In 1993, Environment Canada defined CPs as polychlorinated *n*-alkanes with $C_{10\text{-}38}$, and a chlorine content of 30-70% [7]. Tomy et al. [8] defined them as $C_{10\text{-}30}$ with a chlorine content 30-70%. The term CP is currently also used for carbon chain lengths longer than 30 carbons [2], and shorter than ten [9].
Second, their sub-categorisation may be obsolete. Originally based on the carbon chain length ranges of petroleum feedstock mixtures used for producing CPs, CPs are categorised into three groups: short- ($C_{10\text{-}13}$), medium ($C_{14\text{-}17}$) and long- ($C_{>18\text{-}30}$) chain CPs [7]. China however, currently the world's largest CP producer and consumer [10], produces industrial mixtures irrespective of carbon chain lengths but rather on chlorine content [11]. In addition, their hazard potential is not only based on their carbon chian length but also on their chlorine content.
Around the 2000s, CPs were often described as polychlorinated *n*-alkanes, which is a more accurate term. However, historically introduced names are often very difficult to get rid of. For example, some of the recently international acquired classifications (i.e. POP) are associated with the term SCCPs [11]. The question is how large the differences are between MCCPs with a carbon chain length of 14 (not restricted) versus SCCPs with that of 13 (classified as POP), to classify them as separate groups.
Currently, they are largely known as CPs and their sub-categories. Hence, the term CP

was used throughout this thesis with the following categorisation: short- (C_{10-13}), medium (C_{14-17}) and long- ($C_{>17}$) chain CPs. However, using the term polychlorinated *n*-alkanes with different sub-categories is preferred in the future for more accurate assessments and subsequent regulation. The question is what categories (if any) are useful and how to establish those. To answer this question, individual congener standards are needed that can be studied in detail and form the basis for establishing the relationship between the specific structure of the CPs (i.e. the carbon chain length as well as the position and number of chlorine atoms on that chain) and their fate, bioaccumulation and toxicity.

References

[1] UNEP, 2017. SC-8/11: Listing of short-chain chlorinated paraffins United Nations Environmental Programme Stockholm Convention on Persistent Organic Pollutants. Stockholm, Sweden.

[2] C. Bogdal, T. Alsberg, P.S. Diefenbacher, M. MacLeod, U. Berger, 2015. Fast quantification of chlorinated paraffins in environmental samples by direct injection high-resolution mass spectrometry with pattern deconvolution. Anal. Chem. 87 2852-2860.

[3] K. Kraetschmer, et al., 2018. EU-RL Interlaboratory study on determination of chlorinated paraffins in coconut fat 2017. EURL-PT-CP_1703-CF. Final Version 06 March 2018. Freiburg, Germany.

[4] B.T. Brooks, I.W. Humphrey, 1916. The presence of benzene homologs in the high boiling distillates of petroleum. J. Am. Chem. Soc. 38 393-400.

[5] F.T. Gardner, 1933. Chlorinated paraffin: I. relation of chlorine content to physical properties. Indust. and Eng. Chem. 25 1211-1212.

[6] V. Zitko, E. Arsenault, 1974. Chlorinated parrafins: properties, uses, and potential pollution. Technical Report no. 941 of Department of the Environment Fisheries and Marine Service Research and Development Directorate. Environment Canada.

[7] Environment Canada, 2003. Canadian environmental protection act: priority substances list assessment report chlorinated paraffins.

[8] G.T. Tomy, A.T. Fisk, J.B. Westmore, D.C.G. Muir, 1998. Environmental chemistry and toxicology of polychlorinated n-alkanes. in: G. Ware (Ed.) Rev. Environ. Contam. Toxicol., Springer New York, USA. pp. 53-128.

[9] B. Yuan, V. Brüchert, A. Sobek, C.A. de Wit, 2017. Temporal trends of C8–C36 chlorinated paraffins in Swedish coastal sediment cores over the past 80 years. Environ. Sci. Technol. 51 14199-14208.

[10] J. Glüge, Z. Wang, C. Bogdal, M. Scheringer, K. Hungerbühler, 2016. Global production, use, and emission volumes of short-chain chlorinated paraffins – A minimum scenario. Sci. Total Environ. 573 1132-1146.

[11] POPRC, 2015. Short-chained chlorinated paraffins: Risk profile document UNEP/POPS/POPRC.11/10/Add.2. United Nations Environmental Programme Stockholm Convention on Persistent Organic Pollutants, Geneva, Switzerland.

[12] L.M. van Mourik, C. Gaus, P.E.G. Leonards, J. de Boer, 2016. Chlorinated paraffins in the environment: A review on their production, fate, levels and trends between 2010 and 2015. Chemosphere 155 415-428.

[13] S.H. Brandsma, L. van Mourik, J.W. O'Brien, G. Eaglesham, P.E.G. Leonards, J. de Boer, C. Gallen, J. Mueller, C. Gaus, C. Bogdal, 2017. Medium-chain chlorinated paraffins (CPs) dominate in Australian sewage sludge. Environ. Sci. Technol. 10.1021/acs.est.6b05318.

[14] L. Zeng, J.C.W. Lam, Y. Wang, G. Jiang, P.K.S. Lam, 2015. Temporal trends and pattern changes of short- and medium-chain chlorinated paraffins in marine mammals from the South China Sea over the past decade. Environ. Sci. Technol. 49 11348-11355.

[15] U. Fridén, 2010. Sources, emissions, and occurence of chlorinated paraffins in stockholm, Sweden. . PHd. Dissertation Stockholm University. Stockholm, Sweden.

[16] B. Yuan, T. Alsberg, C. Bogdal, M. MacLeod, U. Berger, W. Gao, Y. Wang, C.A. de Wit, 2016. Deconvolution of soft ionization mass spectra of chlorinated paraffins to resolve congener groups.

Anal. Chem. 88 8980-8988.

[17] B. Yuan, C. Bogdal, U. Berger, M. MacLeod, W.A. Gebbink, T. Alsberg, C.A. de Wit, 2017. Quantifying short-chain chlorinated paraffin congener groups. Environ. Sci. Technol. 51 10633-10641.

[18] D. Xia, L. Gao, M. Zheng, Q. Tian, H. Huang, L. Qiao, 2016. A novel method for profiling and quantifying short- and medium-chain chlorinated paraffins in environmental samples using comprehensive two-dimensional gas chromatography–electron capture negative ionization high-resolution time-of-flight mass spectrometry. Environ. Sci. Technol. 50 7601-7609.

[19] M. Reth, Z. Zencak, M. Oehme, 2005. New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. J. Chromatogr. A 1081 225-231.

[20] F. Wong, G. Suzuki, C. Michinaka, B. Yuan, H. Takigami, C.A. de Wit, 2017. Dioxin-like activities, halogenated flame retardants, organophosphate esters and chlorinated paraffins in dust from Australia, the United Kingdom, Canada, Sweden and China. Chemosphere 168 1248-1256.

[21] A. Gawor, F. Wania, 2013. Using quantitative structural property relationships, chemical fate models, and the chemical partitioning space to investigate the potential for long range transport and bioaccumulation of complex halogenated chemical mixtures. Environ. Sci.: Processes and Impacts 15 1671-1684.

[22] R. Thompson, M. Vaughan, 2014. Medium-chain chlorinated paraffins (MCCPs): a review of bioaccumulation potential in the aquatic environment. Integr. Environ. Assess. Manag. 10 78-86.

[23] W. Gao, J. Wu, Y. Wang, G. Jiang, 2016. Distribution and congener profiles of short-chain chlorinated paraffins in indoor/outdoor glass window surface films and their film-air partitioning in Beijing, China. Chemosphere 144 1327-1333.

[24] C. Wang, W. Gao, Y. Lliang, Y. Wang, G. Jiang, 2018. Concentrations and congener profiles of chlorinated paraffins in domestic products in China. Environ. Pollut. In press.

[25] C. Gallistl, J. Sprengel, W. Vetter, 2018. High levels of medium-chain chlorinated paraffins and polybrominated diphenyl ethers on the inside of several household baking oven doors. Sci. Total Environ. 615 1019-1027.

[26] B. Yuan, A. Strid, P.O. Darnerud, C.A. de Wit, J. Nyström, Å. Bergman, 2017. Chlorinated paraffins leaking from hand blenders can lead to significant human exposures. Environ. Int. 109 73-80.

[27] C. Gallistl, B. Lok, A. Schlienz, W. Vetter, 2017. Polyhalogenated compounds (chlorinated paraffins, novel and classic flame retardants, POPs) in dishcloths after their regular use in households. Sci. Total Environ. 595 303-314.

[28] U.E. Fridén, M.S. McLachlan, U. Berger, 2011. Chlorinated paraffins in indoor air and dust: Concentrations, congener patterns, and human exposure. Environ. Int. 37 1169-1174.

[29] K. Breivik, A. Sweetman, J.M. Pacyna, K.C. Jones, 2002. Towards a global historical emission inventory for selected PCB congeners — a mass balance approach: 1. Global production and consumption. Sci. Total Environ. 290 181-198.

[30] D. Xia, L.-R. Gao, M.-H. Zheng, J.-G. Li, L. Zhang, Y.-N. Wu, L. Qiao, Q.-C. Tian, H.-T. Huang, W.-B. Liu, G.-J. Su, G.-R. Liu, 2017. Health risks posed to infants in rural China by exposure to short- and medium-chain chlorinated paraffins in breast milk. Environ. Int. 103 1-7.