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Environmental risks of medium-chain chlorinated paraffins (MCCPs) - A review

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Abstract

Chlorinated paraffins are industrial chemicals which can be subdivided into short-chain (SCCP), medium-chain (MCCP), and long-chain (LCCP) chlorinated paraffins. The global production volumes of MCCPs are nowadays suspected to be much higher than those of S- and LCCPs, and the few available studies on the environmental occurrence of chlorinated paraffins report often higher MCCP than S- or LCCP concentrations in the environment. The present review focuses therefore on MCCPs specifically and provides a literature overview and a data analysis of the production volumes, PBT properties (persistence, bioaccumulation potential, and toxicity) and the worldwide measured concentrations of MCCP in environmental samples, biota, and humans. Furthermore, we include own measurements of technical CP formulations from China, the

major global producing country, to estimate the global production amounts of MCCPs. The key findings from this review are: 1) MCCPs are toxic to the aquatic environment and the available data suggest that they are also persistent. 2) Available time trends for MCCPs in soil, biota and most of the sediment cores show increasing time trends over the last years to decades. 3) MCCP concentrations in sediment close to local sources exceed toxicity thresholds (i.e. the PNEC). Our study shows that overall MCCPs are of growing concern and regulatory actions should be considered seriously.

INTRODUCTION

Polychlorinated *n*-alkanes, also known as chlorinated paraffins (CPs), are complex industrial chemicals with the molecular formula $C_nH_{2n+2-x}Cl_x$ and a chlorination degree varying from 30% to 70% by weight. According to their carbon chain length, CPs are subdivided into short-chain CPs (SCCPs, C_{10-13}), medium-chain CPs (MCCPs, C_{14-17}), and long-chain CPs (LCCPs, C_{18-30}). Depending on the alkane chain lengths and chlorination degrees, different technical mixtures of S-, M-, and LCCPs have different physicochemical properties[1] and are, therefore, used in various applications. In general, CPs are mainly used as flame retardants, plasticizers and extreme pressure additives.[2] Production and use volumes of CPs are nowadays higher than ever before and exceeded one million tons in 2013.[3–5] Therefore, CPs are among the industrial chemicals with the highest production volumes.

In the last years, the focus of the research community and of regulatory authorities - with respect to chlorinated paraffins - was mainly on SCCPs.[6,7] SCCPs have shown to be persistent,[8–10] bioaccumulative,[11] and toxic,[12] whereas for MCCPs these PBT properties are less well studied and still a matter of debate. MCCPs are more difficult to quantify accurately than SCCPs[13] and many studies have reported only SCCP (but no MCCP) concentrations.

The available data suggest, however, that especially MCCPs could be of critical concern to the environment. The global production amounts of MCCPs are nowadays suspected to be much higher than those of SCCPs,[14] and MCCPs are quite often measured in higher

concentrations in the environment than SCCPs. The US EPA,[15,16] Environment and Health Canada,[17,18] the European Union (EU),[19,20] and the European Chemicals Agency (ECHA)[21] have assessed the risks of MCCPs, but no production or use prohibitions or restrictions are yet in force. This is different for SCCPs which have been substantially restricted in the EU in 2000 and have also been listed in Annex A of the Stockholm Convention (meaning a global ban with time-limited specific exemptions) in 2017. In addition to these global treaties, several national/regional restrictions on the production and use of SCCPs have been enforced.[14] It is expected that due to their listing in Annex A of the Stockholm Convention, the production and use of SCCPs will decrease in the future and SCCPs will be replaced in most applications. The risk management evaluation adopted by the Persistent Organic Pollutants Review Committee proposed alternative products and processes for SCCPs and suggested, among other chemicals, also MCCPs as alternatives for SCCPs.[2] However, they stated clearly that most of the alternatives that have been identified in the risk management evaluation have not been assessed under the Convention and that it is unknown if some of these would exhibit persistent organic pollutant (POP) characteristics.

The present review aims therefore to support the ongoing risk assessment of MCCPs and provides a literature overview and a data analysis of the production volumes, PBT properties and the worldwide measured concentrations of MCCP in environmental samples, biota, and humans after 1995. Furthermore, we include measurements of the composition of technical CPs formulations from the major global producing country, China. So far, only a few technical mixtures have been analyzed for S- and MCCPs. Additional information on the composition of the technical CPs formulations is therefore highly important to estimate global production volumes of MCCPs.

Previous scientific reviews focused always on both SCCPs and MCCPs,[6,22–24] but the amount of information on SCCPs always surpassed those on MCCPs and limited a critical assessment of the MCCPs. Our review focuses therefore specifically on MCCPs and shows information on SCCPs only for comparison.

PRODUCTION AND USE

Production amounts for MCCPs have been reported for North America (17 800 t in 1998),[25] the UK (40 000 t in 1991),[26] and Russia (21 000 t in 2007, 27 000 t in 2011)[4] (Table S1, SI). Production capacities (but no production amounts) have been reported for the EU (45 000−160 000 t in 2004)[19] and Thailand (20 000 t in 1994).[27] Production amounts for MCCPs from the Asian market are not available, because manufacturer in Asia do not differentiate between S-, M-, and LCCPs. However, some information are available on the produced technical mixtures in China. The International Chlorinated Alkanes Industry Association (ICAIA) stated for example that nearly 90% of the CP mixtures produced in China in 2012 were CP-52.[3] CP-52 is characterized by a chlorine content of 52% and can include CPs of all chain length. One study has analyzed the fractions of S-, M-, and LCCPs in three CP-52 mixtures,[28] and four more measurements are available for the fraction of SCCPs in CP-52.[29–32] We analyzed ourselves eleven CP-52 mixtures, obtained in 2017 from nine different producers in China and determined the fractions of S-, M-, and LCCPs (Section S1.2 in the SI). MCCPs in CP-52 ranged (with one exception) between 29% and 67%, with a mean value of 57%. LCCPs were in all CP-52 mixtures below 12% with a mean of 4% and SCCPs ranged (with the one exception) between 24% and 63%. We do not know how representative the samples are, given that there are more than 120 CP producers in China,[14] but the measurements give at least a first indication of the range of the MCCPs in CP-52 as they cover around 10% of the producers. If we take the latest available production figure from China (1 050 000 t in 2013)[5] and assume that the manufacturer did not change the composition of CP-52 in the last five years to a great extent, MCCPs might have been produced in the order of 600 000 t in China in 2013. This number is much larger than any of the production amounts reported in literature for North America, Russia or the EU and indicates that China was the largest producer of MCCPs in 2013. Data for the last five years are missing, but CP production amounts were increasing in China before 2013,[14] and there is no indication that this trend has stopped or reversed.

Information on the use of MCCPs is very scare and restricted to the US,[33] the EU,[19,26,34–38] Norway,[35,39] and Japan[40,41] (Table S1, SI). It is known that the main uses of MCCPs are as secondary plasticizers in polyvinyl chloride (PVC), as extreme pressure additives in metal working fluids and as additives to paints, adhesives, sealants, rubbers and other polymeric materials.[19] However, not much is known about the applications areas in the specific countries. Numbers reported by the European Chemicals Bureau[19] indicate that MCCPs were mainly used as secondary plasticizers in PVC in the EU between 1994 and 1997. The only data further available are for Japan for 2001 and indicate a MCCP usage of around 50% in PVC and 40% as extreme pressure additives in metal working fluids.[40] More information on the uses of MCCPs are therefore urgently needed, especially if emission reduction strategies will become necessary in the future.

CHEMICAL PROPERTIES

MCCPs consists of thousands of congeners and the chain length and chlorination degree of the molecules influence most of the chemical properties. Therefore, for most of the properties exists not one 'true' value, but there is rather a range of values.

Physicochemical properties

Measurements for some physicochemical properties of MCCPs are available,[42–46] but they do not cover all groups of constitutional isomers nor all properties. Therefore, we derived in our previous work a set of property data for SCCPs and MCCPs, based on calculations with the quantum-chemical model COSMO*therm* and validated with data from literature.[1] In brief, the calculated logarithmic octanol-water partition coefficients range for MCCPs between 6.77 (for a C_{14}-CP with 35% chlorine) and 9.85 (for a C_{17}-CP with 70% chlorine) (Table S5, Fig. S2c), which shows the large preference of MCCPs for organic phases such as the lipid tissue of organisms compared to the aqueous phase. The values also indicate that soil and

sediment are likely to be relevant environmental reservoirs for MCCPs. Specific data for the congener groups and measured octanol-water partition coefficients are provided in Table S5. The calculated vapor pressure ranges for MCCPs between $6.64 \cdot 10^{-12}$ Pa (for a C_{17}-CP with 70% chlorine) and $1.31 \cdot 10^{-2}$ Pa (for a C_{14}-CP with 35% chlorine) (Table S4, Fig. S2a). A vapour pressure of $2.27 \cdot 10^{-3}$ Pa has been reported for MCCPs with a chlorine content of 45%,[19] and a vapor pressure of $1.3 - 2.7 \cdot 10^{-4}$ Pa for a C_{14-17}-CPs with 52% chlorine.[42] The calculated solubilities in water range for MCCPs between 0.02 μg/L (for a C_{17}-CP with 70% chlorine) and 40.4 μg/L (for a C_{14}-CP with 35% chlorine) (Table S4, Fig. S2b). Madeley and Gillings[43] determined the solubility of a C_{15}-CP with 51% chlorine to be 5 μg/L, Campbell and McConnell[42] reported the solubility of a C_{16}-CP with 52% chlorine to be 10 μg/L. With these chemical properties ranging over several order of magnitudes, MCCPs are prone to a complex behavior and fate in the environment. Thus, MCCPs partition in the environmental compartments, such as in the atmosphere (gaseous/particulate phase) and in water (dissolved/particulate phase). Therefore, a review about the occurrence of MCCPs in the environment needs to consider all environmental matrices and their sub-phases.

Degradation in the environment

The degradation of MCCPs in the environment has been reported in water and secondary activated sludge. Degradation in air through the reaction with OH radicals, and degradation in soil and sediment through biodegradation might be possible, but studies which confirm these degradation pathways for MCCPs are missing. Estimated half-lives in air and soil from EPI Suite™ are provided in Section S2.1 in the SI; however, it is unclear how realistic the data are.

Photochemical degradation The degradation of CPs in water through photochemical dechlorination was investigated by Koh and Thiemann.[47] The obtained half-lives in water for CP mixtures with 30−53% chlorine ranged between 9.6 hours (for a C_{17-24}-CP with 35%

chlorine) and 12.8 hours (for a C_{12-18}-CP with 52% chlorine). However, these half-lives are only relevant for chemicals in the uppermost water layer. MCCPs in deeper water layers cannot be photochemically degraded due to a lack of UV radiation.

Biodegradation Ready biodegradation tests in secondary activated sludge reported by the MCCP manufacturer in the EU showed no biodegradation for C_{14-17}-CPs with 63.2% chlorine and C_{15}-CPs with 51% chlorine. Only substances/mixtures with a chlorine content below 46% were readily biodegradable.[48] According to these data, MCCP congeners with more than 46% chlorine have to be considered as persistent, which is in line with the estimated data from EPI Suite™ (Table S6). Reliable studies on the biodegradation of MCCPs in water, soil, or sediment are missing.

Transformation pathways and products Bergman et al.[49] reported that synthetic CPs and commercial CP products are transformed into a large number of aromatic hydrocarbons as well as numerous polychlorinated aromatic compounds at temperatures above 300 °C. They stated that dehydrohalogenation of the aliphatic structure, followed by ring formation, is most probably the explanation for the formation of aromatic compounds. Schinkel et al.[50] confirmed dehydrohalogenation reactions of chlorotridecanes (and the formation of chlorinated alkenes) at temperatures above 160 °C. Furthermore, photochemical and bacterial dechlorination of MCCPs have been observed.[47,51] No study has observed yet degradation pathways which could lead to a chain length reduction. However, a break-down of carbon-carbon bonds is considered a critical reaction pathway because this would transform long- and medium-chain to short-chain CPs.

Conclusion Not much has been published so far on the degradation of MCCPs, but the available data from the ready biodegradation tests in secondary activated sludge point out that MCCP congeners with more than 46% chlorine have to be considered as persistent.

Bioaccumulation and biomagnification potential

A review of the bioaccumulation potential of MCCPs in the aquatic environment is available from Thompson and Vaughan [52] from 2013. The following paragraphs summarize the findings of Thompson and Vaughan [52] and describe additionally studies published after 2013.

BCF & BAF No study has reported so far reliable bioconcentration or bioaccumulation factors for MCCPs. Available (omitted) studies are summarized in Table S9 in the SI.

BMF Laboratory-derived biomagnifictation factors were reported by Fisk et al. [53,54,55] However, the results show no clear trend: BMFs for C_{14-17}-CPs ranged between 0.3 and 5, with a mean of 1.6 and a median of 0.99. A detailed data analysis is provided in Section S2.3. Field-derived BMFs for MCCPs were reported by Houde et al. [11] and Zeng et al. [56] BMFs reported by Houde et al. [11] were generally below one. Field-derived BMFs reported by Zeng et al. [56] were above one but questionable (Table S9, SI).

TMF No bioaccumulation of MCCPs was found in the food webs studied by Houde et al. [11], NIVA [57,58,59] and Huang et al. [60] Miljodirektoratet [61] and Zeng et al. [56] otherwise, calculated trophic magnification factors above one, which would indicate an increase in the chemical concentration in the biota with increasing trophical level. However, the TMFs in both studies were derived from concentrations in different tissues and are therefore questionable.

Conclusion It remains so far unclear whether or not MCCPs are bioaccumulative and there is therefore an urgent need for reliable studies that investigate the bioaccumulation and biomagnification potential of these chemicals. Studies on the BMF and TMF should pay attention to compare concentrations in similar tissues. Also, care should be taken that animals are representatives of the same food web.

ECHA [62] considered C_{14}-CPs with 40% to 56% chlorine and C_{15}-CPs with 51% chlorine as potentially bioaccumulative and proposed that the bioaccumulation potential of MCCPs is

decreasing with increasing carbon chain length and chlorine content. However, if we consider the available measured data for SCCPs and MCCPs (Section S2.2), no clear trends with carbon chain length or chlorination degree are visible. ECHA requested aqueous and dietary exposure tests from the registrant manufacturers for C_{14}-CPs with 50−52% and 55−60% chlorine until September 2018,[63] but tests for MCCPs with other carbon chain lengths and chlorination degrees will most probably be necessary to conclude whether or not MCCPs (or single congener groups of the MCCPs) should finally be considered as bioaccumulative.

Eco-toxicity

Toxicity to soil organisms To date, the highest sensitivity of organisms to MCCPs in soil has been observed for the earthworm *Eisenia fetida*.[12,64] The data show that a statistically significant decrease in reproduction occurred at 900 μg/g dry weight (dw) soil. The predicted no-effect concentration (PNEC) in soil for *Eisenia fetida* reproduction was estimated to be 28 μg/g dw soil, based on a no observed effect concentration (NOEC) of 280 μg/g dw and an assessment factor of ten.[12] The organic carbon (OC) content in the study was 4.7%, which gives a PNEC of 5.9 mg/g OC. The study was conducted with a C_{14-17}-CP with 52% chlorine.

Toxicity to sediment organisms Among the organisms tested, *Hyalella azteca* and *Lumbriculus variegatus* have the highest sensitivity to MCCPs in sediment. *Hyalella azteca* showed a statistically significant reduction in mean weight at 270 mg/g dw sediment, *Lumbriculus variegatus* showed a statistically significant reduction in the mean total weight of worms/replicate at 410 mg/g dw sediment.[12,19,65,66] The PNEC in sediment was estimated to be 13 μg/g dw for both organisms, based on a NOEC of 130 μg/g dw sediment and an assessment factor of ten.[12] The organic carbon content in both studies was around 5%, which gives a PNEC of 260 μg/g OC. Both studies were conducted with a C_{14-17}-CP with 52% chlorine.

Toxicity to aquatic invertebrates MCCPs show toxicity to *Daphnia magna* in both short- and long-term exposure.[12] Most of the data available have been generated using a C_{14-17}-CP mixture with 52% chlorine. A 48-hour EC_{50} of 5.9 μg/L was reported for *Daphnia magna*,[12,67] although other studies suggest that the EC_{50} might be higher than this value.[12] Long-term studies with *Daphnia magna* suggest that the 21-day LOEC for MCCPs is at around 18 μg/L and the NOEC at around 10 μg/L.[12,68] The PNEC for MCCPs in water for aquatic invertebrates was estimated to be 1 μg/L, based on the NOEC of 10 μg/L for *Daphnia magna* and an assessment factor of ten.[12]

Toxicity to fish So far, only one study has reported the toxicity of MCCPs to fish. Cooley et al.[69] exposed rainbow trout to different concentrations of C_{14}-CPs in food and found behavioral effects as well as effects on liver and thyroid histology for the C_{14}-CP with 55% chlorine at concentrations of 0.22 and 1.3 μg/g wet weight (ww) whole fish. No effects were observed for the C_{14}-CP with 48% chlorine at concentrations between 0.02 and 0.11 μg/g ww whole fish. We propose here therefore a PNEC for the toxicity of MCCPs to rainbow trout of 11 ng/g ww whole fish, based on the NOEC of 0.11 μg/g ww whole fish and an assessment factor of ten. A lipid content of 0.24 g lipid/g ww whole fish[70] gives a PNEC of 46 ng/g lipid whole fish for rainbow trout.

Conclusion MCCPs meet the toxicity threshold defined under REACH (chronic NOEC or EC_{10} for freshwater organisms below 10 μg/L)[71] and should therefore be considered as toxic to the environment. This is in line with the European CLP Regulation which classified MCCPs as acute and chronic toxic to the aquatic environment.[72]

OCCURRENCE OF MCCPS IN THE ENVIRONMENT, BIOTA, AND HUMANS

The following subsections discuss the world-wide measured concentrations of MCCPs in the environment, biota, and humans. The very first subsection discusses the sources of errors in the measurements to illustrate the uncertainties in the data.

Sources of errors in the measurements

So far, no standard method for analyzing chlorinated paraffins has been available; which means that basically each laboratory has been using its own method. We have recorded the instrumental technique and the quantification method used in the different studies (Tables 1 to 6), but it is beyond this review to evaluate the different methods, as this has been addressed before.[73] However, we would like to point out the largest uncertainties associated with the measurements and discuss the consequences for data interpretation. First, it is important to note that almost all reported MCCP concentrations were obtained by gas chromatography coupled to mass spectrometry (GC-MS) and that MCCPs with 16 and 17 carbon atoms were hardly detected due to their low vapour pressure which results in long retention times and their inseparability in the GC. The use of direct liquid injection mass spectrometry as applied in the new method of Bogdal et al.[74] is an elegant alternative to GC-MS for analyzing MCCPs (and LCCPs) in the future. Also, methods based on liquid chromatography are used now more often[28,75,76] and are interesting alternatives to methods based on GC-MS. Gas chromatography coupled to electron capture negative ionization mass spectrometry (GC-ECNI-MS), as used by most of the laboratories, also has the disadvantage that lower chlorinated CPs ($<Cl_5$) are not detected.[6,23] The reported chlorination degrees of low chlorinated mixtures are therefore systematically too high.[77] Another disadvantage of this method is that the external standard mixture used for quantification must have an average molecular mass and a chlorination degree as similar as possible to the sample.

Basing the quantification on a standard with a significantly different chlorination degree than the sample, can appreciably affect the results and easily falsify the measurements by up to an order of magnitude.[77] Reth et al.[77] suggested to derive a linear relationship between instrumental response and the chlorine content of the external standard mixture, to correct for the inevitable difference in the chlorination degree between the standard mixture and the field sample. We have indicated in Tables 1 to 6 under 'compensation' whether the authors of the studies used such a linear correlation to compensate for differences in the chlorine content of sample and standard. An alternative is to use specific chain-length standards and response factors for each congener group, as recently suggested by Yuan et al.[78] Another important aspect to note is that around 40% of the studies conducted measurements with low resolution mass spectrometry (LRMS). However, mass spectrometers with a resolution below 10 000 FWHM are not able to resolve the commonly occurring mass interferences from different CP congener groups (for example interferences between $^{12}C_{18}{}^{1}H_{30}{}^{35}Cl_4{}^{37}Cl_4$ (533.97 Da) and $^{12}C_{16}{}^{1}H_{25}{}^{35}Cl_8{}^{37}Cl_1$ (533.91 Da)). LCCP congener groups which cannot be resolved from the MCCP congener groups therefore increase the MCCP concentration by at least 15% (for the calculation see Section S3 in the SI.) An increased response factor of the longer-chained CPs will increase this percentage even further.[74] In addition to the commonly occurring mass interferences, other mass interferences from, for example, transformation products[79] or unexpected fragment ions formed during the ionization[80] can complicate the analysis even more. However, Schinkel et al.[79,81] and Yuan et al.[80] showed that it is possible to identify the target congeners when applying deconvolution procedures. Zeng et al.[82] presented a method where they used the isotope abundance of the interferential congeners and an algebraic equation group to obtain the true integrated ion signals. Both procedures (deconvolution and the algebraic equation group) are options to decrease the interferences computationally and we highly recommend to use one of these procedures for the analysis of MCCPs with LRMS.

General remarks

If we go through the Tables 1 to 6, where we have listed all the studies that reported MCCP concentrations in the environment, biota, and humans and check a) which studies have used HRMS, or LRMS with a mathematical procedure to reduce the interferences between the congeners (methods of Bogdal et al.[74] or Zeng et al.[82]) and b) which studies have compensated for the differences between chlorine content in standard and sample, not many studies are left. Taking all the other possible error sources into account, which we have listed above, we have to assume that most of the reported concentrations are not very accurate. We believe, however, that the overall picture from the whole set of measurements and studies is - at least at the order of magnitude - correct and will give valuable insights into the environmental contamination with MCCPs. This is also very reasonable if we consider the results from the available interlaboraty studies with SCCPs.[83–85] Tomy et al.[83] found differences between the assigned values and the reported concentrations from -30% to 310%. The latest interlaboratory study of van Mourik et al.[85] reported differences of up to 54%. Therefore, we will take a more general approach and interpret ranges of the measured concentrations rather than single values. The ranges in the texts in the following paragraphs refer always to the 25^{th} to 75^{th} percentile of the reported data of each study. Thus, outliers which might be due to measurement errors are cut out. We also excluded some of the studies which measured obviously unrealistic concentrations (Table S9, SI). Also, studies before 1995 were excluded because only semi-quantitative analytical methods were available.[86] Values below the limit of detection reported in the original study were predicted using the Robust Regression on Order Statistics implemented in R.[87] This method performs a regression on the data assuming log-normal quantiles. The regression line is used to predict unknown observations and summary statistics are computed based on the predicted and reported observations. This approach was used because it ensures that measurements below the limit of detection are included in the assessment and are not arbitrarily substituted or omitted.

MCCP concentrations in air

MCCP concentrations in air (in the vapor and particulate phase) have been measured in the Arctic, Antarctic, Europe, and Asia (Fig. 1, Tables 1 and S10). However, measurements from other areas of the world like North- or South America, Africa, or Australia are also needed to get a more complete picture of the global distribution of the MCCPs in air. The reported MCCP concentrations in air are lowest in the Arctic and Antarctic (4–140 pg/m^3) and highest in Asia (600–36 500 pg/m^3). Peak concentrations were measured in China[88] with up to 360 000 pg/m^3. MCCP concentrations in air measured in Asia and Europe are in the

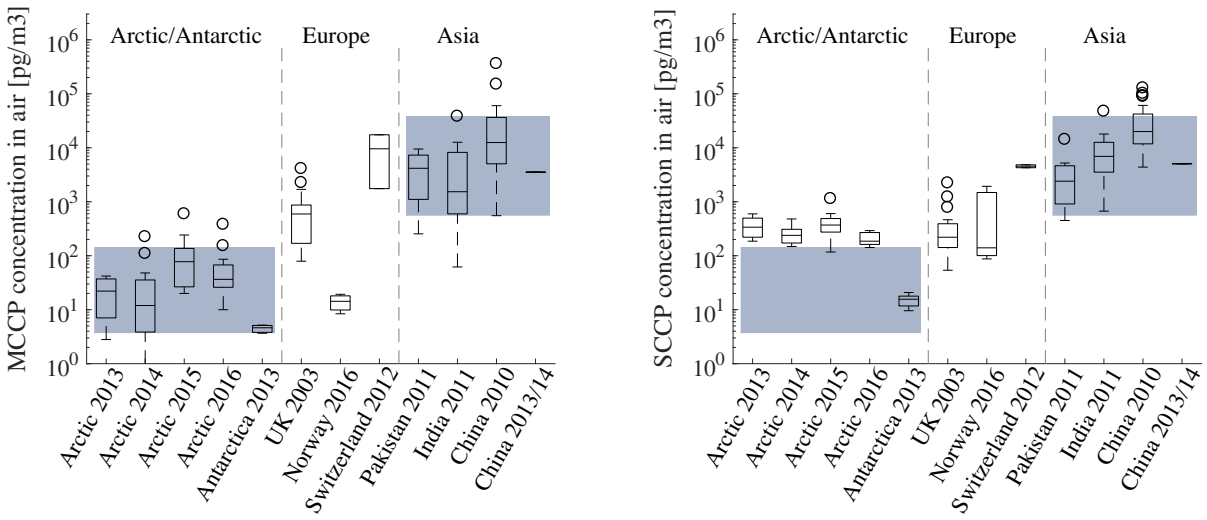

Figure 1: MCCP and SCCP concentrations in air. The blue rectangles indicate the MCCP concentration ranges in the specific regions. The data from the Arctic are only semi-quantitative.

same order of magnitude as SCCP concentrations measured at the same locations and time points (Fig. 1, Table S10). MCCP concentrations in air in the Arctic are, however, around one order of magnitude lower than the SCCP concentrations.[89–92] This indicates a slightly lower long-range atmospheric transport potential of MCCPs compared to SCCPs. However, the data from the Arctic[89–92] have to be considered as semi-quantitative as the contribution of possible contamination during sampling and analyses has not been fully validated and blank levels in some samples were quite high.[92] Also, only C_{14} and C_{15}-CP congeners have

been measured. Thus, final conclusions on the long-range atmospheric transport potential will only be possible if qualitatively better data are available.

MCCP concentrations in water

MCCP concentrations in water bodies that are not directly contaminated by a point source (background sites) are only available for Lake Ontario, Canada[11] and for stormwaters in Oslo, Norway[57,59,93] (Fig. 2, Tables 1 and S10). However, the measured MCCP concentrations in Lake Ontario were conducted with filtered water and are not representative since MCCPs are also attached to particles. MCCP concentrations measured in the stormwaters in Oslo were in the range from 15 to 130 ng/L water and, thus, slightly lower than the SCCP concentrations at the same sites and points in time (Fig. 2). One study reported also MCCP concentrations in a water body close to a local source in the Canadian Arctic. The MCCP concentrations ranged between 24.5 and 102 ng/L and were a factor of five higher than the SCCP concentrations from the same site. The concentrations from both studies were one order magnitude lower than the reported PNEC for MCCPs in water (1000 ng/L).[12] However, the studies are not representative for other areas and given that MCCPs are widely discharged to water bodies after their use as cutting fluids in metal working applications,[19] more measurements of MCCP concentrations in water are urgently needed. Most important would be measurements close to industrial sites to see whether or not MCCPs pose a risk to aquatic organisms close to these sites.

MCCP concentrations in soil

MCCP concentrations in soil are available for Europe, South Africa, and China (Fig. 3, Tables 1 and S10). The measured concentrations do not show large differences between regions, particularly when compared to the ranges observed in air. Measured MCCP concentrations at background sites range between 1 and 37 ng/g dw in Europe and China, and between 15 and 305 ng/g dw in South Africa. The measured MCCP concentrations from Xu et

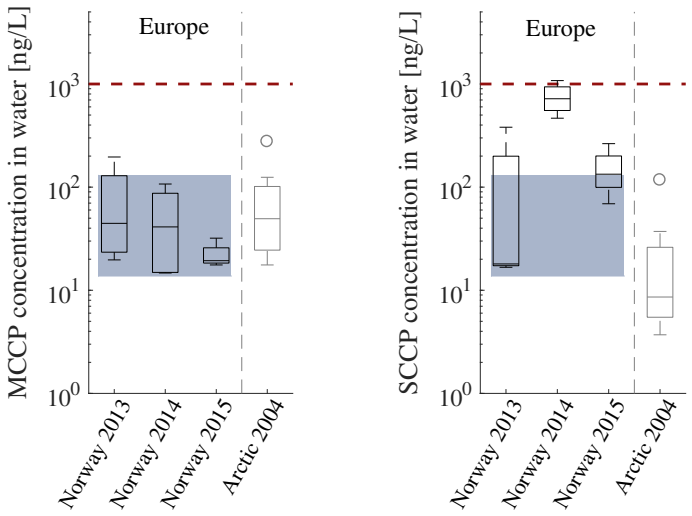

Figure 2: MCCP and SCCP concentrations in surface water. The blue rectangles indicate the MCCP concentration ranges in the background sites. The box plot in grey represents a site close to a local source. The horizontal dashed lines show the PNECs for MCCPs and SCCPs, respectively.

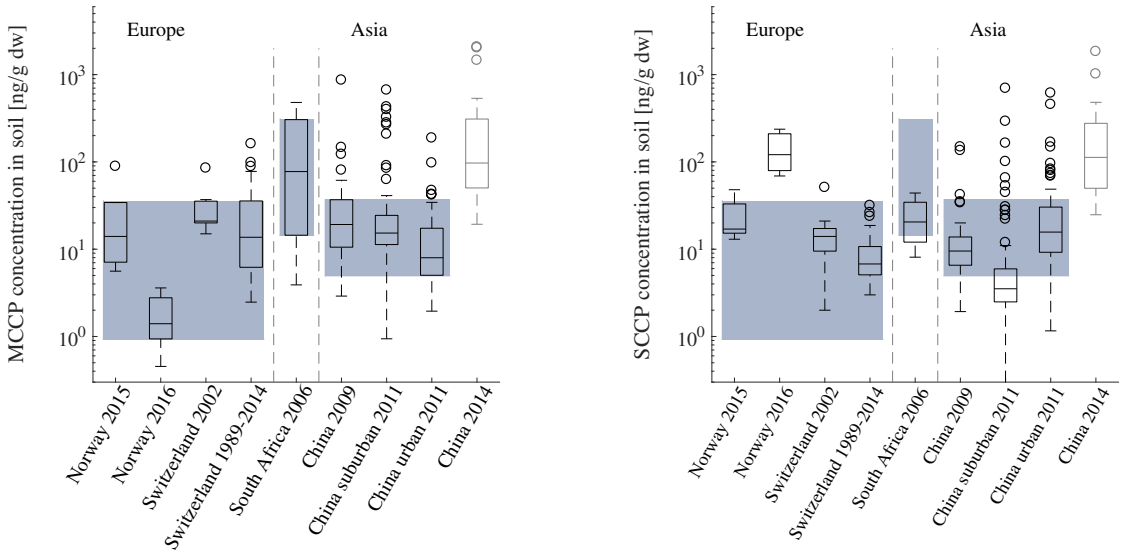

Figure 3: MCCP and SCCP concentration in soil. The blue rectangles indicate the MCCP concentration ranges in background soil in the specific regions. The box plot in grey represents a site close to a local source.

al.,[94] which are from sites close to a CP production plant in China, are in the same range as the background soil concentrations in South Africa (50 to 310 ng/g dw).[95] The MCCP concentrations measured by Bogdal et al.[96] are shown here as one box plot; however, they encompass archived soil samples from six sampling sites in Switzerland, covering the period from 1989 to 2014. The authors could show that MCCP concentrations in soil increased during the whole time period by a factor of two to three, with the highest concentrations occurring in the last sample from 2014.

MCCP concentrations in soil in Europe (except Norway 2016) and China are in the same range as the SCCP concentrations measured at the same sites and points in time (Fig. 3).

Although, the measured MCCP concentrations are still well below the estimated PNEC for soil (28 μg/g dw), continuous monitoring of sites close to local sources and background soils would be important to ensure that levels of MCCPs are not further increasing.

MCCP concentrations in surface sediment

Similar to MCCP concentrations in soil, available MCCP concentrations in surface sediment do not show large differences between regions (Fig. 4, Tables 2 and S11). Concentrations at background sites are in the range of 14–290 ng/g dw (Canada), 1–403 ng/g dw (Europe and South Africa), and 5–1300 ng/g dw (Asia). MCCP concentrations in background surface sediment are thus one order of magnitude higher than MCCP concentrations in background soil. MCCP concentrations in sediment close to local sources in Australia and China range from 1140 to 9760 ng/g dw (Fig. 5) and are more than one order of magnitude higher than concentrations in background sediment. Moreover, some of the measured concentrations in Australia in 2001[97] and in the Pearl River in China in 2010[98] exceeded the PNEC (13 μg/g dw) for MCCPs in sediment. Although these sediment samples are from heavily industrialized and urbanized areas, the high concentrations should not be overlooked because they are from open water bodies that are habitats for aquatic invertebrates, fish, and humans. The high MCCP concentrations in the Pearl River in 2010 were also confirmed by measurements

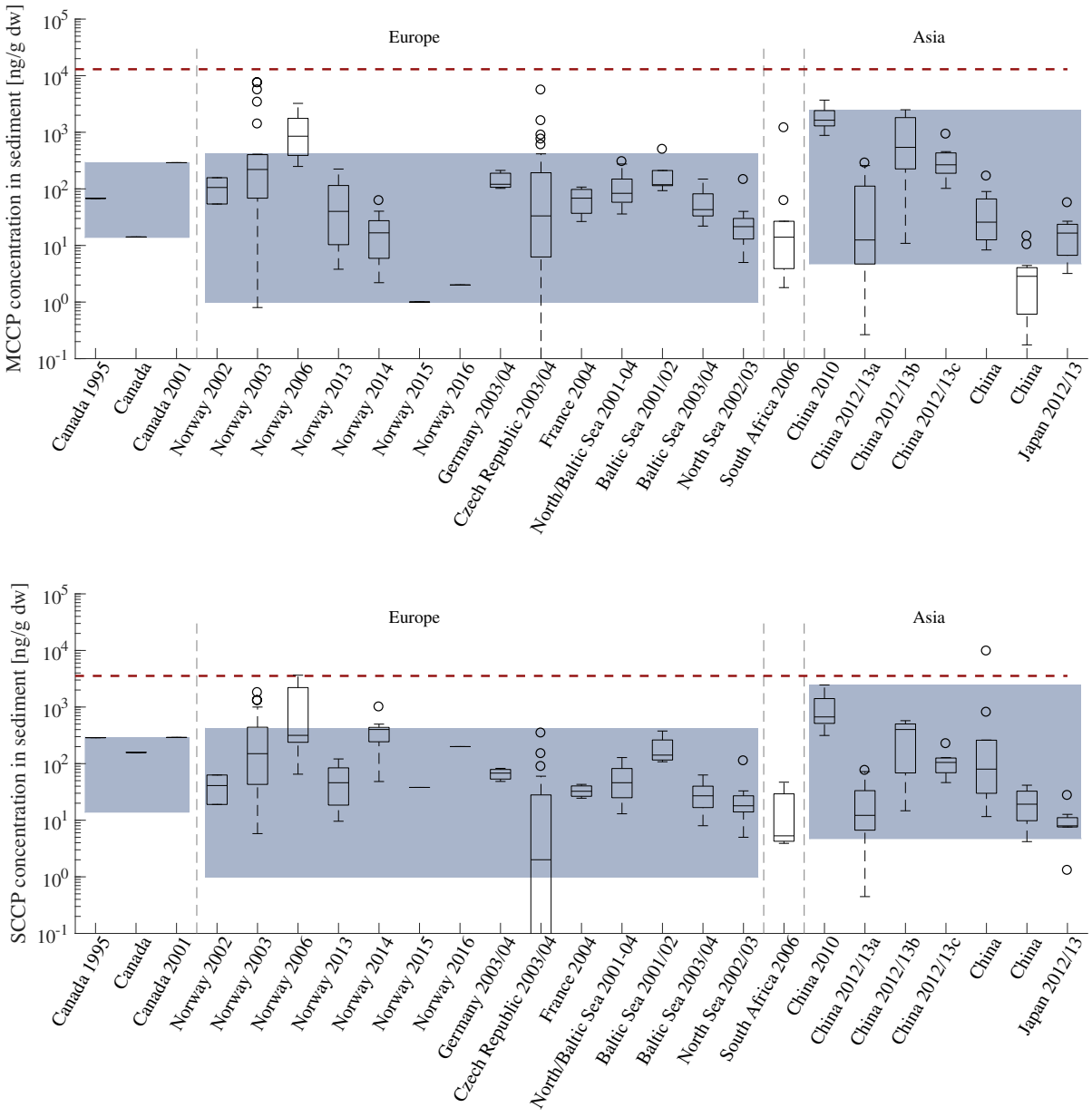

Figure 4: MCCP and SCCP concentrations in surface sediment (background sediment). Studies without an indicated year did not report the sampling year. The blue rectangles indicate the MCCP concentration ranges in the background surface sediment in the specific regions. The horizontal dashed lines show the PNECs for MCCPs and SCCPs, respectively.

359 from Zeng et al.[41] in 2012/2013 who measured only slightly lower levels than Chen et al.[98]
360 in 2010. The MCCP concentrations in sediment close to local sources are also up to one
361 order of magnitude higher than the SCCP concentrations from the same sites and points in
362 time (Fig. 5). The high sediment concentrations close to local sources are very alarming and
363 more measurements are needed in heavily industrialized and urban areas to assess the risks
of MCCPs and to determine the emission sources of the MCCPs in these regions.

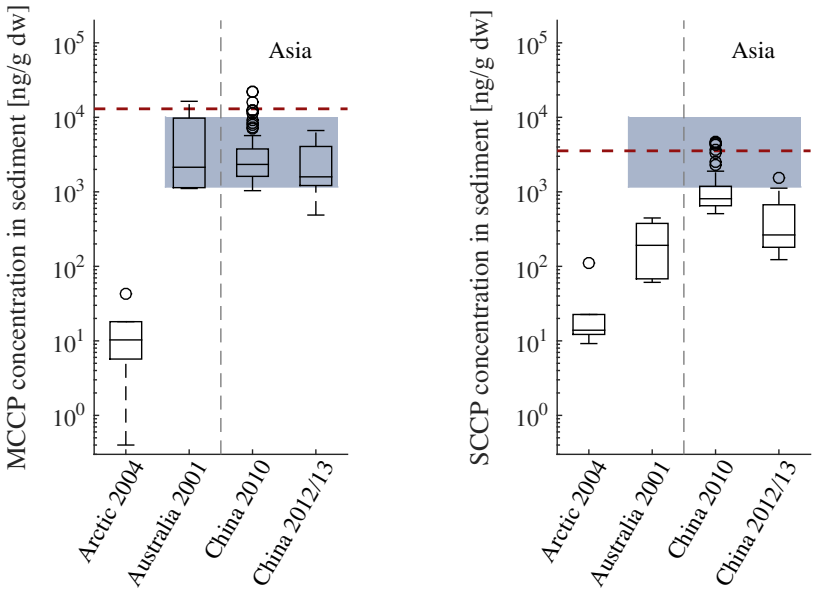

Figure 5: MCCP and SCCP concentrations in surface sediment close to local sources. The blue rectangle indicates the MCCP concentration range in surface sediment close to local sources in Australia and Asia. The horizontal dashed lines show the PNECs for MCCPs and SCCPs, respectively.

364

365 MCCP concentrations in sediment cores

366 MCCP concentrations were reported in eight sediment cores from Switzerland, Sweden,
367 China, and Japan (Fig. S7, Table S14). The core from Lake Thun, Switzerland,[99] two of the
368 cores from Sweden (Baltic Sea),[100] and the two cores from China[41,98] all showed increasing
369 MCCP levels, whereas one of the cores from the Baltic Sea[100] and the two cores from
370 Tokyo Bay, Japan[41] showed decreasing or non-discernible time trends. These trends match

the reported production and use data of MCCPs with decreasing CP levels in Japan and increasing CP levels in China.[14] The cores from Sweden were from urban (decreasing trend) and industrial (increasing trends) sites and show the increasing use of MCCPs in industrial applications in Europe. The occurrence of MCCPs in sediment slices from the 1940s and 50s shows furthermore that MCCPs persist in sediment over decades and degrade only slowly.

MCCP concentrations in fish

MCCP concentrations in fish (Fig. 6, Tables 3 and S12) are available from the Arctic, Canada, the North Atlantic, Europe, and China. The reported concentrations are similar in the Arctic, Canada, Europe and the Liaodong Bay in Northeastern China and range between 12 and 700 ng/g lipid. MCCP concentrations measured in the South China Sea[56] and in paddy fields in the Yangtze River Delta in China[101] were higher and ranged between 1260 and 2600 ng/g lipid. MCCP concentrations in fish from a lake on Bear Island in the Arctic[102] were in the upper 50th percentile of the observed concentrations from Canada and Europe. The contamination of this remote island was explained by two reasons.[103] First, the lake is in a mountainous area and receives a lot of precipitation. Second, large seabird colonies use the lake as resting area and input of guano from these birds causes an increase in POP levels. These observations and the relatively high MCCP concentrations found in the Arctic fish show once more that MCCPs are able to undergo long-range atmospheric transport. The MCCP concentrations measured in Lake Ontario (Canada) between 1979 and 2004[104] are shown here as one box plot; however, they encompass measurements from every four to six years from 1979 to 2004. MCCP concentrations increased by a factor of almost four between 1979 and 1998, and decreased afterwards. However, the decrease in concentrations after 1998 was most likely due to large changes in the Lake Ontario food web and is not statistically significant anymore when corrected for the food-web effect.[104] MCCP concentrations are in the same range as SCCPs in most of the sampled fish (Fig. 6). Toxicological data are only available for MCCPs in rainbow trout; however, none of the studies measured MCCPs in this

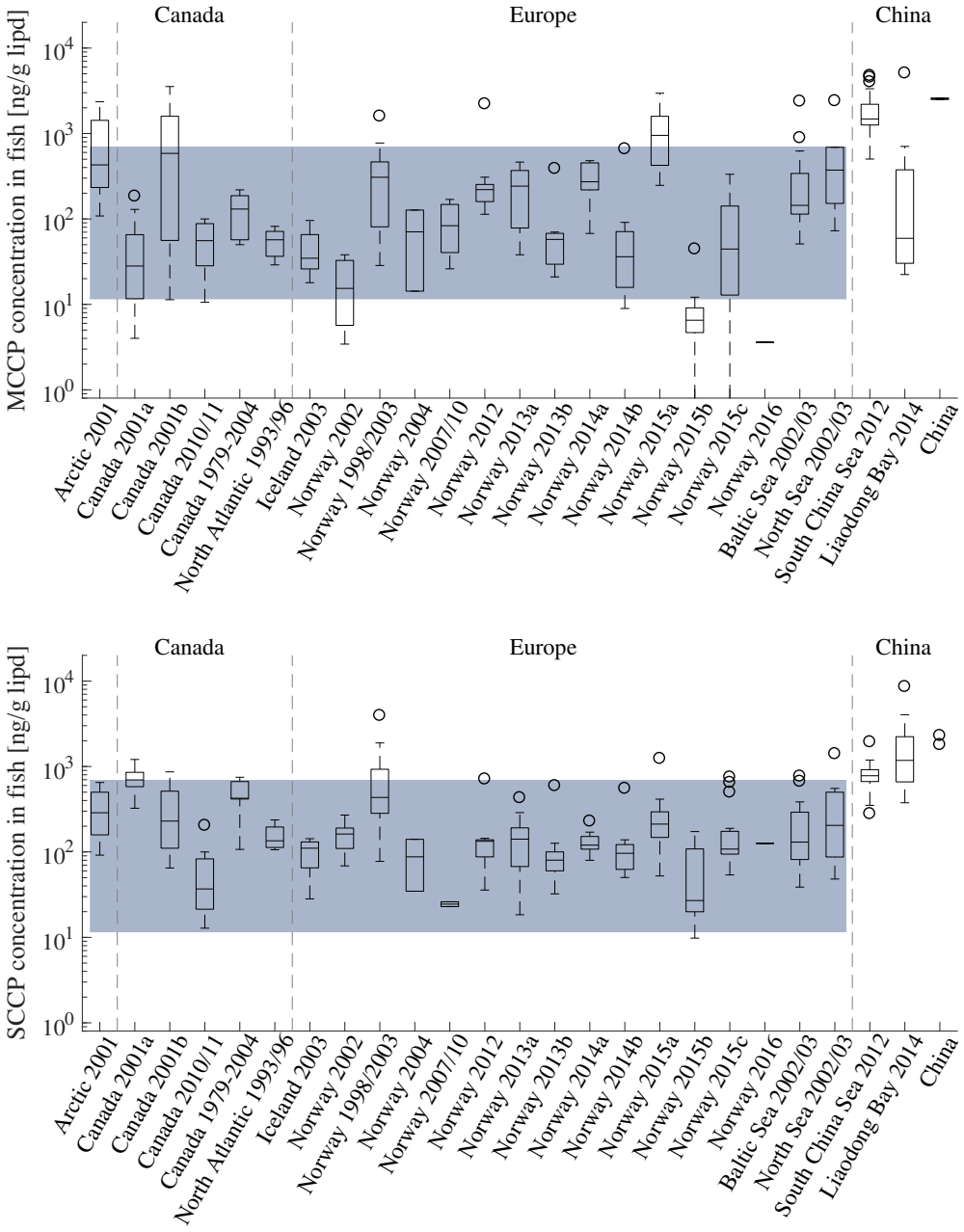

Figure 6: MCCP and SCCP concentrations in fish. The blue rectangle indicates the MCCP concentration range in fish in the Arctic, Canada, and Europe.

fish species. Future research should focus therefore on more toxicological data to assess the risk of MCCPs to fish. Also, studies of food webs to investigate the trophic magnification and biomagnification of MCCPs in aquatic biota would be very important.

MCCP concentrations in birds

Measured MCCP concentrations in bird eggs and bird tissue are available from the Arctic, Norway, and China (Fig. 7, Tables 4 and S12). The concentrations in bird eggs are very similar in the Arctic and in Norway, ranging between 2.1 and 170 ng/g lipid. Lipid normalized concentrations in blood and muscle/liver are around one order of magnitude higher (19−1660 ng/g lipid) than the MCCP concentrations in bird eggs. Data from Søndre Skjælholmen (Osloford, Norway)[57,59,93,105] in eggs and blood were taken every year between 2013 and 2016; however, the measured concentrations show inconsistent time trends. The MCCP concentrations in bird eggs and bird tissue were in the same range or slightly lower than the SCCP concentrations measured in the same animals and points in time (Fig. 7).

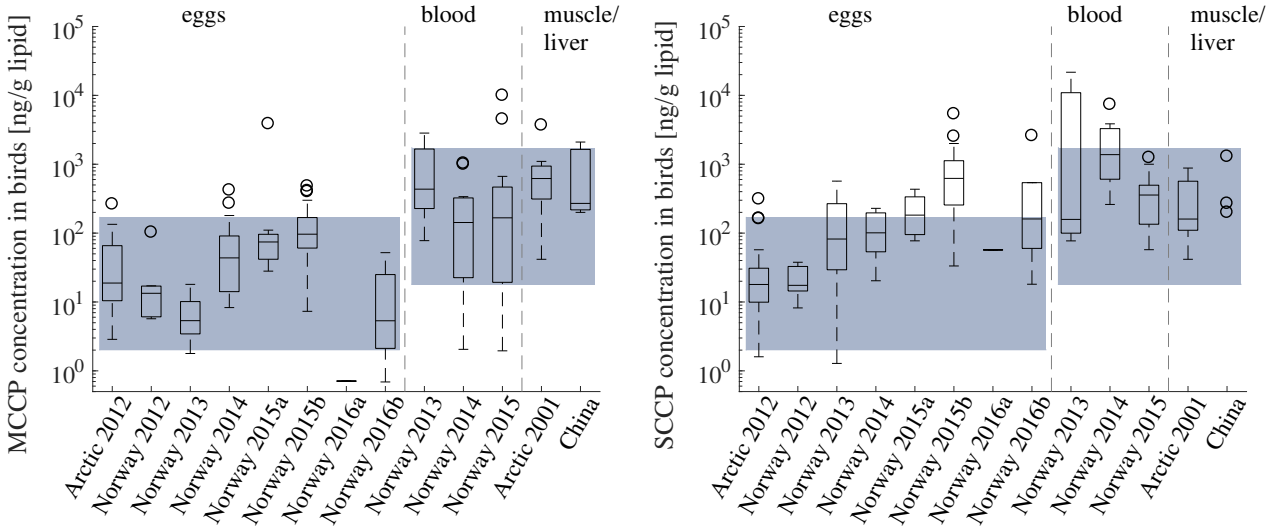

Figure 7: MCCP and SCCP concentrations in birds. The blue rectangles indicate the MCCP concentration ranges in eggs, and in blood and muscle/liver.

MCCP concentrations in mammals

MCCP concentrations in mammals are available for ringed seals and polar bears from the Arctic,[61] and finless porpoise, Indo-Pacific humpback dolphins,[106] and yellow weasels[101] from China (Fig. 8, Tables 5 and S13).

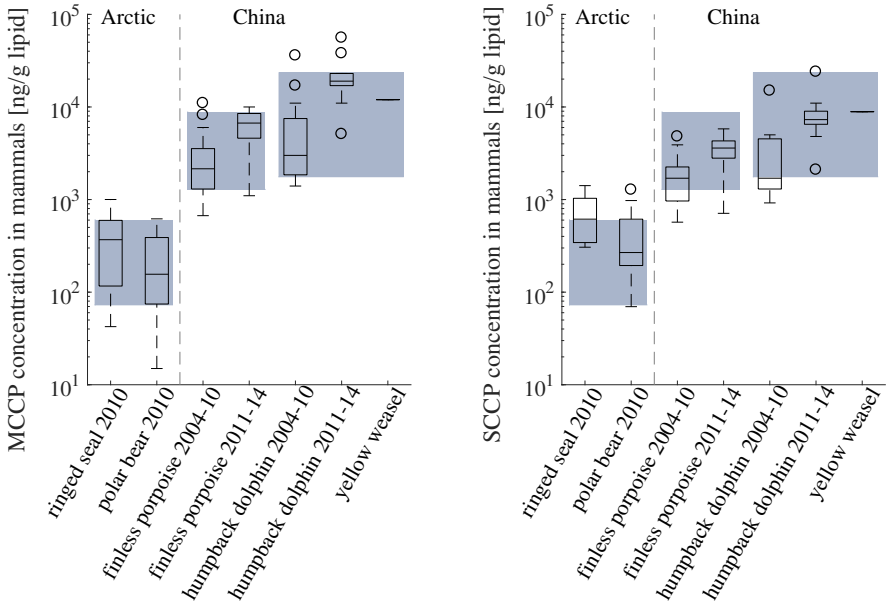

Figure 8: MCCP and SCCP concentrations in mammals. The blue rectangles indicate the MCCP concentration ranges in the specific species and regions.

MCCP concentrations in the plasma of ringed seals and polar bears ranged between 74 and 600 ng/g lipid and were slightly lower than the SCCP concentrations from these animals.[61] MCCP concentrations in the finless porpoises (South China Sea) were in the range from 990 to 9200 ng/g lipid and thus two times higher than the SCCPs concentrations. MCCP concentrations in the Indo-Pacific humpback dolphins (Pearl River Estuary) ranged between 1500 and 51 500 ng/g lipid and were up to 3.5 times higher than the SCCP concentrations. The MCCP concentrations in the finless porpoises and the humpback dolphins showed a statistically significant increase between 2004 an 2014. The higher MCCP concentrations present in humpback dolphins compared to finless porpoises were attributed to species−species differences in feeding habits and biotransformation as well as exposure levels

in their living habitats.[106] MCCP concentrations in yellow weasel from the Yangtze River Delta were in the same order of magnitude as the MCCP concentrations in the humpback dolphins and show that MCCPs accumulate also in terrestrial mammals.

The available studies give a first impression of the levels of MCCPs in mammals, but more measurements in marine and terrestrial mammals from around the world are needed to evaluate the contamination of these animals with MCCPs. Moreover, there is, to our knowledge, so far no study that examined above which level MCCPs pose a risk to the health of mammals. Such a study would be extremely important to judge whether or not the measured MCCP concentrations affect the health of the animals. But independently of this questions, it is for sure that the MCCP levels add to the levels of other toxic pollutants and can, for example, increase the risk of cancer and reproductive problems in whales and dolphins.

MCCPs in human breast milk, placenta, and human blood

MCCP concentrations in human breast milk (Fig. 9, Tables 6 and S13) are available from Europe and China. The measured concentrations show neither temporal nor spatial trends. Also, no significant differences could be observed between rural and urban areas in China.[107,108] The measured MCCP concentrations range between 3.10 and 240 ng/g lipid and are thus one order of magnitude lower than the SCCP concentrations measured in the same samples (with the exception of the concentrations measured in Germany[109]) (Fig. 9). MCCP concentrations measured in human placenta are slightly higher,[110] MCCP concentrations measured in human blood[76] are around one order of magnitude higher than the measured MCCP concentrations in human breast milk. Studies on adverse effects of MCCPs in humans are missing, so it is currently impossible to assess the risk of MCCPs to humans. However, it has repeatedly been shown that toxic pollutants can affect the development of the fetus[111] and it cannot be precluded that MCCPs as well have negative developmental effects.

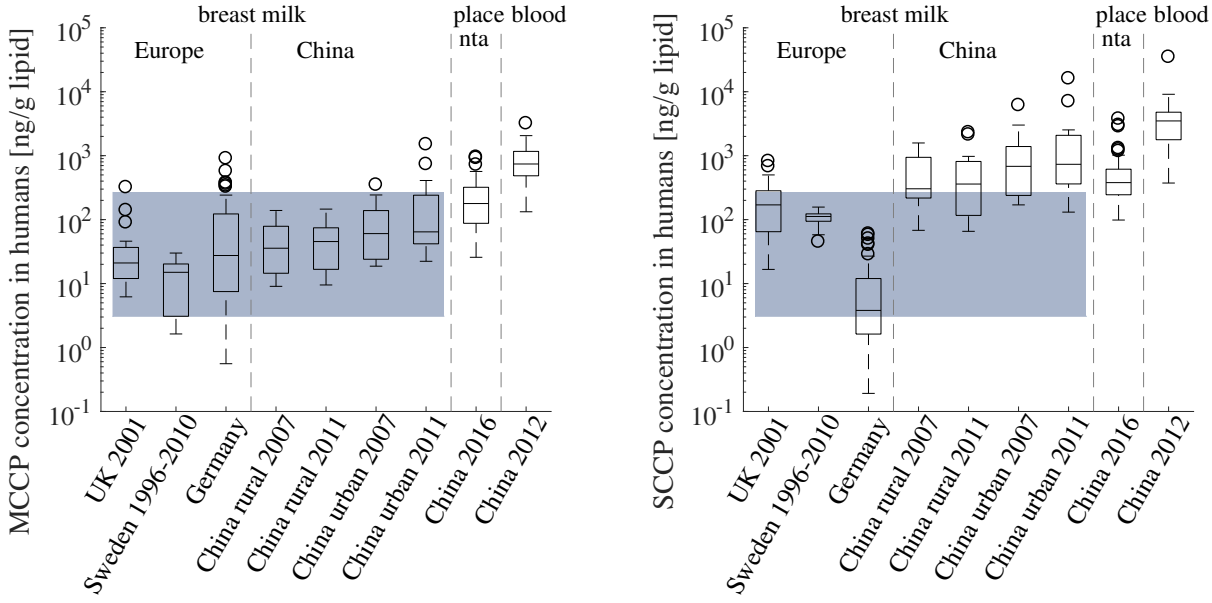

Figure 9: MCCP and SCCP concentrations in human breast milk, placenta, and human blood. The study in Germany did not report the sampling year. The blue rectangle indicates the MCCP concentration range in human breast milk.

CONGENER GROUP PROFILE

Most of the available data for congener groups originate from studies with LRMS. The group congener profiles are therefore more qualitative than quantitative and the differences between the profiles should be interpreted with caution. However, we find that the shorter-chained (C_{14}) and medium-chlorinated (Cl_{7-8}) CPs are the most prevalent MCCPs in environmental matrices (Figs. S8 to S10). $C_{14}Cl_{7-8}$ was also the most prevalent MCCPs in our measured CP-52 samples (Fig. S2). MCCPs with 16 and 17 carbon atoms made up to 30% of the total concentrations in those environmental samples were they could be measured; Pribylová et al.[112] even found a C_{16} content of up to 60% in sediment samples from the Czech Republic. However, robust statements about the congener groups profiles will only be possible if more studies with direct injection or liquid chromatography are available. The congener group profile will otherwise always be affected by the low vapor pressure of the longer-chained MCCPs.

CONCLUSION AND OUTLOOK

The accurate quantification of chlorinated paraffins and especially the quantification of the longer-chained MCCPs and LCCPs is very challenging. This is visible by the fact that many measured concentrations are affected by technical failures. Data generated for example following the method of Tomy and Stern[13] without compensation for the chlorine content differences between standard and sample might substantially under- or overestimate the real concentrations. Concentrations that have been measured with LRMS, without using mathematical procedure to reduce the interferences between the congeners are most probably affected by mass interferences. Studies that quantified only C_{14}- and C_{15}-CPs underestimated the MCCP concentrations. However, we believe that despite these failures, the overall picture from the whole set of measurements and studies is – at least at the order of magnitude – correct and gives valuable insights into the environmental contamination with MCCPs. For future studies, we recommend to use HRMS and the newest analytical methods (for example Bogdal et al.[74] or Yuan et al.[80]) for analyzing CPs, as these are less susceptible to interferences and allow quantification of MCCPs with all chain lengths and LCCPs. Laboratories which have only LRMS available are still encouraged to measure MCCPs, but we highly recommend the usage of the deconvolution procedure to decrease errors due to interferences.

If we look at the obtained overall picture of the environmental contamination with MCCPs, we see that MCCPs have been detected in all environmental compartments, as well as in fish, birds, mammals and human tissues, and they are often measured in higher concentrations than SCCPs. Most alarming to us are the sediment concentrations that reach or exceed the PNEC in sediment as well as the increasing time trends observed for the MCCPs in various locations worldwide. We also observe the potential of the MCCPs to undergo long-range atmospheric transport and their high potential for chronic toxicity to aquatic invertebrates. There is therefore an urgent need to generate data on the degradation of MCCPs in soil and sediment as well as reliable data on the bioaccumulation potential of

MCCPs. ECHA requested aqueous and dietary exposure tests for C_{14}-CPs and aerobic and anaerobic transformation tests in aquatic sediment systems for C_{14} and C_{15}-CPs from the registrant manufacturers until September 2018.[63] However, additional data for MCCPs with other carbon chain length and chlorination degrees will most probably be necessary to draw final conclusions on the MCCPs. Unfortunately, those test are currently difficult to conduct, because only standards of MCCPs mixtures but no chain-length or single congener standards are available. The development of those standards would be a big step forward and would also allow the development of response factors for congener groups or single congeners as done by Yuan et al.[78] for SCCPs.

It would in general also be very important to study whether MCCPs can degrade into SCCPs or other (potentially unknown) compounds of concern and if so, to what extent. There is also a necessity for more long-term monitoring studies in remote and non-remote regions to monitor temporal trends of MCCPs in air, soil, sediment, and biota. Decision makers should otherwise not wait too long for more data to come, because there is already a lot of evidence supporting that MCCPs with more than 46% chlorine are persistent and toxic, and if we apply the precautionary principle, regulatory actions should be considered seriously.

Acknowledgement

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515 Supporting Information Available

516 The Supporting Information includes information about the reported production and use
517 amounts of MCCPs and LCCPs, the physicochemical and kinetic properties, the mass inter-
518 ferences between CP congeners, and the measured concentrations in the environment, biota
519 and humans.

Table 1: Information on the concentrations shown in Figs. 1,2, and 3. The column 'compensation' states whether the chlorine content differences between standard and sample were compensated according to Reth et al. [77]

country	year	month	specific location	type of site	instrumental technique	quantification	compensation	sample no.	literature source
Concentrations in air [pg/m^3]									
Arctic	2013	1-12	Zeppelin, Ny-Alesund	remote	GC-ECNI-HRMS	T	no	12	NILU [89]
Arctic	2014	1-12	Zeppelin, Ny-Alesund	remote	GC-ECNI-HRMS	T	no	12	NILU [90]
Arctic	2015	1-12	Zeppelin, Ny-Alesund	remote	GC-ECNI-HRMS	T	no	12	NILU [91]
Arctic	2016	1-12	Zeppelin, Ny-Alesund	remote	GC-ECNI-HRMS	T	no	12	NILU [92]
Antarctic	2013	1,2	Georgia King Island	remote	GC-ECNI-LRMS	Z+R	yes	10	Ma et al. [113]
UK	2003	4,5	various	rural-urban	GC-ECNI-HRMS	T	no	40	Barber et al. [114]
Norway	2016	7-9	Oslo	urban	GC-HRMS	-	-	3	NILU [115]
Switzerland	2012	8,9	Zurich	urban	GC-ECNI-HRMS	T	yes	2	Bogdal et al. [74]
Pakistan	2011	1	various	rural-urban	GC-ECNI-LRMS	R	yes	10	Chaemfa et al. [116]
India	2006	1	various	rural-urban	GC-ECNI-LRMS	R	yes	20	Chaemfa et al. [116]
China	2010	1-3, 7-9	Pearl River Delta	urban	GC-ECNI-LRMS	R	yes	40	Wang et al. [88]
China	2013/14	1-12	Shenzhen	urban	UPLC-ESI-HRMS	R	yes	24	Li et al. [28]
Concentrations in water [ng/L]									
Norway	2013		Oslo (river[1])	urban	GC-HRMS	-	-	4	NIVA [93]
Norway	2014		Oslo (river[1])	urban	GC-HRMS	-	-	4	NIVA [59]
Norway	2015		Oslo (river[1])	urban	GC-HRMS	-	-	4	NIVA [57]
Arctic	2004		Iqaluit (river)	dump site	GC-ECNI-HRMS	T	no	9	Dick et al. [117]
Concentrations in soil [ng/g dw]									
Norway	2015		Oslo	urban	GC-HRMS	-	-	5	NILU [118]
Norway	2016		Oslo	urban	GC-HRMS	-	-	5	NILU [115]
Switzerland	2002		various	rural-urban	GC-ECNI-LRMS	R	yes	9	Iozza [119]
Switzerland	1989-2014		various	rural-urban	GC-ECNI-HRMS	T	yes	36	Bogdal et al. [96]
S. Africa	2006		Vaal Triangle	rural-urban	GC-EI-HRMS	-	-	12	Quinn et al. [95]
China	2009		Pear River Delta	urban	GC-ECNI-LRMS	R	yes	59	Wang et al. [88]
China	2011		Shanghai	suburban	GC-ECNI-LRMS	R	yes	101	Wang et al. [120]
China	2011		Shanghai	urban	GC-ECNI-LRMS	R	yes	75	Wang et al. [121]
China	2014		Dalian city	industrial	GC-ECNI-LRMS	Z+R	yes	25	Xu et al. [31]

- not stated [1] stormwater [M] quantified according to Moore et al. [122] [R] quantified according to Reth et al. [77]
[T] quantified according to Tomy et al. [86] and Tomy and Stern [13] [Z] quantified according to Zeng et al. [82]

Table 2: Information on the sediment concentrations shown in Figs. 4 and 5. The column 'compensation' states whether the chlorine content differences between standard and sample were compensated according to Reth et al. [77]

country	year	specific location	type of site	instrumental technique	quantification	compensation	sample no.	literature source
Concentrations in surface sediment (background) [ng/g dw]								
Canada	1995	Lake Erie	industrial	GC-ECNI-HRMS	T	no	3	Tomy [123]
Canada	-	Hamilton harbour	industrial	GC-ECNI-HRMS	-	-	1	Muir et al. [124]
Canada	2001	Lake St. Clair		GC-ECNI-HRMS	-	-	20	Gewurtz et al. [125]
Norway	2002	Tromso		GC-ECNI-LRMS	T	no	2	Umweltbundesamt [126]
Norway	2003	various	-	GC-MS	-	-	23	NIVA [127]
Norway	2006	various	-	GC-ECNI-LRMS	T	no	10	Petersen et al. [128]
Norway	2013	Inner Oslojord[1]		GC-HRMS	-	-	9	NIVA [93]
Norway	2014	Inner Oslojord[1]	-	GC-HRMS	-	-	9	NIVA [59]
Norway	2015	Inner Oslojord[2]	-	GC-HRMS	-	-	1	NIVA [57]
Norway	2016	Inner Oslojord[2]	-	GC-HRMS	-	-	1	NIVA [105]
Germany	2003/04	Hamburg harbour	-	GC-ECNI-LRMS	T	no	3	Umweltbundesamt [126]
Czech Rep.	2003/04	various	rural-urban	GC-ECNI-LRMS	C	no	12	Pribylová et al. [112]
France	2004	River Seine	-	GC-ECNI-LRMS	T	no	3	Umweltbundesamt [126]
North/Baltic Sea	2001-04	various	-	GC-CH_4/CH_2Cl_2-NICI-LRMS	T	n.n.	18	Umweltbundesamt [126]
Baltic Sea	2001/02	various	-	GC-EI-MS/MS	H	n.n.	6	Hüttig and Oehme [129]
Baltic Sea	2003/04	various	-	GC-ECNI-LRMS	R	yes	11	Hüttig and Oehme [130]
North Sea	2002/03	various	-	GC-EI-MS/MS	H	n.n.	14	Hüttig and Oehme [131]
S. Africa	2006	various river	[3]	GC-EI-HRMS	-	-	9	Quinn et al. [95]
China	2010	Pear River Delta	[4]	GC-ECNI-LRMS	T	no	39	Chen et al. [98]
China	2012/13	Hong Kong (sea)	urban	GC-ECNI-LRMS	R	yes	35	Zeng et al. [41]
China	2012/13	Shenzhen (sea)	urban	GC-ECNI-LRMS	R	yes	8	Zeng et al. [41]
China	2012/13	Pear River Delta	[4]	GC-ECNI-LRMS	R	yes	7	Zeng et al. [41]
China		Yellow River	rural-urban	GC^2-ECNI-HRMS	R	yes	13	Qiao et al. [131]
China		Yangtze River	rural-urban	GC^2-ECNI-HRMS	R	yes	13	Qiao et al. [132]
Japan	2012/13	Tokyo Bay	urban	GC-ECNI-LRMS	R	yes	8	Zeng et al. [41]
Concentrations in surface sediment close to local sources [ng/g dw]								
Arctic	2004	Iqaluit, river	dump site	GC-ECNI-HRMS	T	no	6	Dick et al. [117]
Australia	2001	Yarraville (sea)	industrial[5]	CSR-GC	-	n.n.	4	Kemmlein et al. [97]
China	2010	Pear River Delta	industrial	GC-ECNI-LRMS	T	no	76	Chen et al. [98]
China	2012/13	Pear River Delta	industrial	GC-ECNI-LRMS	R	yes	9	Zeng et al. [41]

- not stated n.n. not necessary [1] Alne, Bekkelaget, Frognerkilen [2] Cm21 [3] agriculture and industrial region [4] low industry activity area
[5] area influenced by CP manufacturer C quantified according to Coelhan [133] H quantified according to Hüttig and Oehme [134]
R quantified according to Reth et al. [77] T quantified according to Tomy et al. [86] and Tomy and Stern [13]

Table 3: Information on the MCCP concentrations in fish [ng/g lipid] shown in Fig. 6. The column 'compensation' states whether the chlorine differences between standard and sample were compensated according to Reth et al. [77]

country	year	specific location	sample medium	fish type	instrumental technique	quantification	compensation	sample no.	literature source
Arctic	2001	Bear Island, Lake Ellasjoen	liver, muscle	a	GC-ECNI-LRMS	R	yes	4	Reth et al. [102]
US	1995	Lake Erie	whole fish	b,c	GC-ECNI-HRMS	T	no	2	Tomy and Stern [13]
Canada	2001	Lake Michigan	whole fish	d−f	GC-ECNI-HRMS	T	no	11	Houde et al. [11]
Canada	2001	Lake Ontario	whole fish	d,f−h	GC-ECNI-HRMS	T	no	13	Houde et al. [11]
Canada	2010/11	various lakes	whole fish	f, i, j	GC-NCI-HRMS	T	no	84	Saborido Basconcillo et
Canada	1979-04	Lake Ontario	whole fish	f	GC-ECNI-HRMS	T	no	29	Ismail et al. [104]
N. Atlantic	1993-06	-	whole fish	k−o	GC-ECNI-LRMS	-	no	5	Lahaniatis et al. [136]
Iceland	2003	Akureyri, Vestmanna.	liver	p	GC-ECNI-LRMS	R	yes	4	Reth et al. [102]
Norway	2002	various	liver	p	GC-MS	-	-	42	NIVA [127]
Norway	1998/03	various	various	various	GC-MS	-	-	163	NIVA [127]
Norway	2004	Lofoten	liver	p	GC-ECNI-LRMS	R	yes	2	Reth et al. [102]
Norway	2007/10	Lake Stensjön, Sännen and Tjultr.	liver	a, q	-	-	-	39	Nyberg et al. [137]
Norway	2012	various	liver	p	GC-MS	-	-	165	NIVA [138]
Norway	2013	various	liver	p	GC-MS	-	-	82	NIVA [139]
Norway	2013	Oslofjord, Lysakerfj.	liver	r	GC-HRMS	-	-	15	NIVA [93]
Norway	2014	various	liver	p	GC-MS	-	-	119	NIVA [58]
Norway	2014	Oslofjord, Sollerud skole	liver	r	GC-HRMS	-	-	15	NIVA [59]
Norway	2015	various	liver	p	GC-MS	-	-	153	NIVA [140]
Norway	2015	Inner Oslofjord	muscle, liver	m, p	GC-HRMS	-	-	30	NIVA [57]
Norway	-	various	-	q, s	-	-	-	70	NIVA [141]
Norway	2016	Inner Oslofjord	liver	p	GC-HRMS	-	-	13	NIVA [105]
Baltic Sea	2002/3	-	liver	p, r, t	GC-ECNI-LRMS	half T, half R		29	Umweltbundesamt [126]
North Sea	2002/3	-	liver	p, r, t	GC-ECNI-LRMS	T	no	35	Umweltbundesamt [126]
China	2012	South China Sea	muscle/soft tissue	various	GC-ECNI-LRMS	R	yes	51	Zeng et al. [56]
China	2014	Liaodong Bay	whole fish	various	GC^2-ECNI-HRMS	R	yes	73	Huang et al. [60]
China	-	Yangtze River Delta	muscle	u, v	GC-NCI-LRMS	B	n. n.	10	Du et al. [101]

[-] not stated [n. n.] not necessary [a] Arctic char [b] yellow perch [c] channel catfish [d] alewife [e] deepwater sculpin [f] lake trout [g] slimmy [h] rainbow smelt [i] Walleye [j] brook trout [k] sprat [l] redfish [m] herring [n] mackerel [o] halibut [p] cod [q] perch [r] flounder [s] trout [t] north sea dab [u] pond loach [v] rice field eel [B] quantified according to Bogdal et al. [74] [R] quantified according to Reth [T] quantified according to Tomy et al. [86] and Tomy and Stern [13]

Table 4: Information on the MCCP concentrations in birds [ng/g lipid] shown in Fig. 7. The column 'compensation' states whether the chlorine content differences between standard and sample were compensated according to Reth et al.[77]

country	year	specific location	sample medium	bird type	instrumental technique	quantification	compensation	sample no.	literature source
Arctic	2012	Svalbard	egg	a, b	GC-HRMS	-	-	24	Miljodirektoratet[61]
Norway	2012	Sklinna, Rost	egg	b, c	GC-ECNI-MS	-	-	24	Huber et al.[142]
Norway	2013	Oslofj., Søndre Skjælh.	egg	c	GC-HRMS	-	-	15	NIVA[93]
Norway	2014	Oslofj., Søndre Skjælh.	egg	c	GC-HRMS	-	-	14	NIVA[59]
Norway	2015	Oslofj., Søndre Skjælh.	egg	c	GC-HRMS	-	-	15	NIVA[57]
Norway	2015	Oslo	egg	d−f	GC-HRMS	-	-	30	NILU[118]
Norway	2016	Oslofj., Søndre Skjælh.	egg	c	GC-HRMS	-	-	15	NIVA[105]
Norway	2016	Oslo	egg	f	GC-HRMS	-	-	10	NILU[92]
Norway	2013	Oslofj., Søndre Skjælh.	blood	c	GC-HRMS	-	-	3	NIVA[93]
Norway	2014	Oslofj., Søndre Skjælh.	blood	c	GC-HRMS	-	-	10	NIVA[59]
Norway	2015	Oslofj., Søndre Skjælh.	blood	c	GC-HRMS	-	-	13	NIVA[57]
Arctic	2001	Bear Island	muscle, liver	a, g	GC-ECNI-LRMS	R	yes	8	Reth et al.[102]
China	-	Yangtze River Delta	muscle	h−*j*	GC-NCI-LRMS	B	n. n.	18	Du et al.[101]

- not stated [n. n.] not necessary [a] kittiwake [b] common eider [c] herring gull [d] sparrowhawk [e] tawny owl [f] fildfare [g] little auk [h] peregrine falcon [i] collared scops owl [j] common cuckoo [B] quantified according to Bogdal et al.[74] [R] quantified according to Reth et al.[77]

Table 5: Information on the MCCP concentrations in mammals [ng/g lipid] shown in Fig. 8. The column 'compensation' states whether th chlorine content differences between standard and sample were compensated according to Reth et al.[77]

country	year	specific location	sample medium	mammal	instrumental technique	quantification	compensation	sample no.	literature source
Arctic	2010	Svalbard	plasma	Ringed seal	GC-HRMS	-	-	9	Miljodirektoratet[61]
Arctic	2012	Svalbard	plasma	Polar bear	GC-HRMS	-	-	20	Miljodirektoratet[61]
China	2004−14	South China Sea	blubber	finless porpoise	GC-ECNI-LRMS	Z	yes	50	Zeng et al.[106]
China	2004−14	Pear River Estuary	blubber	Indo-Pacific humpback dolphin	GC-ECNI-LRMS	Z	yes	25	Zeng et al.[106]
China	-	Yangtze River Delta	muscle	yellow weasel	GC-NCI-LRMS	B	n. n.	5	Du et al.[101]

- not stated [n. n.] not necessary [B] quantified according to Bogdal et al.[74] [Z] quantified according to Zeng et al.[82]

Table 6: Information on the MCCP concentrations in human breast milk, placenta, and human blood [ng/g lipid] shown in Fig. 9. The column 'compensation' indicates whether the chlorine content differences between standard and sample were compensated according to Reth et al.[77]

country	year	specific location	type of site	instrumental technique	quantification	compensation	sample no.	literature source
UK	2001	Lancaster, London	urban	GC-ECNI-HRMS	T	no	25	Thomas et al.[143]
Sweden	1996-10	Uppsala county	-	GC-ECNI-HRMS	T	no	523	Darnerud et al.[144]
Germany	-	Bavaria	rural-urban	GC-ECNI-LRMS	R	yes	60	Hilger et al.[109]
China	2007	various	rural	GC^2-ECNI-HRMS	R	yes	452	Xia et al.[107]
China	2011	various	rural	GC^2-ECNI-HRMS	R	yes	960	Xia et al.[107]
China	2007	various	urban	GC^2-ECNI-HRMS	R	yes	570	Xia et al.[108]
China	2011	various	urban	GC^2-ECNI-HRMS	R	yes	800	Xia et al.[108]
China	2016	Henan	–	GC-NCI-HRMS	G	yes	54	Wang et al.[110]
China	2012	Shenzhen	urban	UPLC-ESI-LRMS	R	yes	50	Li et al.[76]

- not stated R quantified according to Reth et al.[77] T quantified according to Tomy et al.[86] and Tomy and Stern[13]
G quantified according to Gao et al.[30]

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Graphical TOC Entry