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Report of the Persistent Organic Pollutants Review Committee on the work of its eighteenth meeting

Addendum

Risk profile for chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight

At its eighteenth meeting, in decision POPRC-18/4, the Persistent Organic Pollutants Review Committee adopted a risk profile for chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight on the basis of the draft text contained in document UNEP/POPS/POPRC.18/5/Add.1, as revised during the meeting. The text of the risk profile as adopted is set out in the annex to the present addendum, without formal editing.

Annex*

Chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight

Risk profile

September 2022

^{*} The studies and other information referred to in this document do not necessarily reflect the views of the Secretariat, the United Nations Environment Programme (UNEP) or the United Nations. The designations employed and the presentation of the material in such studies and references do not imply the expression of any opinion whatsoever on the part of the Secretariat, UNEP or the United Nations concerning geopolitical situations or the legal status of any country, territory, area or city or its authorities.

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Executive summary

- 1. This risk profile concerns chlorinated paraffins (CPs) with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight. These are the principal constituents of substances called "medium-chain chlorinated paraffins" ("MCCPs") in Europe, North America and Australia, and major constituents of several products manufactured in Asia (e.g., CP-52). Due to the possible confusion regarding different product names, the proposal for listing is based on specific chain lengths and degrees of chlorination. Nevertheless, most of the available hazard and monitoring information is available from assessments on the substance called "MCCPs". The substance itself is a widely used industrial chemical which is estimated to be supplied in the order of 800,000 tonnes per year globally. It has a broad range of uses, primarily as a flame retardant and secondary plasticiser in polymers such as polyvinyl chloride (PVC), and in metal working fluids.
- 2. CPs with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight meet the persistence criteria of the Convention. The C_{14} chain length is considered to have a half-life exceeding 180 days in two types of aerobic sediment based on a laboratory test. Assessment of the persistence screening data indicates that the constituents with chlorination levels at or exceeding 45% chlorine by weight would also be expected to be persistent in sediment. Persistence in sediment is supported by sediment core monitoring data, where "MCCPs" can be detected at similar orders of magnitude across horizons spanning the last 8 years (and longer) in the same core. The persistence conclusion for the C_{14} chain length can be applied to the C_{15-17} chain lengths because they will be more adsorptive based on the measured and predicted trends for water solubility and log K_{OW} . This is supported by the detection of these chain lengths in sediment, and notably, where data are available, the congener profile detected reflects that in commercial substances.
- CPs with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight meet the bioaccumulation criteria of the Convention. All constituents have log Kow values exceeding 5. Two recent laboratory fish bioaccumulation studies using C₁₄ chain lengths show measured or estimated bioconcentration factor (BCF) values well above 5,000 L/kg. The available fish bioaccumulation laboratory studies for the C_{15} , C_{16} and C_{18} chain lengths were not performed to current test guidelines nor to such a high standard as the modern tests for C₁₄. Nevertheless, they indicate a high bioaccumulation potential for all three "MCCPs" chain lengths (although C_{17} was not tested, its bioaccumulation potential can be inferred to lie between that of C_{16} and C_{18}). A non-guideline invertebrate bioaccumulation study using a C₁₄₋₁₇ 45% Cl wt. substance measured a BCF value well in excess of 5,000 for Daphnia magna. Field monitoring studies indicate that all chain lengths are bioavailable and can be detected in biota, including in top predators as well as in sensitive life stages (such as birds' eggs). Where data are available, the congener profile in organisms is similar to the congener profile in environmental matrices such as soil and sediment, and wastewater treatment plant sludge, suggesting congener uptake reflects exposure. Overall, the bioaccumulation behaviour of the longer chain lengths appears to be broadly similar to C₁₄. A number of field biomagnification studies are available, where biomagnification factors (BMFs) or trophic magnification factors (TMFs) both above and below 1 were calculated. Each field study has limitations, but the data indicate that the possibility of biomagnification of "MCCPs" cannot be excluded.
- 4. CPs with carbon chain lengths in the range C₁₄₋₁₇ and chlorination levels at or exceeding 45 per cent chlorine by weight are shown to meet the long-range environmental transport potential criteria of the Convention. The predicted atmospheric half-life values are between 37 and 140 hours, principally dependent on the degree of chlorination: more highly chlorinated constituents will be more photolytically stable and more adsorptive to particulates. There are uncertainties regarding both the model training set, and the effect of the fraction adsorbed to aerosols (which is reliant on the predicted log K_{OA}). Modelling using the OECD Screening tool indicates long-range environmental transport (LRET) comparable to, but slightly below, that for short-chain chlorinated paraffins (SCCPs), which is a listed POP. The "MCCPs" LRET also falls within the range of other listed POPs. The modelling is also affected by the fraction adsorbed to aerosols, which could be higher than the OECD tool predicts, and would result in greater LRET potential. Monitoring data support the modelling conclusion. Detection of "MCCPs" in air (gaseous and particulate) and water (dissolved and particulate) suggests a number of pathways exist to deliver "MCCPs" to remote locations. While "MCCPs" are rarely included in monitoring campaigns in remote regions, the available data indicate detection in air in the Arctic, Antarctic and Tibetan Plateau, sediment of the Arctic, and multiple detections in Arctic biota including predators. In some instances, the monitoring data indicate levels of "MCCPs" comparable or exceeding levels of SCCPs and some other listed POPs in remote regions.
- 5. CPs with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight are shown to meet the adverse effects criteria of the Convention. A C_{14-17} chlorinated n-alkane, 52% Cl wt. is very toxic to *Daphnia magna* in both acute and long-term studies. This indicates significant toxicity to aquatic invertebrates which are an important part of aquatic food chains. Effects on organisms at this trophic level may reduce food availability at higher levels of the food chain with potential population-level effects. Regulatory testing is designed to protect all organisms living in the environment, and is limited in scope for practical and ethical reasons. Therefore, high toxicity observed in one organism within a trophic level means that it cannot be excluded that others are equally or more affected (a general principal of regulatory ecotoxicology). For chemicals that are also shown to be persistent and bioaccumulative, the concern is also for unpredictable effects within the food chain. Internal

haemorrhaging and death have been observed in rodent offspring in a mammalian reproduction study. This observation suggests that potential adverse effects could occur in mammals living in the environment and exposed to MCCPs via their diet. As the (eco)toxicity tests used a substance containing C_{14-17} chain lengths, all chain lengths are considered to contribute to the observed effects. The tests are also used to support regulatory submissions by suppliers covering all "MCCPs" products on the market (not just 52% Cl wt.) indicating the applicability of the studies to a broad range of chlorination levels.

- 6. The available monitoring data generally show widespread occurrence of "MCCPs" in surface water, sediment, soil, biota, sludge and air, in multiple regions of the world, including remote regions. The substance can be widely detected in environmental biota including predators, as well as human tissues. In some instances, tissue concentrations up to 23 mg/kg lw have been detected. Increasing detections in local biota have been observed where trend information is available.
- 7. The most recent biota monitoring studies have usually provided chain length and congener level information, which indicates the bioavailability of all chain lengths. Where data are available, "MCCPs" chain length / congener profiles detected in biota are consistent with those detected in environmental matrices and wastewater treatment plant sludge.
- 8. Following national and international restrictions on the use of SCCPs, the supply of "MCCPs" has increased significantly as it appears to be the main drop-in replacement for SCCPs. The increase in supply (with consequent environmental emission) is reflected in environmental monitoring trends: increasing levels of "MCCPs" are detected where multi-year sampling has been undertaken. Sediment core data also indicate a decline in SCCPs with a concurrent increase in "MCCPs" in more contemporaneous cores. As the switch from SCCPs to "MCCPs" has only occurred in recent years, "MCCPs" detection can be expected to increase in the absence of risk management.
- 9. The concentrations detected in biota in more contaminated areas shows that high levels can be attained in organisms. If environmental exposure of "MCCPs" is increasing in more remote areas as suggested by the limited trend data available, this indicates that increasing levels in remote biota can similarly be expected.
- 10. The concern for "MCCPs" is its demonstrated persistence, bioaccumulation and toxicity, together with similarities in the long-range environmental transport potential to SCCPs. The underlying concern is that "MCCPs" poses similar types of risk to SCCPs. While the two substances are not identical, they are sufficiently similar to warrant action to address the potential risk from "MCCPs". The very high levels of estimated emissions to the environment (around 2,400 to 24,000 tonnes/year) are reflected in widespread detection, together with indications that these levels are increasing, including in remote areas. Given the bioavailability and increasing trend in the detection of a known persistent, bioaccumulative and toxic substance, it can be expected that levels in remote environments will continue to increase, and levels in biota will also continue to increase with consequent risk of unpredictable impacts unless risk management measures are implemented.
- 11. Based on evidence of its persistence, bioaccumulation and adverse effects, widespread occurrence in environmental compartments and frequent detection in biota in remote regions, it is concluded that chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight are likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted.

1. Introduction

12. In April 2021, the United Kingdom of Great Britain and Northern Ireland (UK) submitted a proposal to list chlorinated paraffins (CPs) with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight (Cl wt.) in Annexes A, B and/or C of the Convention. The proposal was submitted in accordance with Article 8 of the Convention and was reviewed by the Persistent Organic Pollutants Review Committee (POPRC) at its seventeenth meeting held in January 2022.

1.1 Chemical identity

1.1.1 CAS number, chain length and chlorination

- Chlorinated paraffins (CPs) are manufactured substances consisting of predominantly linear chloroalkanes, with different degrees of chlorination and chain length distributions depending on the application and feedstock. This Risk Profile focuses on any CP product that has constituents with 14 to 17 carbon atoms (C_{14-17}) and a chlorination level at or exceeding 45% Cl wt. These congeners are the principal constituents of substances called "medium-chain chlorinated paraffins" ("MCCPs") in Europe, North America and Australia, and major constituents of several products manufactured in Asia (e.g., CP-52). Due to the possible confusion regarding different product names, the proposal for listing is based on specific chain lengths and degrees of chlorination. Nevertheless, most of the available hazard and monitoring information is available from assessments on the substance called "MCCPs", and so the term "MCCPs" is used in these instances. As a consequence of the manufacturing process, "MCCPs" is a substance of 'Unknown or Variable composition, Complex reaction product or Biological material' (UVCB), containing many individual constituents. For clarity, a CP constituent is an individual structural isomer, i.e., chlorine atoms are in defined molecular positions on the carbon chain. Congeners are groups of isomers with the same structural formula such as $C_{14}Cl_{5}$, without the chlorine position being defined. CP homologues are groups of constituents with the same carbon chain length but varying number of chlorine atoms, e.g., the C_{14} homologue.
- 14. Key information for CPs with C_{14-17} chain lengths and chlorination levels at or exceeding 45 per cent Cl wt. is provided in Table 1. This is based on the substance identity for "MCCPs" from the European Union's (EU) REACH Substance Evaluation (Environment Agency, 2019a). An indicative list of relevant CAS numbers is provided in Table 3 of document UNEP/POPS/POPRC.18/INF/10, together with further information. Around forty CAS numbers have been used to identify the CPs at various times. Some of these clearly cover CPs in the C_{14-17} range, and it is possible that some of the remainder may be used for products containing CPs in this range too.

Table 1. Substance identity (based on CAS No. 85535-85-9, adapted to the scope proposed in the nomination)

IUPAC name	Alkanes, C ₁₄₋₁₇ , chloro*		
CAS number	85535-85-9*		
EC number	287-477-0		
Molecular formula	$C_x H_{(2x-y+2)}Cl_y$, where $x = 14$ to 17 and $y = \ge 5$ to 17		
Molecular weight range	370–826 g/mole (approximately)		
Synonyms	Medium-chain chlorinated paraffins ("MCCPs"); Chlorinated paraffins, C _{14–17} (used in Annex VI of the EU CLP Regulation)		

^{*} The IUPAC name and CAS number cover a broader range of chlorination than the scope proposed in this document.

- 15. The predominant chain lengths of "MCCPs" are in the range C_{14-17} , reflecting the hydrocarbon feedstocks used in its manufacture within Europe, North America and Australia. Information presented in Environment Agency (2019a) indicates that chlorinated C_{14} carbon chain lengths are the dominant congener group in commercially supplied "MCCP" products. They also contain some constituents outside of the C_{14-17} range in small amounts.
- 16. CPs produced in Asian countries such as India and China are differentiated based on their chlorine content (or viscosity) rather than by the carbon chain lengths of their constituent congeners. An example is the product CP-52, which accounted for 80% of the total commercial CP production in China in 2005 (cited in Wei *et al.*, 2016). Li *et al.*, (2018) cites data showing CP-42 and CP-52 together accounted for >80% of Chinese production. The Chinese industry standard HG/T 2092 defines CP-52 as a product with a chlorine content between "50%-54%" by weight (CCPIA, 2022). CP-52 contains C_{9-30} chain lengths with a significant fraction in the range C_{14-17} (Castro *et al.*, 2018). Niu *et al.*, (2021) noted marked variation in the C_{10-17} congeners in 7 different batches of CP-52, which was suggested to be due to the varying composition of the n-alkane feedstock used for production. Li *et al.*, (2018b) examined the

congener profiles for three Chinese CP products. In the CP-52 sample, they found the predominant "MCCPs" chain length was C₁₇, although due to the form of analysis used in the study this conclusion is uncertain. Glüge *et al.*, (2018) analysed 11 CP-52 mixtures from 9 Chinese producers and found that (with one exception) C₁₄ was present in these products between 29% and 67%, with a mean value of 57%. The C₁₄Cl₇₋₈ congeners were the most prevalent. Xia *et al.*, (2021) analysed 18 commercial Chinese CP products, including 13 CP-52 products. They found "MCCPs" composed 34.3% to 69.1% of the CP-52 products with C₁₄ congeners dominant, contributing 46.1–79.5% of the total "MCCPs" detected. Similar results were observed for CP-42 (2 products). The three CP-70 products were noted to have two dominant congeners, C₁₄ and C₁₇. Wang *et al.*, (2018) noted that C₁₄ was the dominant "MCCPs" chain length in a wide range of Chinese polymer products. For both "MCCPs" and products such as CP-52, chain lengths below C₁₄ are structurally analogous to the range described as short-chain chlorinated paraffins (SCCPs).

- 17. The chlorine content of commercial products (e.g., "MCCPs" and CP-52) varies according to the applications they are used for but is generally within the range 40% to 63% by weight; the majority of products have a chlorine content between 45% and 52% by weight. The chlorination process is random, and so all of these products contain many thousands of constituents (Yuan *et al.*, 2020; Tomy *et al.*, 1997).¹
- Table 2 indicates the molecular formulae of possible constituents of the different product types (adapted from information originally presented in the EU Existing Substances Regulation assessments (EC, 2000 and 2005)). The "blocks" in the table each contain one or more groups of positional isomers. Each group contains a large number of individual isomers (constituents). The main constituents in the majority of product types have between five and seven chlorine atoms per molecule. This was verified by Yuan *et al.*, (2020) who examined five C_{14} (37.75–60.14% Cl wt.) and four C_{15} (40.3–57.75% Cl wt.) homologues using both APCI-QToF-MS and NMR.² Molar plots of the detected congeners using both detection methods generated pseudo-normal and non-normal distributions for the top 100 isomers of each homologue, respectively. Nevertheless, it should be noted that percentage chlorine content only represents an average level of chlorination and so a much wider range of constituents may be present in any particular product. Therefore, higher and lower chlorination levels will be present for a product with a given average chlorination level. For example, due to the manufacturing process, some of the congeners (e.g., C_{14-15} with four or five chlorine atoms) that make up CP products with C_{14-17} and a chlorination level at 45% Cl wt have also been shown to be present in CP products with C_{14-17} and a chlorination level of 40% Cl wt (Du *et al.*, 2019; Du *et al.*, 2020; Yuan *et al.*, 2020).

Table 2. Theoretical chlorine content of constituents for C₁₄₋₁₇ chain lengths

Chlorine content,	Carbon chain length				
70 W/W	C ₁₄	C ₁₅	C ₁₆	C17	
<40	$C_{14}H_{29}Cl$ to $C_{14}H_{27}Cl_3$	C ₁₅ H ₃₁ Cl to C ₁₅ H ₂₉ Cl ₃	C ₁₆ H ₃₃ Cl to C ₁₆ H ₃₀ Cl ₄	C ₁₇ H ₃₅ Cl to C ₁₇ H ₃₂ Cl ₄	
40–45	C ₁₄ H ₂₆ Cl ₄	C ₁₅ H ₂₈ Cl ₄	C ₁₆ H ₂₉ Cl ₅	C ₁₇ H ₃₁ Cl ₅	
45–50	C ₁₄ H ₂₅ Cl ₅	C ₁₅ H ₂₇ Cl ₅	C ₁₆ H ₂₈ Cl ₆	C ₁₇ H ₃₀ Cl ₆	
50–55	C ₁₄ H ₂₄ Cl ₆	C ₁₅ H ₂₆ Cl ₆ & C ₁₅ H ₂₅ Cl ₇	C ₁₆ H ₂₇ Cl ₇	C ₁₇ H ₂₉ Cl ₇	
55–65	C ₁₄ H ₂₃ Cl ₇ to C ₁₄ H ₂₁ Cl ₉	C ₁₅ H ₂₄ Cl ₈ to C ₁₅ H ₂₂ Cl ₁₀	C ₁₆ H ₂₆ Cl ₈ to C ₁₆ H ₂₃ Cl ₁₁	C ₁₇ H ₂₈ Cl ₈ to C ₁₇ H ₂₅ Cl ₁₁	
>65	C ₁₄ H ₂₀ Cl ₁₀ and higher number of Cl atoms	C ₁₅ H ₂₁ Cl ₁₁ and higher number of Cl atoms	C ₁₆ H ₂₂ Cl ₁₂ and higher number of Cl atoms	C ₁₇ H ₂₄ Cl ₁₂ and higher number of Cl atoms	

Note: Bold text indicates those blocks within scope of the proposal.

19. Available regulatory laboratory testing for "MCCPs" has been undertaken using substances with a specified chlorine content, such as 50% Cl wt. The exact constituents of "MCCPs" will always be variable (as it is a UVCB) and a block approach as shown in Table 2 is a recognised way of addressing this uncertainty. An alternative approach

¹ Tomy et al. (1997) includes a formula for the calculation of the number of isomers.

² Atmospheric pressure chemical ionisation-quantitative time of flight-mass spectrometry, Nuclear Magnetic Resonance.

is to assess the substance based on the number of chlorine atoms per chain length. For laboratory studies this requires an assumption about which congeners were present in the test, and at what abundance, as in many cases congener-specific analysis is not available. Applying the alternative approach would require an assumption of equality, rather than trends, across the different congeners to interpret each test for a specific property. Where congener-specific analysis is available, it also requires verification of the accuracy of the analysis to quantify the individual congener concentrations (including their representativeness where extrapolation from specific constituents to the whole congener group is made). The assessment approach for the Risk Profile is therefore aligned with the laboratory data. The analytical challenges associated with "MCCPs" are described elsewhere, particularly the preferred forms of analysis and their capabilities.

1.1.2 Structural formula

20. Two example structures of CPs with C_{14} and C_{17} chain lengths are shown in Figure 1 (skeletal formulae, i.e., hydrogen atoms not shown for simplicity).

Figure 1. Structures of two representative constituents of CPs with C14 and C17 chain lengths

1.1.3 Analogues

- 21. SCCPs (containing C_{10-13} carbon chain lengths) and long-chain chlorinated paraffins (LCCPs, containing C_{18-30} carbon chain lengths) are structural analogues of "MCCPs". SCCPs was listed as a Persistent Organic Pollutant in the Stockholm Convention 2017. Commercial "MCCPs" contains C_{10-13} constituents that may be analogous to SCCPs, at levels typically below 1% by weight (often much lower), although the identity and actual concentration of the individual constituents are not known. The unintentional trace contaminant threshold specified in the Annex A listing of SCCPs is 1%. The agreed Risk Management Evaluation (RME) of SCCPs indicated that "MCCPs" was one of the main alternatives to SCCPs (UNEP/POPS/POPRC.12/11/Add.3). The main uses of "MCCPs" (section 2.1.2) are very similar to uses for SCCPs previously identified in the RME document.
- 22. HSE (2008) indicated that LCCPs based on a C_{18-20} carbon chain length may contain up to 20% C_{17} CPs. A related UK report assessing LCCPs (Environment Agency, 2009) was recently updated (Environment Agency, 2022) following the substance evaluation of "MCCPs" in the EU. This concluded that further data were required to assess the PBT properties of the substance. As pointed out above, some Asian products (e.g., CP-52) contain LCCP chain lengths together with "MCCP" and SCCP chain lengths (and $C_{<10}$ constituents) in a single product.
- 23. Further details of the analogues are provided in document UNEP/POPS/POPRC.18/INF/10.

1.1.4 Physico-chemical properties

24. Key physico-chemical data are summarised in Table 3. The complexity and variability of the commercial substance means that many of the measured values represent averages or are ranges. For example, the $\log K_{OW}$ will have a range covering several orders of magnitude, reflecting the wide variety of congeners present. These values may change for products with different degrees of chlorination.

Table 3. Physicochemical properties for CPs with C₁₄₋₁₇ chain lengths

Property	Value	Source of information/remarks
Physical state at 20 °C and 101.3 kPa	Liquid	EC (2005)
Melting / freezing point	Pour point -50 °C to 25 °C (chlorination dependent)	EC (2005)
Boiling point	Decomposition ~200 °C before boiling	EC (2005)
Vapour pressure	C ₁₄₋₁₇ (52% Cl wt.) 1.3 x 10 ⁻⁴ -2.7 × 10 ⁻⁴ Pa (20 °C)	Campbell and McConnell (1980)

Property	Value	Source of information/remarks
	$\begin{array}{c} C_{14-17} \ (52\% \ Cl \ wt.) \\ 1.1 \times 10^{-3} \ Pa \ (45 \ ^{\circ}C) \\ 6.0 \times 10^{-3} \ Pa \ (60 \ ^{\circ}C) \\ 0.051 \ Pa \ (80 \ ^{\circ}C) \\ < 1 \ x \ 10^{-6} - 0.0042 \ Pa \ for \ C_{17} \ Cl_{1-15} \end{array}$	BUA (1992) as cited in EC (2005) Glüge <i>et al.</i> , (2013); Predicted vapour pressure values using COSMOtherm ² .
Water solubility	$0.0061~mg/L$ at $20~^{\circ}C$ for C_{14} chlorinated nalkane, 50% Cl wt.	Unpublished (2019a), discussed in Environment Agency (2019); non-GLP¹ OECD Test Guideline (TG) 105. Analytical method: APCI-ToF-HRMS. Study considered to be "reliable without restriction".³
	0.005–0.027 mg/L at 20 °C for C_{15} chlorinated n-alkane, 51% Cl wt.	Madeley <i>et al.</i> , (1983a); non-standard method. Analytical method: thin-layer chromatography and radioactivity measurements. Key study used in EC (2005) and considered to be a realistic upper limit for this substance.
	0.01 mg/L in freshwater and 0.004 mg/L in seawater at 16–20 °C for C ₁₆ chlorinated n-alkane, 52% Cl wt.	Campbell and McConnell (1980); method unknown. Analytical method: radioactivity measurements
	$\begin{array}{c} 1.90272~\mu\text{g/L} \text{ for } C_{14} \text{ with } Cl_{112} \\ 0.5068.1~\mu\text{g/L} \text{ for } C_{15} \text{ with } Cl_{113} \\ 0.1542.2~\mu\text{g/L} \text{ for } C_{16} \text{ with } Cl_{113} \\ 0.7212.7~\mu\text{g/L} \text{ for } C_{17} \text{ with } Cl_{115} \end{array}$	Glüge <i>et al.</i> , (2013); Predicted water solubility values using COSMOtherm ² .
Partition coefficient noctanol/water (log Kow)	6.58 ± 0.09 for C_{14} chlorinated n-alkane, 50% Cl wt.	Unpublished (2019b); non-GLP OECD Test Guideline (TG) 123 (slow stir). Analytical method: APCI ToF HRMS (only dominant congeners). Very little variability in K _{OW} was observed between differently chlorinated congener groups due to the chosen analytical method. Study considered to be reliable with restrictions.
	6.30 (5.56–7.71) C ₁₄ , 47.0% Cl wt. 6.65 (5.84–7.81) C ₁₅ , 50.4% Cl wt. 6.81 (5.78–8.38) C ₁₆ , 61.0% Cl wt. 6.67 (5.57–7.90) C _{14–17} , 46.7% Cl wt.	Hilger <i>et al.</i> , (2011a); reverse-phase HPLC method based on OECD 117 using UV detection. Considered to be reliable with restrictions as a non-GLP study. A fuller résumé is provided in document UNEP/POPS/POPRC.18/INF/10.
	7.2 (4.7–8.3) for C_{16} chlorinated n-alkane, 35% Cl wt.	Fisk <i>et al.</i> , (1998a); key study used in EC (2005). Analytical method: high performance liquid chromatography (HPLC). Study considered to provide indicative information only (due to lack

 $^{^{3}}$ Reliability assessed here and elsewhere in the document using Klimisch et al 1997.

Property	Value	Source of information/remarks
	$ 5.52 \text{ to } 8.21 \text{ for } C_{14-17} \text{ chlorinated } \text{n-alkane}, \\ 45\% \text{ Cl wt.}; \\ 5.47 \text{ to } 8.01 \text{ for } C_{14-17} \text{ chlorinated } \text{n-alkane}, \\ 52\% \text{ Cl wt.} $ $ 7.93-10.21 \text{ for } C_{14} \text{ with } \text{Cl}_{1-16} \\ 8.49-10.91 \text{ for } C_{15} \text{ with } \text{Cl}_{1-17} \\ 9.04-11.16 \text{ for } C_{16} \text{ with } \text{Cl}_{1-16} \\ 9.60-11.84 \text{ for } C_{17} \text{ with } \text{Cl}_{1-18} $	of information about internal standards and reference substances). Renberg <i>et al.</i> , (1980); non-GLP nonguideline study. Analytical method: reversed-phase high performance thin layer chromatography (RP-HPTLC). Study considered to provide indicative information only. (due to lack of information about internal standards and reference substances). Endo (2021); Predicted log K _{OW} with COSMOtherm. ⁴ A fuller résumé is provided in document UNEP/POPS/POPRC.18/INF/10.
	$6.2-8.25 \text{ for } C_{14} \text{ with } Cl_{1-14} \\ 6.63-8.76 \text{ for } C_{15} \text{ with } Cl_{1-15} \\ 7.07-9.28 \text{ for } C_{16} \text{ with } Cl_{1-16} \\ 7.33-9.8 \text{ for } C_{17} \text{ with } Cl_{1-17} \\ 7.94-9.1 \text{ for } C_{14} \text{ with } Cl_{4-10} \\ 8.43-9.84 \text{ for } C_{15} \text{ with } Cl_{4-11} \\ 8.92-10.36 \text{ for } C_{16} \text{ with } Cl_{4-12} \\ 9.59-11.04 \text{ for } C_{17} \text{ with } Cl_{5-13}$	Predicted log K _{OW} with log P methods of ACD/Labs Percepta ⁵ (provided in ECHA, 2021a). Predicted log K _{OW} using KOWWIN v1.68 ⁶ within EPIWIN TM . A fuller résumé is provided in document UNEP/POPS/POPRC.18/INF/10. Based on Glüge <i>et al.</i> , (2013), the COSMOtherm results are preferred to the EPIWIN results.
Partition coefficient noctanol/air (log KoA)	$7.56{-}16.42 \text{ for } C_{14}Cl_{1-16} \\ 8.05{-}17.56 \text{ for } C_{15}Cl_{1-17} \\ 8.54{-}18.21 \text{ for } C_{16}Cl_{1-17} 9.03{-}19.17 \text{ for } \\ C_{17}Cl_{1-18}$	Predicted log K _{OA} generated using COSMOtherm (see UNEP/POPS/POPRC.18/INF/10).

Note: Good Laboratory Practice (GLP).

1.2 Conclusion of the Review Committee regarding Annex D information

25. At its seventeenth meeting, the POPRC evaluated the proposal to list chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight in Annex A, B and/or C to the Convention. The Committee decided that, in accordance with paragraph 4 (a) of Article 8 of the Convention, it was satisfied that the screening criteria specified in Annex D to the Convention were met, with certainty for the C_{14} chain lengths and chlorination levels at or exceeding 45 per cent chlorine by weight (decision POPRC-17/5). The Committee noted that information relating to the screening criteria on bioaccumulation for chlorinated paraffins with carbon chain lengths in the range C_{15-17} was less certain, but the information relating to the remaining screening criteria specified in Annex D was conclusive. The Committee decided that more detail on bioaccumulation data should be included in the draft risk profile. The Committee also decided that issues related to chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight should be dealt with in developing the draft risk profile.

1.3 Data sources

26. The draft risk profile on chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight is based on the following data sources:

⁴ COSMOconfX 20, TURBOMOLE 7.4 and COSMOthermX 20 (all from COSMOlogic, Biovia, Dassault Systemes).

⁵ ACD/Labs release 2019.2.1, Advanced Chemistry Development, Inc., 2019.

⁶ Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency, Washington, DC, USA.

- (a) Proposal to list chlorinated paraffins with carbon chain lengths in the range C_{14-17} and chlorination levels at or exceeding 45 per cent chlorine by weight in Annex A, B or C to the Convention submitted by the UK;
- (b) Information presented at the seventeenth meeting of the POPs Review Committee (POPRC-17) and its pre-meeting;
- (c) Information submitted in accordance with Annex E to the Convention by the following Parties and observers and others: Belarus, Canada, European Union (EU), Germany, Monaco, the Netherlands, Norway, Sweden, New Zealand, the International Pollutants Elimination Network (IPEN) and Alaska Community Action on Toxics (ACAT), Lanxess, World Chlorine Council, and Chlorinated Paraffins Industry Association (CPIA);
 - (d) Peer-reviewed scientific literature, and grey literature;
 - (e) Registration dossier submitted for "MCCPs" under the EU's REACH Regulation;
- (f) EU REACH Substance Evaluation report for "MCCPs" prepared by the UK (Environment Agency, 2019a);
- (g) European Chemicals Agency (ECHA) Substance of Very High Concern support document for "MCCPs" (ECHA, 2021a); and
 - (h) Environment Canada and Health Canada review (Canada, 2008).

1.4 Status of the chemical under national and regional regulations and international forums

- 27. "MCCPs" (alkanes, C₁₄₋₁₇, chloro; CAS No. 85535-85-9) was assessed in the EU under the Existing Substances Regulation (EC) No. 793/93 (EC, 2005; EC, 2007; HSE 2008), and via a transitional Annex XV dossier under the REACH Regulation (Environment Agency, 2010). Subsequently "MCCPs" underwent Substance Evaluation under EU REACH, and the published report prepared by the UK concludes that it meets the REACH Annex XIII criteria for Persistent, Bioaccumulative and Toxic (PBT) and very Persistent, very Bioaccumulative (vPvB) properties (Environment Agency, 2019a). "MCCPs" was subsequently identified as a Substance of Very High Concern due to its PBT/vPvB properties in the EU (ECHA, 2021a). The EU SVHC listing for "MCCPs" was defined as UVCB substances consisting of more than or equal to 80% linear chloroalkanes with carbon chain lengths within the range from C₁₄ to C₁₇. This Risk Profile is principally based on the EU REACH Substance Evaluation report, which focused on the assessment of environmental endpoints. A further analysis prepared by Germany indicates concern for several uncontrolled risks for human health from "MCCPs", and uncertainty for specific toxicological endpoints (BAUA, 2020; Zellmer *et al.*, 2020). Following the European SVHC identification, a proposal to restrict "MCCPs" in the EU has recently been published (ECHA, 2022a).
- 28. A proposal for an EU restriction of "MCCPs" in electrical and electronic equipment under the Restriction of the use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) Directive (2011/65/EU) was prepared by Sweden in 2018 (KEMI, 2018). As part of preparatory work, a supporting report suggested risks to workers in certain scenarios where Personal Protective Equipment was not worn, and also environmental risks for some specific scenarios (KEMI, 2017).
- 29. The Australian Department of Health published a hazard assessment of "MCCPs" in June 2020 (NICNAS, 2020). The review concluded that "MCCPs" meets Australia's domestic PBT criteria, and that some congener groups may meet the Annex D screening criteria for POPs under the Stockholm Convention.
- 30. Environment Canada and Health Canada reviewed the CPs group in 2008 (Canada, 2008) and concluded that "chlorinated alkanes that have the molecular formula $C_nH_xCl_{(2n+2-x)}$ in which $10 \le n \le 20$ " are "toxic" as defined in paragraphs 64 (a) and (c) of the Canadian Environmental Protection Act, 1999. This includes CPs of the chain lengths for "MCCPs" covered in this Risk Profile.
- 31. In their review of Pre-Manufacture Notifications for two "MCCPs" products manufactured and supplied in the United States of America (USA), the US Environmental Protection Agency concluded that these *may be very persistent and very bioaccumulative*, and *may present an unreasonable risk following acute and chronic exposures to aquatic organisms* (USEPA, 2015).

⁷ The substance is entering, or may enter, the environment in quantities or concentrations or under conditions that: have or may have an immediate or long-term harmful effect on the environment or its biological diversity, or constitute or may constitute a danger in Canada to human life or health.

2. Summary information relevant to the risk profile

2.1 Sources

2.1.1 Production and trade

- 32. Guida *et al.*, (2020) review the history of manufacturing of CPs which began in the 1930s and note that currently, "MCCPs" and LCCPs represent the largest components of CP production. Both "MCCPs" and LCCPs are replacing SCCPs in their applications in the short- or medium-term following the listing of SCCPs under the Stockholm Convention.
- 33. The available supply data for "MCCPs" is summarised in Table 4. China is the main country producing CP products containing C_{14-17} chain lengths. More details of the country-specific volumes are provided in document UNEP/POPS/POPRC.18/INF/10. Based on the information current global production of CPs with C_{14-17} chain lengths could be in the region of 800,000 tonnes per year.

Table 4. Global supply volumes and number of producers (collated from Guida *et al.*, (2020), Chen *et al.*, (2022), Li *et al.*, (2018b), ECHA (2022b), ECHA (2022c), Altair Chimica (2021), NICNAS (2020), Glüge *et al.*, (2018), Republic of Korea Annex E information, Canada Annex E information, IPEN Annex E submission, USEPA (2015)

Country or region	Volume manufactured (tonnes/year)	Number of producers	
Australia	1,000–9,999 (2006)	Not known	
Bangladesh	19,500 (2011)	Not known	
Canada	550 (2017)	Not known	
China	450,200 (2019)	100–150	
Europe	110,000 (2021)	11 (EU REACH registrants) 549 (CLP notifiers)	
India	150,000 (2011)	Not known	
Jordan	12,000 (2015)	Not known	
Republic of Korea	36 (2018)	Not known	
Russian Federation	27,000 (2011)	Not known	
Thailand	20,000 (1994)	Not known	
USA	15,529 (2015)		
Japan, Egypt, South Africa and Brazil	Supply of CPs or "MCCPs" indi	icated in the literature but no numerical data	

2.1.2 Uses

- 34. Based on information from Altair Chimica (2021), EC (2005), ECHA (2022b), Chen *et al.*, (2022), USEPA (2015), Norway and Canada (Annex E submissions), the following uses of "MCCPs" are known: as a secondary plasticiser in PVC, adhesives, sealants, paints and coatings; a flame retardant in PVC rubber compounds and other polymers, adhesives, sealants, paints and coatings, and textiles; an extreme pressure lubricant and anti-adhesive for metal working fluids; a waterproofing agent for paints, coatings and textiles; a carrier solvent for colour formers in paper manufacture; fat liquors for leather processing; and carbonless copy paper. "MCCPs" in polymers/rubber (all uses), adhesives and sealants represents the vast majority of all uses in the EU, whereas Chen *et al.*, (2022) noted PVC products dominate "MCCP" usage in China.
- 35. MCCPs have been detected in the following: polymeric packaging (e.g., polyethylene terephthalate, polypropylene and polyethylene) including for food-related products, toys and animal feed; articles including consumer cables such as headphones, toys including rubber ducks, kitchen appliances, dishcloths (following their use in domestic kitchens), mobile phone protective cases, PVC products such as a pool mat and jump rope, clothing; plastic sports courts and synthetic turf; and do-it-yourself spray one-component polyurethane foams (McGrath *et al.*, 2021; Netherlands (Annex E submission); Brandsma *et al.*, 2021; Wang *et al.*, 2018; Su *et al.*, 2020; Kutarna *et al.*, 2022; Sprengel and Vetter, 2021a; Yuan *et al.*, 2021; Gallistl *et al.*, 2017; Gallistl *et al.*, 2018; Li *et al.*, 2021).
- 36. Recent research in waste goods has indicated the presence of "MCCPs" in furniture textiles, end-of-life vehicles, waste electrical and electronic equipment (WEEE), PVC cabling and several other PVC products (NEA,

2021). "MCCPs" have also been detected in end-of-life car tyres, 8 rubber granulates made from car tyres, and playground tiles made from rubber granulates (Brandsma *et al.*, 2019).

2.1.3 Releases to the environment

- 37. CPs can potentially be released to the environment throughout their lifecycle from production, use in industrial processes, during the service life of consumer products, and disposal.
- 38. As part of the Risk Management Options Analysis for "MCCPs" in the EU, the release estimates for the different lifecycle stages were estimated based on information⁹ in the REACH Registrants' Chemical Safety Reports (Environment Agency, 2019b). The values are provided in Table 5 and Table 6. A total of 305 tonnes per year is estimated to be emitted to the environment within the EU. The total estimated release to surface water in Table takes account of the removal of "MCCPs" from aqueous waste streams by wastewater treatment plants. This diverts approximately 149 tonnes per year of "MCCPs" to sludges, which may be landfilled, used in agriculture or incinerated.

Table 5. Estimated total releases of "MCCPs" to the EU environment by use from all lifecycle stages (Environment Agency, 2019b)

Use	Total releases per year (tonnes)
"MCCPs" manufacture	0
PVC and rubber (formulation, conversion, service life)	41
Adhesives/sealants (formulation, use, service life)	126
Metalworking fluids (formulation and use)	100
Textiles (formulation and service life)	13
Paints/coatings (formulation, use, service life)	10
Paper manufacturing/recycling	15
TOTAL	305

Table 6. Estimated total releases of "MCCPs" to the EU environment from all lifecycle stages

Release route	Total releases per year (tonnes)
Water	4
Air	91
Soil	61
Sewage sludge, which may be used in agriculture, landfilled or incinerated	149

- 39. Emissions from "MCCPs" in products were reported to have decreased slightly from 2010 to 2019 in Norway (Annex E information, Norway).
- 40. Chen *et al.*, (2022) estimated that 3 800 and 4 100 tonnes of "MCCPs" were emitted into China's environment in 2018 and 2019.
- 41. Based on the EU emissions estimates, if the proportion of "MCCPs" released per year in the EU (305 tonnes) is applied to the estimated global supply tonnage, ¹⁰ this suggests between 2,400 and 24,000 tonnes per year is being released to the environment at a global scale. Clearly the global tonnage is an approximation, and this calculation assumes that the EU use pattern and emission controls are similar across the world. Based on the estimates of Chen *et al.*, (2022) and Guida *et al.*, (2020) emissions as a proportion of the volume of "MCCPs" supplied at a global level may be higher (for example Guida *et al.*, (2020) cite several studies detecting "MCCPs" at CP production sites in China and USA). Through modelling of the lifecycle, Chen *et al.*, (2022) estimated that cumulative global emissions of "MCCPs" in 2020 were approximately 2.08 million tonnes (40% of 5.2 million tonnes of total CPs). The authors identified wastewater treatment as the dominant emission source for CPs (accounting for ~84% of the cumulative CP

⁸ The authors propose that the levels detected indicate that "MCCPs" contamination may occur during car tyre manufacture, rather than specific inclusion to provide a property such as flame retardancy.

⁹ Tonnage relevant for the lifecycle and quoted emission factor.

 $^{^{10}}$ 305 tonnes/year released from the range of 10,000 to 100,000 tonnes supplied in the EU applied to the estimated global use volume of 800,000 tonnes/year.

emissions), followed by in-use stock of CPs (~9%), with emissions from industrial processes (production of CPs and industrial processing of CP-containing products), accounted for ~4%.

2.2 Environmental fate

2.2.1 Chemical analytical challenges

42. The highly complex nature of CPs means that there are considerable analytical challenges associated with their detection and quantification. In their pure form strong mass interferences can be evident i.e., where high molecular weight "MCCPs" and low molecular weight LCCPs cannot be differentiated due to low mass resolution of the detection method (Schinkel et al., 2018). The most common methods for quantifying "MCCPs" at a homologue and congener level are LC-API-HRMS, 11 GC-ECNI-HRMS12 (including direct injection APCI-HRMS)13 and GC-ECNI-LRMS, 14 respectively. Each of these analytical methods corresponds to the following form of evaluation pattern deconvolution, homologue specific, and linear regression, detailed in Bogdal et al., (2015), Yuan et al., (2017a) and Chen et al., (2011), respectively. These three methods are respectively capable of discerning different CP congeners (same carbon chain length with a given number of chlorine atoms, e.g., CnClm, also referred to as groups of positional isomers), congener groups (a selected range of carbon chain lengths, usually with an averaged degree of chlorination), and homologues (same chain length but varying number of chlorine atoms). Direct injection into HRMS instruments has been shown to provide a relatively large amount of relevant data only for 'clean' samples (Kraetschmer et al., 2019). No chromatographic method is currently available that allows for the separation of congeners into their different isomers. NMR analysis is required for this level of detail (Sprengel et al., 2019) and can only confirm the structure of single isomers (van Mourik et al., 2021). The degree of chlorination can also be important, especially if the substance in a sample differs from the analytical standards used. Based on work of Brandsma et al., (2017), Bogdal et al., (2015) and Yuan et al., (2017), there remains uncertainty with the identification and quantification of "MCCP" congeners with fewer than 5 chlorine atoms where methods used ECNI (van Mourik et al., 2015). In addition. higher-chlorinated homologues are preferentially ionised and produce a stronger signal in MS detectors (e.g., Meziere et al., 2020). Furthermore, some commonly used low resolution mass spectrometry methods may be subject to interferences from both the matrix and other contaminants (such as chlordanes, polychlorobiphenyls and toxaphenes) unless highly efficient sample clean-up procedures are used. Measured values reported in academic literature pre-2011 should be considered indicative but not quantitative. After 2011, detections of "MCCPs" in biota and the environment are considered to be semi-quantitative in the following discussion. This is due to the number of different methods, instruments and laboratories involved. The most recent HRMS methods (2015 onwards) where mathematical corrections have been applied to account for variance between 'standards' and samples are considered accurate but cannot be described as fully quantitative due the absence of certified reference standards. The vast majority of monitoring studies whether of biota, sediment, soil or air matrices are limited to the detection of "MCCP" congeners with only 5-10 chlorine atoms. This is linked to the reference standards used as well as analytical limitations (Kraetschmer et al., 2019). Unless the text indicates otherwise, it should be assumed congener detection was limited to these chlorination ranges.

2.2.2 Persistence

2.2.2.1 Abiotic data

43. Data for photodegradation in air are discussed in the Potential for Long-Range Environmental Transport section 2.2.4.1. There are no reliable data for photodegradation in other media such as water. Due to their structure, CPs are not expected to hydrolyse significantly.

2.2.2.2 Biotic data

2.2.2.2.1 Biotic screening data

44. Predicted biodegradation data are presented by ECHA (2021a) for the following "MCCP" congener groups: C₁₄Cl₁₋₁₄; C₁₅Cl₁₋₁₅; C₁₆Cl₁₋₁₆; and C₁₇Cl₁₋₁₇, using BIOWIN 2, 3, and 6¹⁵ models. Using the ECHA persistence screening criteria (ECHA, 2017), ECHA concluded that the C₁₄Cl₁, C₁₅Cl₁ and C₁₆Cl₁ congeners did not screen as either persistent or very persistent. The C₁₄Cl₂, C₁₅Cl₂, C₁₆Cl₂, C₁₇Cl₁ and C₁₇Cl₂ congeners screened as "potentially either persistent or very persistent with more information required". The congeners C₁₄Cl₃, C₁₅Cl₃, and C₁₇Cl₃,

¹¹ LC-API-HRMS: Liquid chromatography-atmospheric pressure ionisation-high resolution mass spectrometry.

 $^{^{\}rm 12}$ GC-ECNI-HRMS: Gas chromatography-electron capture negative ionisation-high resolution mass spectrometry.

¹³ APCI-HRMS: Atmospheric pressure chemical ionisation-high resolution mass spectrometry.

¹⁴ GC-ECNI-LRMS: Gas chromatography-electron capture negative ionisation-low resolution mass spectrometry.

¹⁵ Using the BIOWIN v4.10 program of EPIsuite v4.1.

screened as "potentially persistent or very persistent". All "MCCP" congeners with more than 3 chlorine atoms also screened as "potentially persistent or very persistent", although for one of the models the congeners were not within the applicability domain due to the number of chlorine atoms. The predictions for the Cl₃ and Cl₄ congeners are given a low weight in this assessment as these data are at odds with the observed high levels of degradation seen in the measured screening studies covering the relevant chlorination range described elsewhere. Overall, while the predicted data suggest a trend in biodegradation with degree of chlorination, the measured data indicate greater levels of chlorination are needed before persistence occurs.

- 45. A number of biodegradation screening studies have been performed in the same laboratory to investigate the influence of chain length and chlorination level on biodegradation potential of CPs with C_{14-17} chain lengths (CPIA Annex E submission). These were mostly 16 based on the OECD TG 301 (ready biodegradation) using modified conditions by including a surfactant (alkylphenol polyalkoxylate) to increase bioavailability, and in some cases, an extended time period for the test. A summary of all the test results presented in Environment Agency (2019a) is provided in document UNEP/POPS/POPRC.18/INF/10. The summary below focuses on tests where the conditions are judged suitable for the Annex D/E assessment.
- 46. Under the conditions of these studies, C_{14} chlorinated n-alkanes with a chlorine content of 41.3% and 45.5% were readily biodegradable within 28 days (>60% mineralisation). C_{14} chlorinated n-alkane, 50% Cl wt. failed to meet the 60% pass threshold within 28 days but did meet it after 56 days.
- 47. Both a 55% and 60% Cl wt. C_{14} chlorinated n-alkane failed to meet the pass threshold of 60% degradation even after 60 days. A C_{15} chlorinated n-alkane, 51% Cl wt. also failed to meet the pass threshold after 60 days.
- 48. C_{14-17} chlorinated n-alkane, 45.5% Cl wt. achieved 51% degradation after 28 days (and so was not readily biodegradable), although a test using an extended timescale was not available. C_{14-17} chlorinated n-alkane, 51.7% Cl wt. was not readily biodegradable in 28 days (achieving 27% degradation) and although it was extensively degraded over an extended period (57% degradation after 60 days) in the same test it still failed to reach the 60% threshold. C_{14-17} chlorinated n-alkane, 63.2% Cl wt. only achieved 10% degradation under the same conditions.
- 49. In summary, these ready biodegradation studies indicate that substances with a lower level of chlorination can be extensively degraded by micro-organisms under conditions of enhanced bioavailability. The trend in the data shows that degradability reduces as the average number of chlorine atoms per molecule increases. There are no screening degradation data for specific C_{16} or C_{17} substances alone. However, it should be noted that the mixture of C_{14-17} substances was less degradable than its C_{14} or C_{15} counterparts at the same level of chlorination. This suggests that these longer chain lengths are less degradable (otherwise the mixtures should have been more degradable than reported). This observation fits with the general expectation that degradation will decrease with increasing carbon chain length, due to decreasing water solubility (Glüge *et al.*, 2013) and greater adsorption capacity (Gawor and Wania, 2013). The same trend in degradation was also observed by Knobloch *et al.*, (2021) for SCCP congeners. In the case of simple hydrophobic substances such as "MCCPs", water solubility will be inversely proportional to K_{OW} , and K_{OC} will be proportional to K_{OW} . As can be seen from the predicted log K_{OW} values in Tables 6 and 10 of document UNEP/POPS/POPRC.18/INF/10, there is a clear increasing trend in log K_{OW} values with increasing carbon chain length.
- 50. It should be noted that it is not possible to extrapolate information from these screening tests to an environmental half-life.
- 51. A test according to OECD TG 314B (biodegradation in activated sludge) and Good Laboratory Practices (GLP) has recently been performed using a 52% Cl wt. C_{14-17} substance. The test material was radiolabelled using tritium, and the 28-day test was conducted using Triton X-100 solubiliser (Eurofins EAG Agroscience, 2022). The test concentration was 54.7 μ g/L, the inoculum concentration was 2.5 g/L (as suspended solids) and solubiliser concentration was 322 μ g/L. The test temperature was between 19.5 °C and 21.3 °C. The study suggested 87.4% mineralisation (based on formation of 3 H₂O) in 24 hours under the conditions of the test. This contrasts with the significantly more limited degradation observed in other screening studies. There was no specific analysis to confirm if the measured mineralised radioactivity related to parent substance rather than the kinetics of the radio tracer. This is an important drawback of the study since tritium is known to exchange with hydrogen atoms of protein-related substances of which there would be many present in the test system (Nivesse *et al.*, 2021). The test guideline also does not offer the option of a solubiliser to administer the substance to the test vessels. Furthermore, the conditions are considerably more favourable to biodegradation compared to other (standard) screening studies (e.g., the concentration of suspended solids is approximately 300 times that of the OECD TG 310). Due to these factors, the

¹⁶ A number of studies used pre-adapted inoculum, which is not appropriate for current REACH Annex XIII assessments and is similarly not considered appropriate for the Annex D screening criteria. Three tests were also performed using OECD TG 302A (Inherent Biodegradability: Modified SCAS Test); the high inoculum concentrations used in these studies mean that the results are not relevant for persistence assessment. In both cases these data are not summarised in this risk profile.

results of the study are not considered to be reliable for the purposes of this assessment. It should also be noted that the OECD TG 314B does not provide a measure of ready biodegradability nor a relevant environmental half-life.

52. A second GLP OECD 314B study was performed under the same conditions and to an identical protocol (Eurofins EAG Agroscience, 2022b). The test substance was prepared by combining tritiated and non-radiolabelled C_{14-17} 52% Cl wt. in a proportion of 1:195. The test concentration was reported to be 150 times the one used in the first study, however the nominal or confirmed initial test concentrations are not clear. The report does not provide a table of percentage biodegradation against sample time, but the text indicates significant degradation was observed within 23 h (no value reported), with >90% biodegradation based on radioactivity achieved by Day 9. Confirmation of biodegradation was severely compromised through interferences in both the biotic and abiotic vessels. It appears that the addition of mercuric chloride compromised the separation and detection in the GC- μ ECD in abiotic vessels, and no analysis of spiked inoculum blanks or spike extraction procedural blanks were reported for the biotic vessels. During the test, there were significant changes in the 'MCCPs' region in GC- μ ECD spectra with poorly resolved regions appearing (when compared to analysis of the standard), which could be interpreted as an indication of biodegradation. Large areas of unresolved and deteriorated peak shapes were observed in the supporting figures. However, in the absence of further work and identification of potential transformation products, the concerns raised for the first (solely tritiated) study remain but with further issues. Overall, without secondary analytical confirmation it is not possible to be confident that degradation is occurring. The results of this study are considered unreliable.

2.2.2.2.2 Environmental simulation data

53. An OECD TG 308 (aerobic and anaerobic transformation in aquatic sediment systems) study has been conducted using non-radiolabelled C_{14} chlorinated n-alkane, 50% Cl wt., in accordance with GLP (Unpublished, 2019c and 2019d). This is described in detail in Environment Agency (2019a). The test was conducted under aerobic conditions using two types of sediment and a nominal test substance concentration of 5 μ g/g dry weight (dw) in sediment. Test vessels were sacrificed on days 0, 15, 30, 45, 60, 91 and 120 (the test guideline specifies that the test should not be run for longer than 100 days). Chemical analysis was performed using APCI-ToF-HRMS. Apart from a single measurement at 91 days, the mean measured concentrations from all sampling intervals did not deviate by greater than 8% (calculated relative standard deviation; RSD) of the applied nominal concentration. Congener-specific analyses¹⁷ for the extracted samples showed no significant variation between these extracts, the extracted spiked sand and the original test substance. Overall, the chemical analysis showed no observable biotransformation in two different sediments, and so the sediment half-life was >120 days at 12 °C. The study is assessed to be reliable with restrictions due to the incomplete mass balance resulting from the lack of a radiolabel and the form of extraction used for the sediment samples.

2.2.2.2.3 Environmental compartment monitoring

- 54. Environmental monitoring data are summarised in section 2.3.1 and in document UNEP/POPS/POPRC.18/INF/10. CPs have been detected in sediment cores taken from several locations around the world, and this section focuses on these studies as they are relevant to the laboratory data summarised in section 2.2.2.2.2.
- 55. Iozza *et al.*, (2008) took a sediment core covering the period 1899–2004 from Lake Thun, Switzerland in May 2005. The lake is in a mainly rural Alpine catchment area without any known point sources (e.g., metal or polymer industries). The level of "MCCPs" measured using GC-ECNI-LRMS in the sediment core showed an increasing trend from 1965 onwards reaching a level of $26 \mu g/kg$ dw in the surface layer (i.e., 2004). Concentrations between 15 and $20 \mu g/kg$ dw were evident in the samples dated to the 1980s. The C_{14} carbon chain length was the most abundant present (accounting for 41 to 64% of the total "MCCPs"), although it is noted that that all chain lengths could be detected in all core sections. Chlorine content of "MCCPs" was slightly higher in the more recent core sections between 1994 and 2004 (generally around 56% wt. with little variation). Over a longer period back to 1961 chlorine content decreased to around 53.3% wt.). The range of chlorination seen for SCCPs was wider over this period (63.7–69.5 %), but with a peak level around 1986. The authors offered two explanations of the chlorination trend: a change to higher chlorine content CPs or dechlorination of CPs in older sediments. C_{14} chain length were dominant for "MCCPs" with C_{16} most frequently detected. C_{15} congeners made up between 2 and 7% of the detected "MCCPs" congeners.
- 56. Chen *et al.*, (2011) took a sediment core from the Dongjiang River within Dongguan city in the Pearl River Delta (PRD) area of south China. This city is the largest manufacturing base of electronic products in the PRD. The sediment core was thought to contain about 15 years of deposition. Using GC-ECNI-LRMS analysis, the concentrations of "MCCPs" were higher in the upper layers of the core than in the deeper layers; 1,400 to 3,800 μg/kg

¹⁷ There may be uncertainty regarding the analysis of lower chlorinated congeners (<5 chlorine atoms).

¹⁸ A further possible explanation not mentioned in either paper is that heavily chlorinated congeners are likely to be more strongly bound to sediment, and so more difficult to extract for analysis, particularly with increasing time since deposition.

dw between 0 and 32 cm depth compared with 1,100 to 1,400 μ g/kg dw between 36 and 68 cm depth. The increasing concentrations in the upper layers were thought to be a result of increasing use of "MCCPs" in the area. The "MCCP" concentrations in the lower layers were relatively constant. It was noted that there was a higher relative abundance of C_{16} and C_{17} substances in the upper layers (from 0 cm to around 44 cm depth) than in the lower layers, with the relative proportion of C_{14} substances being slightly higher in the lower layers than the upper layers. It was suggested that this may reflect changes in the composition of "MCCPs" used in the area over time. Nevertheless, the C_{14} chain length dominated with around 60% of the total "MCCPs" detected. Little variation in the chlorination of "MCCPs" was seen across the core compared to SCCPs. The authors suggest that this was because longer chained CPs (i.e., "MCCPs") had a lower potential to dechlorinate. Cl_{5-10} congeners were detected with Cl_{7-9} congeners most often detected, the level of variation in chlorination is similar to the observations of Iozza *et al.*, (2008) for a similar period of time.

- 57. Sediment cores were taken by Yuan *et al.*, (2017) at three different locations in Sweden (downstream of a wastewater treatment plant, near to an industrial wood processing area, and to a steel factory). Using APCI- QToF-MS analysis, the authors detected "MCCPs" at concentrations of < 6.5 to 93 μ g/kg dw. This included detection in sediment from cores dated as 1954 and 1960. Furthermore, within the ~80 years of sedimentation spanned by the cores, temporal trends could be seen indicating a decrease in SCCPs reflecting their restriction, and a concurrent increase in "MCCPs". At a congener level all four "MCCPs" carbon chain lengths were detected and presented as summed total "MCCP" concentrations. The C₁₄ congener dominated in two of the cores (up to 89%), but all four congeners were evenly distributed in the steel factory core. The analytical method allowed detection of Cl₃₋₁₅ congeners and found for "MCCPs" the average degree of chlorination varied from 48–55%, but the paper does not report the trend in congeners in the different cores.
- 58. Sediment cores were taken from 2 urbanised coastal locations: waters around Hong Kong SAR (1 core, taken in 2004) and Tokyo Bay (2 cores taken in 2012) by Zeng *et al.*, (2017a). These were analysed for SCCPs and "MCCPs" using GC-ECNI-LRMS. "MCCPs" were detected in horizons that were estimated to have been deposited in the late 1950s in both locations. Surface concentrations were 20.3 μg/kg dw in waters around Hong Kong SAR, and 7.9 and 29.3 μg/kg dw in the cores (2–4 cm) from Tokyo Bay, although these represent different sampling times so are not comparable. The maximum historic concentration in the cores were from the late 1980s: 180 μg/kg dw in the cores from Tokyo Bay, and 7.3 μg/kg dw in the core from waters around Hong Kong SAR. Declines in both SCCPs and "MCCP" concentrations were noted in Tokyo Bay from the 1990s to more recent periods, which were suggested by the authors to reflect declining manufacture and use due to regulatory controls introduced in the early 2000s. However, in both cores the concentration in the uppermost core slice are within an order of magnitude of the levels in core slices from the previous 8 years. Recent trends in the core from waters around Hong Kong SAR cannot be discerned due to the older core sampling date. At a congener level all four "MCCPs" carbon chain lengths (and Cl₅₋₁₀) were detected and presented as summed total "MCCP" concentrations. From a figure in the supplementary information, C₁₄ was the most prevalent chain length (66.8–79%), with the detection frequency for the remaining chain lengths between 7.0 and 28.1%.
- Zhang et al., (2019) took sediment cores from the deepest location of 9 lakes in China, including 2 located in areas remote from industry (Lake Qinhgai and Lake Bosten, situated in the Tibetan Plateau and Mengxin lake regions of north-western China were remote from areas of industry). Most cores were taken in 2006 and cover a period from about 1930. Complementary surface sediment samples were taken in 2018 and 2019, together with four shallower sediment cores taken between 2011 and 2019 from the non-remote lakes. All cores were analysed for CPs using UPLC-QToFMS¹⁹ (analysis appears to have been performed in 2019). "MCCP" concentrations are presented as total "MCCPs" based on summed congener level analysis. Graphically presented data indicate Cl₆₋₁₀ were detectable. Concentrations were low or below 5.0 µg/kg dw (the limit of detection) until the 1970s, after which the lowest surface "MCCP" concentrations (35 to 269 µg/kg dw) were observed in the remote lakes, with higher surface "MCCP" concentrations in lakes near to larger cities and manufacturing industries (643 to 3 390 µg/kg dw. For the more contemporary cores from non-remote lakes, "MCCP" concentrations in the top slice are similar to those in the slices representing the early 1990s. The homologue profile of "MCCPs" was noted to be similar in nearly all lakes, with the C₁₄ chain length and the Cl₇ and Cl₈ chlorination levels dominant. The authors indicate the distribution observed is similar to CP-42, a commercial Chinese product. "MCCPs" as a proportion of overall detected CPs in the cores was noted to be increasing, with SCCPs decreasing. Zhang et al., (2019) also proposed that the presence of CPs in the two remote lakes (in cold areas at high elevations) could be the result of long-range atmospheric transport through cold trapping and deposition.
- 60. "MCCPs" were detected at concentrations ranging from 400 to 1,200 μg/kg dw in sediment core layers dating between 1972 and 1995, from Lake St. Francis, downstream of Cornwall, Ontario, Canada (Muir *et al.*, 2002). Based on the data, Canada (2008) estimated the half-life of "MCCPs" in sediments to be longer than 1 year.
- 61. In summary, measurable levels of "MCCPs" are present in deeper (older) sediment layers that are of the same order of magnitude as levels in surface (recent) layers. This provides indirect evidence that the substance may be

¹⁹ Ultra-Performance Liquid Chromatography to Quadrupole Time-Of-Flight Mass Spectrometry.

persistent in sediments over many years. It is acknowledged that degradation conditions (e.g., redox potential) will vary with depth, and levels will also depend on the environmental emission at the time of deposition. Where congener analysis was performed, all four carbon chain lengths were detected. Based on the above studies C_{14} was generally the dominant chain length, with the chain length profile noted to align with commercial CP products in several papers. As C_{14} appears to dominate commercial products, the preponderance of the detection C_{14} congeners in the field is likely to be due to this, and does not imply any heightened persistence relative to other longer carbon chain congeners.

62. "MCCPs" have been detected to a limited extent in several studies analysing marine sediment collected in the Arctic. These are described in more detail in section 2.3.1.4.1. Detection of "MCCPs" at wastewater treatment plants is summarised in section 2.3.1.3.

2.2.2.3 Persistence synthesis

- 63. The key data are the absence of transformation of a C_{14} chlorinated n-alkane, 50% Cl wt. substance after 120 days in two sediments in an OECD TG 308 study (Unpublished, 2019c and 2019d; as described in Environment Agency, 2019a). The absence of degradation at 120 days in the study suggests that it is very unlikely that significant degradation would subsequently occur between 120 and 180 days. This hypothesis is supported by the sediment core monitoring data, where levels of "MCCPs" in recently deposited horizons are of a similar order of magnitude to those horizons in the same core which represent deposition from 8 or more years ago. While a modified screening biodegradation test using C_{14} chlorinated n-alkane, 50% Cl wt. indicated extensive biodegradation after 56 days, no degradation occurred in the OECD TG 308 study using the same test substance. Since the simulation test is more environmentally relevant, it is given the greatest weight in the assessment of persistence. The negligible degradation rate in aerobic sediment may reflect a reduction in bioavailability caused by adsorption.
- All of the "MCCPs" substances that were tested in the modified and enhanced ready tests (section 2.2.2.2.1) and shown to be less degradable than C₁₄ chlorinated n-alkane, 50% Cl wt. are likely to therefore have similar or longer sediment half-lives as the C₁₄ (50% Cl wt.) congener block. Given the predicted and observed trends in physico-chemical properties (Table 3), it can be reasonably expected that C₁₅₋₁₇ constituents with similar or higher chlorine contents to C₁₄ chlorinated n-alkane, 50% Cl wt. will be equally or more adsorptive to sediment. They are therefore likely to be equally or more persistent in sediment (i.e., the sediment half-lives will exceed 180 days). This hypothesis is supported by the detection of all four relevant chain lengths in the older horizons of sediment cores where congener level analysis was performed (e.g., ; Cl₆; 51% Cl wt. average Yuan *et al.*, 2017; C₁₄₋₁₇; 62% made up of Cl₇₋₈ Wu *et al.*, 2020) (see UNEP/POPS/POPRC.18/INF/10). In several of these publications it is clear that C₁₄ is the dominant chain length often with Cl₇₋₈ the dominant congeners. In many of them Cl₅₋₁₀ are frequently detected (Iozza *et al.*, 2008; Chen *et al.*, 2011; Yuan *et al.*, 2017; Zeng *et al.*, 2017a; Zhang *et al.*, 2019). Furthermore, where the comparison was made, the chain length profile in the sediment cores is similar to commercial CPs i.e., the profile appears unchanged following emission, suggesting that degradation has not occurred.
- 65. "MCCPs" have also been detected in remote regions such as sediments in Lake Qinhgai and Lake Bosten in China, and the Arctic (see UNEP/POPS/POPRC.18/INF/10). Such detection far away from point sources suggests that the "MCCPs" can persist following deposition as a result of long-range environmental transport. Further supporting data from surface sediment sampling is provided in section 2.3.1.4.
- 66. C_{14} chlorinated n-alkanes with a low chlorine content (\leq 45% Cl wt.) are readily biodegradable based on the available measured data. In contrast, a C_{14-17} chlorinated n-alkane, 45.5% Cl wt. was not readily biodegradable although there was extensive mineralisation (51%) after 28 days. It is possible that adsorption could cause these substances to have longer sediment half-lives than expected, but no robust data are available to allow a conclusion to be drawn.
- 67. It is acknowledged that the OECD TG 308 study using a C_{14} chlorinated n-alkane, 50% Cl wt. (equivalent to 35.32–72.98% Cl wt), with congener specific analysis showed a degradation half-lives > 180 days. However, there are considered to be uncertainties regarding the conclusions that can be drawn for the analysis of congeners with <Cl₅ atoms in this study. These are the analytical issues described in 2.2.1, and the low proportion of these congeners present in the 50% Cl wt. test substance that was used.
- 68. For UVCB substances, there could be uncertainties regarding degradation as it is possible that persistent constituents might be present in the <45% Cl wt. fraction used in the screening studies. Additionally, the contribution of the different congeners to the overall degradation is unknown, and information regarding the congener specific composition of the test substance is lacking. However, the high level of mineralisation (as the OECD criteria for ready biodegradation was met) attained in these specific screening studies suggests that the concentration of any potentially persistent constituents present is likely to be low.
- 69. Given that the readily biodegradable test results for two specific tested C_{14} substances would meet the OECD definition of "readily biodegradable", chain lengths below 45% Cl wt. are excluded from this proposal.
- 70. Overall, the half-life for sediment is assessed to exceed 180 days for all C_{14-17} chain lengths with chlorination levels \geq 45% Cl wt.

2.2.3 Bioaccumulation

2.2.3.1 Screening information

- As shown in Table 3, the constituents of CPs with C₁₄₋₁₇ chain lengths have a range of log K_{OW} values, but all measured and predicted values exceed 5. C₁₄ chlorinated n-alkane, 50% Cl wt. has a reliable measured log K_{OW} of 6.6. Hilger *et al.*, (2011a) determined a range of measured log K_{OW} values between 5.56 and 8.68 for C₁₄₋₁₆ chain lengths with different chlorination levels. This used an HPLC method (indirect method for the determination of logK_{OW}) identical to OECD TG 117, which allowed for an analysis across the range of "MCCPs", with log K_{OW} results all exceeding 5, further details of the study are available in document UNEP/POPS/POPRC.18/INF/10. Predictions of log K_{OW} using COSMOtherm and ACD/Labs software show good agreement with the available measured data (Glüge *et al.*, 2013; Endo, 2021; ECHA, 2021a; Gawor and Wania, 2013). In comparison, predictions of physico-chemical properties using EPIWIN^{TM20} provide poorer agreement²¹ (Glüge *et al.*, 2013; Environment Agency, 2019a). The predictions indicate that log K_{OW} values are relatively independent of chlorine content for a given carbon chain length, up to a chlorine content of 55% Cl wt. Log K_{OW} is likely to increase with chlorine content above 55% Cl wt. for a given chain length. In other words, there is little change in log K_{OW} values from Cl₁ to around Cl₅, and then an increase above this level of chlorination. Log K_{OW} also increases with increasing carbon chain length. Further details of predictions of log K_{OW} for specific congeners using COSMOtherm can be found in document UNEP/POPS/POPRC.18/INF/10.
- 72. According to OECD TG 117 It is preferable that the reference substances should be structurally related to the test substance. The reference substances used in the study were aromatic (monopolar) compounds, and so are not close structural analogues of chlorinated paraffins, which are apolar. The choice was made as there was a lack of sufficient log K_{OW} data of compounds with a structure similar to CPs. Nevertheless, OECD TG 117 further states If data on the partition coefficients of structurally related substances are not available, a more general calibration, established with other reference substances, may be used.
- 73. As further support to the results of the test, the log K_{OW} of 6.58 measured in the recent GLP slow stir study (OECD TG 123) for C_{14} 50% Cl wt. is comparable to the result reported by Hilger et al (2011) for C_{14} 47% Cl wt (6.30).
- 74. Al Overall, the weight of evidence is that log K_{OW} is greater than 5 for all constituents of CPs with C_{14-17} chain lengths with chlorination >45% using predicted and measured data. The values tested for C_{15-17} chlorinated paraffins with chlorination >45% are considered to be reliable with restrictions and this does not prevent a conclusion being drawn from the tests.

2.2.3.2 Aquatic fish bioaccumulation studies

- A reliable fish bioconcentration study with Rainbow Trout (*Oncorhynchus mykiss*) was conducted according to OECD TG 305 and GLP using a 14 C radio-labelled C_{14} chlorinated n-alkane, 45% Cl wt. product (Unpublished, 2010a and 2010b). This is detailed in Environment Agency (2010). The test used a single measured aquatic exposure concentration of $0.34~\mu g/L$ during uptake, which was well below the water solubility limit. Dimethyl formamide was used as a solvent (0.004~mL/L). The fish were exposed to the substance for 35 days followed by a 42-day depuration period, under flow-through conditions. In follow-up analytical work, it was determined that around 79% of the measured radioactivity was likely to be parent substance (Unpublished, 2010b). The remaining 21% was associated with non-polar non-extractable metabolites. These were not further identified, and so it is not known whether these are toxic or accumulative. For the purpose of the Risk Profile, the fish bioconcentration factor (BCF) is calculated using a conservative assumption that all measured radioactivity is relevant. The growth-corrected and lipid-normalised kinetic BCF is therefore 14 600 L/kg. If the apparent metabolites are ignored, the value would be around 11 530 L/kg for parent substance alone. The study is assessed to be reliable without restriction based on regulatory assessment against the test guideline.
- A reliable fish dietary bioaccumulation test with Rainbow Trout (O.mykiss) was conducted according to OECD TG 305 and GLP using a C_{14} chlorinated n-alkane, 50% Cl wt. substance in a flow-through system (Unpublished, 2019e and 2019f). This is detailed in Environment Agency (2019). A dosed treatment containing the test substance at a nominal concentration of 15 μ g/g, and a positive control treatment dosed with both a nominal 15 μ g/g of test substance plus 3 μ g/g of hexachlorobenzene (HCB) were used. An uptake period of 14 days was followed by 56 days of depuration during which the fish were fed non-dosed food. Chemical analysis was performed using APCI-QToF-HRMS. The growth-corrected depuration half-life was 108.9 days and the growth-corrected and lipid-normalised kinetic biomagnification factor (BMF $_{KgL}$) was 0.468 (Unpublished, 2019e). For HCB (positive control), the growth-corrected depuration half-life was 26 days and the BMF $_{KgL}$ was 1.41. The study is assessed to be reliable

²⁰ Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency, Washington, DC, USA.

²¹ Based on log Kow values for 29 "MCCPs" congener groups using COSMOtherm and EPISuiteTM.

without restrictions based on regulatory assessment against the test guideline. As shown in Environment Agency (2019a), using the measured depuration half-life and each of the 15 uptake (k₁) models within the OECD TG 305 BCF estimation tool (OECD 2017a), the BCF significantly exceeds 5,000 L/kg in this study in all cases.

77. Several more studies provide information about fish bioaccumulation for other relevant constituents, which are described below and summarised in Table . These are assessed to be of lower reliability (discussed below) than the two studies summarised above, but still provide useful information.

Table 7. Results of additional fish bioaccumulation tests considered to be supporting studies

0/ 614	Carbon chain length					
% Cl wt.	C ₁₄	C ₁₅	C ₁₆	C ₁₇	$\mathbf{C_{18}}^{\dagger}$	
<40			>5,000 L/kg Fisk <i>et al.</i> , 1996#			
40–45						
45–50	>5,000 L/kg Fisk <i>et al.</i> , 1998b [#]				>5,000 L/kg Fisk <i>et al.</i> , 2000#	
50–55		2,072 L/kg* Thompson <i>et al.</i> , 2000				
55–65	>5,000 L/kg Fisk <i>et al.</i> , 2000 [#]					
>65			>5,000 L/kg Fisk <i>et al.</i> , 1996#			

Note: * Not lipid corrected. # Extrapolated from a dietary test. † Not a constituent of "MCCPs" but provides an upper boundary.

- 78. The bioaccumulation of a C₁₅ chlorinated n-alkane, 51% Cl wt. substance in Rainbow Trout (*O. mykiss*) was measured by Thompson *et al.*, (2000). This was a GLP study performed according to OECD TG 305. It used flow-through exposure and a ¹⁴C radiolabelled test substance. Two test concentrations (nominally 1 μg/L and 5 μg/L) were used, although the higher concentration was considered to have exceeded the water solubility limit as lower BCF values were determined. Fish lipid content was not measured so lipid normalisation is not possible. BCF values were calculated based on total radioactivity in fish and mean-measured water concentrations. The growth-corrected kinetic BCF for the low concentration was 2 072 L/kg, and the growth corrected depuration half-life was 29 days. While the BCF value is significantly lower than for a lower chlorine content C₁₄ substance, the depuration half-life suggests significant concern for bioaccumulation (a depuration half-life around 8 to 10 days is indicative of a lipid-normalised and growth-corrected BCF above 5,000 L/kg according to the analysis in Environment Agency (2012) and discussed in OECD (2017b)). The apparent and unexplained disparity between BCF value and depuration half-life indicates that the test results should be treated with caution. It is considered to be a supporting study.
- Fisk et al., (1996, 1998b and 2000) performed a series of fish dietary bioaccumulation studies using Rainbow Trout (O. mykiss) from which BCF values can be derived using the OECD estimation tool (OECD, 2017a). These used C₁₄ (in two separate studies), C₁₆ and C₁₈ chain lengths with varying chlorination levels, and several SCCP chain lengths, some of which were run together in the same experiment. The test substances were specifically synthesised and had chlorine atoms on the terminal carbon atoms (which could have affected metabolic potential). The tests were not conducted to a standard test guideline or GLP, and key information to validate the studies run in 1996 and 1998 is not available; mortality was also observed in one of the studies. There is therefore uncertainty regarding the reliability of these studies. The issues are discussed in more detail in document UNEP/POPS/POPRC.18/INF/10. The results from the studies indicate that depuration half-lives were between 29 and 91 days, with estimated BCF values exceeding 5,000 L/kg for all constituents. As described above, depuration half-lives this long are indicative of BCF values above 5,000 L/kg. The C₁₈ result suggests that a similar result would have been seen if a C₁₇ constituent had been tested. The findings of Fisk et al., (1998) using C₁₄ 42-53% Cl wt. constituents are consistent with the results of the two reliable fish bioaccumulation studies (Unpublished, 2010a/b; and Unpublished, 2019e/f) that cover similar levels of chlorination for the same C₁₄ chain length. This provides some confidence that the methodology used by Fisk et al., (1996, 1998b and 2000) gave results that are broadly comparable to more recent bioaccumulation studies, and so the bioaccumulation results for other chlorination levels or carbon chain lengths measured in the Fisk et al., (1996, 1998b and 2000) studies and described in the previous paragraph are useable.

- 80. Collectively the four laboratory studies (Fisk *et al.*, (1996, 1998b and 2000) and Thompson *et al.*, (2000)) indicate that constituents with carbon chains longer than C_{14} may have significant bioaccumulation potential in fish, but this cannot currently be confirmed definitively based on laboratory data alone. They are considered to be supporting studies.
- 81. The results of an analysis using the BAT v2.0 tool have been provided (CPIA, Annex E submission). This provides a review and interpretation of nearly all of the available laboratory bioaccumulation data and one of the field biomagnification studies, together with several *in silico* models. The BAT report does not provide any new experimental data, and the main technical points raised for the existing measured data are already discussed in Environment Agency (2019a) and this Risk Profile. The weight-of-evidence approach concluded that 82% of the reliable measured data indicated that "MCCPs" were not bioaccumulative. However, this is based on a single study (Houde *et al.*, 2008; detailed in document UNEP/POPS/POPRC.18/INF/10) and predicted data for 88% of the overall evidence base, which is not considered to provide a reasonable reflection of the available data. The fugacity ratio concept included in the output has not been recognised or validated for regulatory purposes within the UK or EU. Therefore, the BAT report is not discussed further in this document.

2.2.3.3 Other aquatic taxa of potential concern

- Castro et al., (2019) assessed a number of commercial CP products including a C₁₃₋₁₈ chlorinated n-alkane (45% Cl wt.) substance in a non-standard, non-GLP laboratory bioaccumulation study using the water flea Daphnia magna. The test used a passive dosing system with CP substances loaded onto the silicone at 1 mg CP/g silicone. Five replicates were used for each treatment (with sufficient numbers to allow 35 daphnids per replicate to be sampled during uptake and depuration), and exposure conditions were in accordance with OECD TG 202. The <24-h old juvenile daphnids were exposed to CPs for 48 hours (uptake) followed by a 24-h depuration phase. Although the exposure time was relatively short, previous investigations by the authors indicated the system equilibrated within 24 hours in a passive dosing system for CPs. The BCF was calculated from the ratio of the concentration in daphnids exposed via water alone to a single measured water concentration that was made in the absence of the organisms. A BAF was also calculated for daphnids exposed via both water and food from concentrations measured at the end of each phase. ECHA (2021a) and ECHA (2022e) address several uncertainties discussed in Environment Agency (2019) and consequently the study is considered to provide supporting information. The issues are detailed in document UNEP/POPS/POPRC.18/INF/10. Congener level chemical analysis was made using APCI-QTOF-MS. The study author has indicated that this analysis should be treated as semi-quantitative as the method does not allow for quantification of single congeners (Pers. Comm., 2021). Comparison of the congener fingerprints in the test material and the Daphnia show that these are visually analogous, with exception at the extremes of chlorination (e.g., Cl₂ and Cl_9). This indicates a proportional accumulation for C_{14-17} chain lengths (e.g., no data indicated a disproportional or preferential accumulation of individual chain lengths). ECHA (2021a) presented a water content corrected BCF of around 50 000 L/kg ww (the original data are presented in terms of dry weight).
- 83. Three further tests also suggest significant bioaccumulation of C_{14-17} CPs in aquatic invertebrates (the sediment worm *Lumbriculus variegatus* and Blue mussel *Mytilus edulis*) (Renberg *et al.*, (1986), Madeley & Thompson (1983), Fisk *et al.*, (1998a)). Due to methodological issues (discussed in document UNEP/POPS/POPRC.18/INF/10), the studies are not considered sufficiently reliable to support the proposal, but they do indicate a concern that other aquatic taxa besides fish and *Daphnia* may experience high bioaccumulation of CPs with C_{14-17} chain lengths.
- 84. In summary, laboratory bioaccumulation studies using fish indicate high levels of bioaccumulation for different constituents of CPs with C_{14-17} chain lengths. In particular, reliable aqueous and dietary exposure studies for C_{14} chain lengths with chlorine contents in the range 45–50% Cl wt. have measured or extrapolated BCF values above 5,000 L/kg. Several other supporting fish bioaccumulation studies that were not performed to current test guidelines, nor to such a high standard as the modern tests for C_{14} , suggest BCF values ranging from around 2 000 L/kg to above 5,000 L/kg for carbon chains longer than C_{14} . A non-GLP, non-guideline laboratory bioaccumulation study using *Daphnia magna* reported a very high BCF value for a C_{13-18} 45% Cl wt. substance. Other available laboratory bioaccumulation data for invertebrates are less reliable but support the concern that high bioaccumulation is unlikely to be limited to fish.

2.2.3.4 Field biomagnification and monitoring studies

85. Yuan *et al.*, (2019) analysed for CPs with a chain length up to C_{30} in the Swedish environment using APCI-QToF-MS. In the marine food web, concentrations of C_{14-17} congeners from tissue samples of White-tailed Seaeagles, Grey Seal, Harbour Seal and Harbour Porpoise (around 0.2 to 0.5 mg/kg lipid weight (lw)) were generally similar to or higher than those in Herring (around 0.03 to 0.44 mg/kg lw). "MCCPs" were reported as summed congeners, and the authors detected all four "MCCPs" chain lengths (chlorination levels detected varied from Cl_4 up to Cl_{10}), including in top predators. Using data from Yuan *et al.*, (2019), De Wit *et al.*, (2020) estimated the biomagnification potential for CPs where they were definitively measured in predator-prey species sourced from identified spatial areas. Ratios of mean lipid weight concentrations of SCCPs, "MCCPs" and LCCPs for possible

predator/prey pairings range from 1.5–5.0 for SCCPs, 0.40–3.1 for "MCCPs" and 0.90–3.3 for LCCPs. The highest ratios for "MCCPs" were seen for Harbour Seal/Herring (2.4) and Sea Eagle/Guillemot pairs (3.1). Lower BMF values for "MCCPs" were found in: Guillemot/Herring pairs (0.4), Sea Eagle/Eider pairs (1.1), Grey Seal/Herring (1.4) and Harbour Porpoise/Herring pairs (1.8). These values should be considered with considerable caution as they are based on tissue measurements which may not be representative of whole-body burdens, and small sample numbers (just 2 samples in some cases). Also, the predators and their potential prey were not collected at the same sites or times. In addition, the temporal trends of the CPs in the Baltic Sea are unknown. Taken together Yuan *et al.*, (2019) and De Wit *et al.*, (2020) are considered to provide strong evidence that "MCCPs" constituents can accumulate in a wide range of aquatic species and are found in tissues of organisms at the top of the food chain. However, further contemporaneous data from biota within the same specific food webs and supporting stable isotope data would be required to strengthen the evidence and confirm biomagnification between predator and prey species.

- 86. Du *et al.*, (2019, 2020) analysed tissue from Black-spotted frogs and two snake species (terrestrial Short-tailed Mamushi and the semi-aquatic Red-backed Rat Snake) sampled from the paddy fields of the Yangtze Delta using APCI-QTOF-MS. Animals were sampled at the same times and place in 2011. All four "MCCPs" chain lengths were detected in tissues with C_{14} the most abundant, and congener-specific analysis indicated uptake variation between tissue types. Congeners were dominated by Cl_{5-6} isomers. Du *et al.*, (2020) calculated mean BMF values for "MCCPs" of 1.8 (maximum BMF 2.8) in the Black-spotted Frog Red-backed Rat Snake food chain based on muscle concentrations. Calculations of BMFs were from tissue specific concentrations (not whole body), and sample numbers for the snakes were low. Measurement of δ^{13} C and δ^{15} N indicated that the two species were part of the same food chain, but it is not possible to verify that the snakes exclusively ate frogs (in a different paper, Du *et al.*, 2018 indicates that the Red-backed Rat Snake eats frogs, snails, small fish such as Pond Loach and eels). There is therefore uncertainty in the reliability of the reported BMFs. Nevertheless, the study indicates the possibility of biomagnification. Furthermore, the high concentrations (up to 14 mg/kg lw) of "MCCPs" measured in tissues in contaminated areas including those of predators indicate that the substance is bioavailable.
- 87. Huang *et al.*, (2017) studied the bioaccumulation of SCCPs and "MCCPs" in biota from Liaodong Bay, north China, by sampling 10 species of fish and 5 invertebrates (covering trophic levels between 2.31 and 3.81 based on δ^{15} N) in 2014. Analysis was performed using 2D GC-HRMS. "MCCPs" were detected in all samples with the highest and lowest concentrations measured in Turbot (mean 5,097 μg/kg lw) and Mantis Shrimp (16.72 μg/kg lw), respectively. Congener profiles were dominated by C₁₄ homologues (60.7–96.5%), followed by C₁₅ (6.7–24.0%), C₁₆ and C₁₇. "MCCPs" chain lengths were predominantly chlorinated with 7 to 9 atoms (90.1%). Bioaccumulation Factors (BAFs) were not calculated for "MCCPs" as water concentrations were not available. Trophic Magnification Factors (TMFs) for "MCCP" congeners (C_{14–17}Cl₅₋₁₀) ranged from 0.23 to 2.92, but none were statistically significant (p < 0.05), and nearly all the plots had very low r^2 values. The ΣMCCPs TMF was similarly not significant. Around one quarter of the SCCPs congener plots had $r^2 > 0.5$ and TMFs above one (and were statistically significant). The TMF for ΣSCCPs was not however statistically significant. The authors concluded that biomagnification of "MCCPs" in fish was not occurring, but was for SCCPs. Given the limited number of fish samples at the higher trophic level (2-3 fish in several instances), absence of defined predator-prey relationships in the sampled biota (including for example r^{13} C analysis), and the quality of the correlations for both substances, there is uncertainty associated with the conclusions of the study. Overall, the biomagnification data are given a low weight in the assessment.
- Zeng et al., (2017b) collected 4 mollusc species, 7 crustacean species, and 16 fish species from the subtropical waters around Hong Kong SAR of the South China Sea and analysed these for "MCCPs". These values were then compared to average concentrations of the CPs in blubber from two cetacean species: Finless Porpoise (mean 5.5 mg/kg lw) and 3 Indo-Pacific Humpback Dolphins (mean 13 mg/kg lw) sampled in the same year and region and detailed in an earlier paper (Zeng et al., 2015) described in section 2.3.1.6.2. Biomagnification Factors (BMFs) and TMFs were calculated using the fish muscle tissue, the mollusc soft tissue and the cetacean blubber concentrations (all lipid weight normalised). Calculated BMF and TMF values exceed 1. While the concentrations in the mammals are notably higher than the prey, there is considerable uncertainty for whether the mammals exclusively consume these prey items in the sample area or would have also consumed prey from a wider – and possibly more contaminated - area (for example the Dolphin is indicated to prefer feeding in brackish estuarine waters, which would appear to be some distance from the prey sampling site). Further uncertainty results from the low sample numbers of the predators; the use of a single pooled value for each predator in the TMF calculation; and the use of tissue rather than whole body concentrations. Therefore, the BMF and TMF values are not considered to be reliable. Nevertheless, the high average concentrations observed in the cetaceans' blubber suggest the possibility of high bioaccumulation resulting from exposure to "MCCPs". Chain length level analysis indicated uptake of all four chain lengths in both cetacean species, with C_{14} the most prevalent.
- 89. Harju *et al.*, (2013) collected Ringed Seal plasma, Polar Bear plasma, Black-legged Kittiwake eggs, Common Eider eggs, Glaucous Gull plasma and Atlantic Cod liver and whole Polar Cod from Svalbard (in the Norwegian Arctic) and analysed these for CPs and several other contaminants using GC-HRMS. Samples were collected in 2012 (except for the seal samples which were collected in 2010). Measured concentrations included 100–740 μg/kg lw (Seal plasma) and <LOD–600 μg/kg lw (Bear plasma). The estimated TMFs were 2.3 for SCCPs and 2.0 for "MCCPs". The TMF for PBDE-47 in the study was 1.1. Due to the complex nature of SCCPs and "MCCPs"

and variability between samples for a species, the authors indicate that a TMF > 1 can only be applied as an indication for bioaccumulation of S/"MCCPs" (it is further noted that the r^2 coefficient for the concentration / trophic position plot was 0.52 for SCCPs and 0.31 for "MCCPs"). The authors indicate that the tissues used have a much shorter turnover than their preferred muscle tissue, which is longer. The use of tissue, particularly different tissues, rather than whole body concentrations also causes uncertainty, as does the unknown temporal variability of the sampling (not just the seals). Overall, there is uncertainty in the derived TMF values, which are assigned a low weight for this assessment.

90. Several other older field monitoring studies, including Houde *et al.*, (2008), are detailed in document UNEP/POPS/POPRC.18/INF/10.

2.2.3.5 Terrestrial organisms

- 91. An earthworm-soil accumulation factor of 2.4 for adults and 2.3 for juveniles was determined for a C_{15} chlorinated n-alkane, 51% Cl wt. in a 56-day study using *Eisenia fetida* (Thompson *et al.*, 2001). This is assessed to be reliable with restrictions.
- 92. Liu *et al.*, (2020) studied the biomagnification of "MCCPs" in a terrestrial food web covering 7 species of insects, 2 amphibians, 1 lizard and several insectivorous birds. Biota were sampled over 14 months across an area where e-waste recycling and farming were taking place in Guangdong Province, south China. "MCCPs" were analysed using GC-MS-ECNI. Congener level analysis covering C_{14–17} and Cl_{5–10} detected all congeners in all organisms, with C₁₄Cl_{7–9} the most abundant "MCCPs" homologues. The calculated TMF for the insect amphibian/lizard food chain for the sum of "MCCPs" was 2.45. A significant, positive correlation was noted between δ¹⁵N and the percentage chlorination of "MCCPs". This suggests that higher biomagnification potential was linked to higher levels of chlorination. The paper provides evidence that the amphibians were in the same food chain as the insects. However, the numbers of amphibians and lizards sampled are low compared to the number of insects, BMFs were calculated from predator muscle tissue but insect whole body, sampling took place at different times over more than one year, and the range of trophic levels occupied by single predator species (1.7 to 3.8) was higher than expected (so birds were excluded from the TMF calculations). There is therefore uncertainty in the derived TMF values, which are assigned a low weight for this assessment.
- 93. Several other studies have indicated that "MCCPs" can undergo maternal transfer to birds' eggs, which represent a sensitive life stage (species include Common Eider (Green *et al.*, 2018); Tawny Owl (Heimstad *et al.*, 2018 & 2020); Common Eider, Guillemot, White-tailed Sea-eagle, Common Kestrel and Tawny Owl (Yuan *et al.*, 2019); and Herring Gull (Ruus *et al.*, 2018)). The highest reported concentration was 0.135 mg/kg wet weight (ww). Eggs collected from free range chickens living in the vicinity of a former Chinese e-waste recycling plant had "MCCP" concentrations between 0.125 and 91.1 mg/kg lw, with median values around of 1 mg/kg lw (Zeng *et al.*, 2018).

2.2.3.6 Mammalian data relevant to bioaccumulation

- 49. Laboratory data for mammals using rats were assessed in EC (2007). Mammalian studies using radiolabelled "MCCPs" have shown that absorption following oral exposure is significant (probably at least 50% of the administered dose; however, the concentration reached in the organism is generally lower than that in food). Following absorption there is an initial preferential distribution of the radiolabel to tissues of high metabolic turnover/cellular proliferation. Subsequently there is a re-distribution of radiolabel to fatty tissues where half-lives of up to 8 weeks have been determined for abdominal fat. Of special interest is the study by CXR Biosciences Ltd (2005a) that found that a steady-state concentration in white adipose tissue was reached after approximately 13 weeks' dietary exposure. The elimination from this tissue was found to be biphasic with an initial half-life of 4 weeks followed by a markedly slower second phase with a terminal half-life of approximately 43 weeks.
- 95. Dong *et al.*, (2020) extrapolated results from a rat physiologically-based pharmacokinetic (PBPK) model to a human PBPK model. Based on a comparison of volumes of distribution and half-lives, CPs were predicted to accumulate in the liver and fat. The authors estimated the half-life of "MCCPs" in humans to be 1.2 years, which is much longer than in rats above.
- 96. Human biomonitoring is summarised in section 2.3.2. This includes multiple studies detecting "MCCPs" in breast milk and other tissues such as blood.
- 97. The toxicokinetics of CPs as a group is discussed in a recent review by Darnerud and Bergman (2022). Specific conclusions are presented on "MCCPs" alone for absorption only. "MCCPs" are absorbed from the gastro-intestinal tract and probably also from the lungs. Absorbed CPs are widely distributed. CPs are metabolised in the liver and excreted mainly via the bile and faeces. Some elimination also occurs via breast milk.

2.2.3.7 Other data relevant to bioaccumulation

98. As described in section 2.3.4, a number of environmental monitoring studies provide chemical analysis for "MCCPs" at a congener level. Where this relates to either environmental matrices such as sediment and soil, or at emission points such as wastewater treatment plants, the shorter "MCCPs" chain lengths predominate, particularly C_{14} . The biota monitoring where congener level information is available shows a similar pattern. Glüge *et al.*, (2018) noted that $C_{14}Cl_{7-8}$ was the most prevalent in environmental samples and the most prevalent congeners in the CP-52 commercial samples that they analysed. Xia *et al.*, (2021) also noted the prevalence of C_{14} congeners in both the commercial products and air-borne particulate matter, sediment, food, and human tissue monitoring. The authors determined a close correlation between the congener profiles of environmental and biota samples, and two CP-52 commercial samples to identify these as the likely sources based on a principal component analysis.

2.2.3.8 Bioaccumulation synthesis

- 99. The constituents of CPs with C_{14-17} chain lengths have a range of log K_{OW} values, but all measured values exceed 5 (Hilger *et al.*, 2011). Predicted data, which align well with the measured congener level information, indicate all chain lengths will have log K_{OW} values exceeding 5.
- 100. Two reliable fish bioaccumulation studies (Unpublished, 2010a and b; Unpublished 2019e and f) conducted according to OECD TG 305 and to GLP show that a C_{14} chlorinated n-alkane, 45% Cl wt. product has a measured BCF value significantly in excess of 5,000 L/kg in Rainbow Trout, and that a C_{14} chlorinated n-alkane, 50% Cl wt. substance has a calculated BCF from dietary exposure significantly in excess of 5,000 L/kg.
- Supporting laboratory evidence indicates that there is likely to be a high bioaccumulation potential in fish for CPs with chain lengths longer than C_{14} (Fisk et al., 1996, 1998b, and 2000; Thompson et al., 2000). These data are from an aqueous exposure test performed with a C₁₅ chlorinated n-alkane, 51% Cl wt. substance and a series of dietary bioaccumulation studies using C₁₄, C₁₆ and C₁₈ chain lengths with different levels of chlorination. The dietary studies are of unknown reliability, but measured and estimated BCF values range from around 2 000 L/kg to above 5,000 L/kg. Additionally, all substances had long depuration half-lives which are consistent with a BCF exceeding 5,000 L/kg. Further supporting evidence is provided by the very high BCF value determined in a laboratory bioaccumulation study using Daphnia magna for a C₁₃₋₁₈ 45% Cl wt. substance. Other available invertebrate laboratory bioaccumulation data are less reliable but provide some supporting evidence that other taxonomic groups might bioaccumulate C₁₄₋₁₇ CPs significantly. As described in section 2.2.3.3, these invertebrate studies are of lower reliability than the fish studies, and are therefore considered to carry a lower weight in this assessment. There are eight available field bioaccumulation studies where calculated BMFs or TMFs were both above and below 1 (Houde et al., 2008; Yuan et al., 2019; de Wit et al., 2020; Du et al., 2020; Liu et al., 2020; Zeng et al., 2017b; Harju et al., 2013). All of these have major methodological limitations (particularly limited sample numbers, use of samples collected at different times, and reliance on single tissue concentrations), which affects their reliability. Nevertheless, while the food chain data are not definitive in terms of demonstrating a high bioaccumulation potential, they show that "MCCPs" are bioavailable, and can accumulate throughout the food chain, including in top predators.
- Aquatic and terrestrial biota monitoring evidence is summarised in section 2.3.1.6. Despite the general uncertainty in the available data due to the analytical challenges described elsewhere, CPs with C_{14-17} chain lengths are present in a wide range of organisms living and feeding in locations that are close to input sources (i.e., industrial and urban areas), including at sensitive life stages such as birds' eggs. Biota concentrations can exceed 1 mg/kg lw in contaminated areas, for example 14 mg/kg lw in Chinese snake species. Whilst more limited in number, "MCCPs" have also been detected in samples from remote regions, including the Arctic, as well as in top predators. Only limited information is available on the actual carbon chain length distribution and chlorine contents of "MCCPs" detected in most environmental samples, although advances in analytical methodologies have meant that this has been increasingly possible in more recent studies. C₁₄ chain lengths are frequently the predominant constituents of "MCCPs" when more detailed information is available for biota, although C_{15} , C_{16} and C_{17} chain lengths are also detected. The C₁₄ chain length is a significant constituent of commercial product types in Europe and the USA. The pattern is less certain in the Asian products such as from China, nevertheless in Chinese soil and sediment, the C₁₄ does appear to predominate. Where the observed congener patterns in biota are available, these are similar to the congener patterns found in either commercial products or environmental matrices (i.e., there appears to be little relative enrichment of one congener compared to others). This suggests that the bioaccumulation behaviour of the C₁₅- $_{17}$ chains is likely to be similar to C_{14} . There is good evidence that C_{14} CPs bioaccumulate significantly in fish in the laboratory, and so based on the biota measurements, it is reasonable to expect that the higher chain lengths could exhibit similar levels of bioaccumulation. This hypothesis is supported by the Fisk et al., (1996, 1998 and 2000) fish dietary bioaccumulation studies, and the invertebrate bioaccumulation study of Castro et al., (2019), where high levels of bioaccumulation of the longer chain lengths were observed in laboratory animals (although the studies themselves are of unknown or lower reliability).
- 103. "MCCPs" have been shown to have relatively long elimination or depuration half-lives in fish and mammals. The substance is estimated to have a half-life in humans of 1.2 years based on PBPK modelling (Dong *et al.*, 2020).

The study parameterised a human PBPK model based on experimental data derived from a rat study as well as human dietary exposure data.

104. Overall, there is good evidence from screening data, laboratory tests and field biomonitoring data that all chain lengths meet the bioaccumulation criteria of the Convention.

2.2.4 Potential for long-range environmental transport

2.2.4.1 Atmospheric half-life

105. No measured atmospheric half-lives are available for CPs with C_{14-17} chain lengths. AOPWIN v1.92²² has been used to make predictions of the hydroxyl radical rate constant (k_{OH}) to estimate atmospheric half-lives. The model is based on a training set of 667 organic chemicals, of which 1-chlorohexane is the closest analogue to the chlorinated C_{14-17} structures. Using a hydroxyl radical concentration of 5 x 10⁵ OH/cm³ (ECHA, 2016),²³ atmospheric half-lives for 14 representative constituents of "MCCPs" covering all chain lengths with >45% Cl wt. were estimated from the predicted k_{OH} . The various half-lives ranged from 37 to 140 hours, as detailed in document UNEP/POPS/POPRC.18/INF/10. These estimates should be treated with caution, as the closest chlorinated alkane in the model training set is a C_6 alkyl substance with a single chlorine atom, and there are no measured data with which to directly compare the current estimates. For a given chain length, increasing the chlorination level increases the half-life whereas for a given chlorination level increasing the chain length will decrease the half-life, due to fewer or more C-H bonds for reaction with the hydroxyl radicals, respectively. The same pattern can also be seen in the half-lives for SCCPs (UNEP, 2015). The high adsorption of CPs to atmospheric particles at low temperatures, typical of conditions at high latitudes, may also limit the atmospheric oxidation pathway and increase the half-life.

106. Li *et al.*, (2014) investigated the relationship between measured and predicted (AOPWIN v1.92) hydroxyl rate constant values in SCCPs, which indicated under-prediction of atmospheric half-life particularly for higher chlorination levels. The work is detailed in document UNEP/POPS/POPRC.18/INF/10, but the comparison suggests that AOPWIN v1.92 may under-predict atmospheric half-life values for "MCCP" congeners.

2.2.4.2 Modelling of long-range environmental transport

107. The OECD P_{OV} & LRTP Screening Tool (OECD, 2006) has been used to estimate the long-range transport potential (LRTP) of a representative range of C_{14} , C_{15} , C_{16} and C_{17} constituents of "MCCPs" with differing degrees of chlorination. The input parameters use log K_{AW} , log K_{OW} and log K_{OA} values predicted by COSMOtherm (Glüge, Pers. Comm., 2021 & 2022), and environmental fate values predicted by EPISuiteTM, including the predicted atmospheric half-lives described in the previous section. These are all detailed in document UNEP/POPS/POPRC.18/INF/10.

108. The results from the OECD Screening Tool for the 14 constituents show that the Characteristic Travel Distance (CTD) and Transfer Efficiency (TE %) increases with percentage chlorination of the constituents (~40% to ~67%) with a predicted TE % ranging between 1% and 13% for most of the constituents. CTD and TE % also increase with increasing carbon chain length, with the most heavily chlorinated longest carbon chain length constituents having the largest predicted LRTP. More details are provided in document UNEP/POPS/POPRC.18/INF/10.

109. For further comparative and sensitivity considerations, the results of four constituents illustrating the lower and higher end of the LRET range (and terminal and non-terminal chlorination patterns) are shown in Table 8 and discussed below.

110. To provide a comparison, data for SCCPs (which is already listed as a POP) have also been considered. SCCPs with >48% Cl wt. were the focus of the Risk Profile (UNEP, 2015). The LRTP modelling for this substance (referred to as "SCCP 5" below) used an atmospheric half-life value of 88.8 hours (Wegmann *et al.*, 2007), although the specific congener modelled is not stated. Two further SCCP constituents have been modelled, with a chlorination level of 61%, which is considered to be representative of the typical 50% to 70% chlorination levels used for most commercial SCCP products (the input parameters are provided in document UNEP/POPS/POPRC.18/INF/10). The input parameters for these constituents rely on physico-chemical values derived using COSMOtherm and atmospheric half-life values predicted by EPISuiteTM.

²² Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency, Washington, DC, USA.

²³ The value used is taken from ECHA (2016), rather than the hydroxyl concentration used within the AOPWIN model. The selected value (5×105 OH/cm³) may not be typical of northern latitudes since hydroxyl radical concentrations decline with latitude.

	C ₁₄ constituent (52.6% Cl wt.)		C ₁₇ constituent (51.6% Cl wt.)	
Predictions	Non-terminal chlorine (MCCP-1)	Terminal chlorine (MCCP-2)	Non-terminal chlorine (MCCP-3)	Terminal chlorine (MCCP-4)
Characteristic Travel Distance (CTD) (km)	1,603	1,466	2,826	2,821
Transfer Efficiency (TE) (%)	3.95	3.10	12.41	12.39
Overall persistence, P _{OV} (days)	518	518	519	519

- 111. Similar to the "MCCPs" modelling, the SCCP congeners are modelled with both terminal and no terminal chlorine atoms. These four constituents have predicted atmospheric half-lives between 84.7 and 144.3 hours. All five SCCP constituents have been run in the OECD P_{OV} & LRTP Screening Tool together with the four "MCCPs" constituents. These results together with those for other available POP reference chemicals in the database (aldrin, α -HCH, HCB, PCB-28, PCB-101 and PCB-180) are shown in Figure 2. Figure 3 provides a zoomed extract of Figure 2 to show the CP positions. These indicate that the LRTP of "MCCPs" is similar to, but slightly less than, SCCPs. Given the lower atmospheric half-life predicted for the C_{14} and C_{17} constituents compared to SCCPs, this position is not surprising.
- As noted in section 2.2.3.1 COSMOtherm is preferred to EPISuiteTM to predict physico-chemical values for CPs. A sensitivity analysis between the use of EPISuiteTM and COSMOtherm physico-chemical values to model the LRET is provided in document UNEP/POPS/POPRC.18/INF/10.

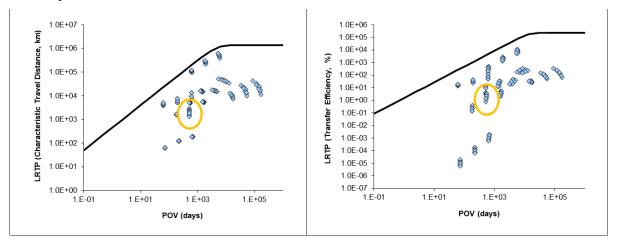


Figure 2. Output plots of CTD and TE for 4 "MCCP" and 5 SCCP constituents (within orange circle) (derived using inputs from COSMOtherm)

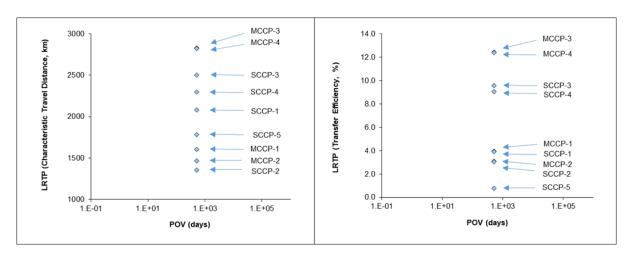


Figure 3. Output plots for CTD and TE for 4 "MCCP" and 5 SCCP constituents (expanded view of Figure 2, with labelled constituents) (derived using inputs from COSMOtherm)

- 113. The high K_{OW} and low vapour pressure values of "MCCPs" suggests that it will strongly partition to organic matter, including adsorption into and onto aerosol particles in air, as well as to suspended solids in water. Long-range transport of CPs with C_{14-17} chain lengths to remote regions is likely to be governed by the relative proportions present in the gaseous and particulate-sorbed phases with subsequent deposition to soil, vegetation and water when conditions permit. CPs with C_{14-17} chain lengths are also likely to be transported via water while adsorbed to suspended particles. In relation to atmospheric LRET, sorption to particulates reduces the potential for photodegradation during atmospheric transport relative to the gaseous phase. COSMOtherm predictions by Endo (2021) shows that K_{OA} , and hence sorption to particles, increases with both increasing chlorination and increasing carbon chain length (see discussion in document UNEP/POPS/POPRC.18/INF/10). The high log K_{OA} value suggests that the proportion of CPs with C_{14-17} chain lengths present in the gas phase is very low. As COSMOtherm estimates higher log K_{OA} values than EPISuiteTM based on the respective predicted physico-chemical parameters, the OECD Screening Tool predicts a very high binding potential to particles for C_{14-17} chain lengths compared to EPISuiteTM (refer to document UNEP/POPS/POPRC.18/INF/10, which results in the greater LRET predicted by COSMOtherm values).
- 114. A final consideration is the fraction sorbed to airborne particulates (phi) predicted within the OECD Screening Tool itself, which affects the LRET modelling using EPISuiteTM physico-chemical values. The OECD Screening Tool predicts the fraction in aerosols in air to be between 0.73% and 33% for C_{14-17} chain lengths at ~52% Cl wt., 0.04% to 2.1% at ~42% Cl wt. and 75% to 100% at ~66% Cl wt. respectively when using physico-chemical values from EPISuiteTM. The AEROWIN v1.0 model (also within EPISuiteTM) has three methods for estimating phi from the predicted substance properties. Using the same physico-chemical properties, the phi values predicted by AEROWIN v1.0 for CPs with C_{14-17} chain lengths at ~52% Cl wt. (1.68% to 63.8%) are higher than predicted by the OECD Tool for C_{14-17} chain lengths at ~52% Cl wt. and this trend is repeated for the other levels of chlorination. This implies that a lower proportion of the CPs with C_{14-17} chain lengths may be available for degradation in air than is predicted by the OECD Tool and therefore the long-range transport potential in air is potentially underestimated. Little effect of changing phi is seen when using the COSMOtherm values due to the already high particle sorption. Phi values for "MCCPs" and SCCPs are discussed further in document UNEP/POPS/POPRC.18/INF/10.
- 115. The absence of degradation in the OECD TG 308 study could be a result of strong binding to the sediment phase, and consequent lack of bioavailability. This adsorption would also then suggest the level of gaseous partitioning may be over-estimated by the OECD tool. Jiang *et al.*, (2021) indicate that "MCCPs" detected in Antarctica were present as 72.1% gas phase and 27.9% in the particle phase (based on 3 commercial products with 42%, 52% and 57% Cl wt. as the analytical standards). Greater partitioning of higher molecular weight CPs was shown by Al Saify *et al.*, (2021) in air sampling development work using the same analytical standards, where "MCCPs" in the gaseous phase was exclusively 42% Cl wt., whereas more than half of the particle-bound "MCCPs" was composed of congeners with 52 to 57% Cl wt.
- 116. Gawor and Wania (2013) analysed predictions of log K_{AW} and log K_{OA} for a number of complex halogenated chemical mixtures, including CPs, to forecast their LRET. They suggest that substances with a log K_{OA} between 6.5 and 10 are "multiple hoppers" (which undergo repeated cycles of deposition and re-evaporation to reach higher latitudes). Substances with log $K_{OA} \ge 10$ are likely to be "single hoppers" (sorbed to aerosols, which would need to undergo LRET without being deposited along the way in order to accumulate in remote locations like the Arctic). They expect "MCCPs" with around 4 to >6 chlorine atoms would be single hoppers based on the authors' prediction of log $K_{OA} > 10$ (estimated using ACD/Labs software). Using experimental data (see UNEP/POPS/POPRC.18/INF/10, Table 7) for the C_{14} , 51% Cl wt. constituent, a log K_{OA} of 8.58 can be estimated. This suggests that the K_{OA} predicted by ACD/Labs is over-estimated for "MCCPs", and that the C_{14} constituent would be a multiple hopper. Gawor and Wania (2013) concluded that "MCCPs" with ~5–6 and ~6–7 chlorine atoms, respectively, were predicted to have the highest LRET potential (see UNEP/POPS/POPRC.18/INF/10).
- 117. The long-range atmospheric transport potential for CPs with C_{14-17} chain lengths has also been assessed by Canada (2008). They concluded that the atmospheric half-lives for vapour phase "MCCPs" ranged from 2.7 to 7.1 days (64.8 to 170.4 hours). Canada (2008) further concluded that "MCCPs" have estimated vapour pressures and Henry's Law constants in the range of values for several POPs that are known to undergo long-range atmospheric transport, such as lindane, heptachlor and mirex.

2.2.4.3 Air monitoring data

118. Several monitoring studies have reported the detection of "MCCPs" in the air of remote areas such as the Arctic (Svalbard and Finland), Antarctic and the high-altitude Tibetan Plateau, which provides evidence that long-range transport occurs (Bohlin-Nizzetto *et al.*, 2014, 2015, 2017, 2018, 2019, 2020; Bohlin-Nizzetto & Aas, 2016; Jiang *et al.*, 2021; Ma *et al.*, 2014; Wu *et al.*, 2019; Schlabach *et al.*, 2022). These are summarised in document UNEP/POPRC.18/INF/10. Concentrations in Antarctica (~10 pg/m³) were lower than those in the Arctic (Svalbard) (~200 pg/m³). Higher concentrations were observed in the Tibetan Plateau than the Polar regions, although the years that were monitored do not fully overlap. Congener-specific information indicated that in the Antarctic the Cl₇₋₈ congeners were dominant in the particulate phase, with Cl₆₋₇ predominating in the gas phase (Jiang *et al.*, 2021). In the Tibetan Plateau, Wu *et al.*, (2019) comment that the homologue profiles were similar to those in South China

air and Beijing indoor air, and in accordance with the compositions of the major industrial CP products manufactured in China.

- 119. The values observed at Svalbard between 2013 and 2019 by Bohlin-Nizzetto *et al.*, (2020) were noted to be similar to monitoring of rural air in Canada, but significantly lower than measurements in urban and rural sites in China and India (see UNEP/POPS/POPRC.18/INF/10 for other air monitoring data). Furthermore, the levels of "MCCPs" were generally an order of magnitude higher than the concentrations of most of the other studied POPs (including polybrominated diphenyl ethers (PBDEs) such as decabromodiphenyl ether), but 1 to 2 orders of magnitude lower than concentrations of summed polyaromatic hydrocarbons (PAHs). Jiang *et al.*, (2021) similarly found that concentrations of "MCCPs" in the Antarctic exceeded those of PBDEs and polychlorinated biphenyls (PCB).
- 120. Bohlin-Nizzetto *et al.*, (2020) note that at Zeppelin in Svalbard, 42% of "MCCP" samples taken in 2019 had higher or similar concentrations to SCCPs, which is different to previous years where <10% of "MCCP" values exceeded SCCP concentrations. The trend continued in the 2020 sampling, where "MCCP" concentrations were higher than SCCP concentrations in most samples, and an increasing trend in "MCCP" concentrations over the last two years noted (Bohlin-Nizzetto *et al.*, 2021).
- 121. Jiang *et al.*, (2021) also record a significant increasing trend in the ratio of total "MCCPs" to total SCCPs from 2014 to 2018 detected in both aerosol particle and gaseous phases in Antarctica, although "MCCP" concentrations remain significantly below SCCPs. Wu *et al.*, (2019) similarly note an increasing trend in their measurements of "MCCPs" at the Tibetan Plateau, which was thought to reflect increasing production and use in China.
- 122. Data from the Chinese Bohai Sea (Ma *et al.*, 2018) provide further supporting evidence of the potential mechanisms of LRET as the researchers detected "MCCPs" in air samples (both gaseous and particulate) and seawater samples (both dissolved and particulates). Several studies summarised in section 2.3.1.6 detected "MCCPs" in marine biota indicating exposure via sea water.
- 123. According to Glüge *et al.*, (2018), "MCCP" concentrations in air measured in Asia and Europe are in the same order of magnitude as SCCP concentrations measured at the same locations and points in time. "MCCP" concentrations in air in the Arctic are, however, around one order of magnitude lower than the SCCP concentrations which indicates a slightly lower long-range atmospheric transport potential of "MCCPs" compared with SCCPs (Glüge *et al.*, 2018). This observation aligns with monitoring data above, and the OECD model prediction for LRET for "MCCPs" and SCCPs.

2.2.4.4 Other environmental monitoring data

- 124. Wu *et al.*, (2020a) detected SCCPs and "MCCPs" in soil, pine needles, tree bark, lichen and moss in four regions of the Tibetan plateau using GC-qTOF-NCI-MS. "MCCPs" were detected in all samples taken between 2010 and 2016. The mean concentration in soils was 2.4 mg/kg Total Organic Carbon (TOC), with levels in the biota around 2 mg/kg lw. The dominant congener profiles in samples were noted to be similar to those detected in soils at an e-waste dismantling site, and the Pearl River Delta in China. SCCPs were detected at marginally higher concentrations than "MCCPs", which was suggested to reflect a higher LRET of the substance, although there was a temporal difference in sampling which could also influence the findings. Different air currents and sources were thought to influence detection across the 700 000 km² sampling area. The same research group detected "MCCPs" in air sampled from the Tibetan Plateau, described in section 2.2.4.3 above (Wu *et al.*, 2019).
- 125. Iozza *et al.*, (2009a and 2009b) detected "MCCPs" at concentrations of between 0.0052 to 0.095 mg/kg in spruce needles collected from 8 remote locations in the European Alps in October 2004. Samples were taken at different altitudes of between 700 and 1 900 metres above sea level. C₁₄ substances with 6 to 8 chlorine atoms per molecule dominated, although 5, 9 and 10 chlorine atom substances (and substances with longer chain lengths) were also detectable at a few percent relative abundance. Schlabach *et al.*, (2022) detected "MCCPs" in pine needle samples taken in Norway and Sweden from remote locations although there is uncertainty in the analytical quantification. The findings of Wu *et al.*, (2020a), Iozza *et al.*, (2009a and 2009b) and Schlabach *et al.*, (2022) are likely to reflect atmospheric deposition rather than plant uptake. This is supported by the detection of "MCCPs" in urban tree bark and pine needles by Niu *et al.*, (2021) and Wang *et al.*, (2016), as summarised in document UNEP/POPS/POPRC.18/INF/10.
- 126. Section 2.3.1.4.1 details the detection of "MCCPs" in Arctic sediment, specifically in surface marine sediments from the Norwegian Sea, and to a more limited extent the Barents Sea, over several years (Bakke *et al.*, 2008; Boitsov and Klungsøyr, 2018; Boitsov *et al.*, 2019). As there are no obvious significant local sources of "MCCPs" in these locations this suggests detection of the substance is likely to have resulted from long-range environmental transport. As described in section 2.3.1.6.1 several monitoring studies detect "MCCPs" in other matrices and biota at remote locations. The biota studies include Reth *et al.*, (2006), Harju *et al.*, (2013), Green *et al.*, (2018, 2019), Schlabach *et al.*, (2018), and Casa *et al.*, (2019). This indicates that "MCCPs" transported to remote

locations is bioavailable to the biota living there. In several of the studies "MCCP" concentrations detected in biota were around or above those of SCCPs.

2.2.4.5 Long-range transport synthesis

- 127. The predicted atmospheric half-life for relevant C_{14} and C_{17} constituents are between 37 and 140 hours. It is difficult to validate these estimated values due to the lack of experimental data, and so they are considered uncertain. The modelled C_{14} constituents are at or above the 48-hour threshold of Annex D. Predicted half-lives for longer chain lengths are below 48 hours at lower levels of chlorination, but these constituents are less relevant for (gaseous) atmospheric photodegradation as a greater fraction will be adsorbed to aerosols. More highly chlorinated constituents will be more photolytically stable and more adsorptive.
- 128. Using the OECD Screening Tool and EPISuiteTM predicted physico-chemical properties, the LRET for these constituents are comparable to, but slightly below those for SCCPs, which is a POP. It also falls within the range of other listed POPs. CPs with C₁₄₋₁₇ chain lengths have low volatility and are expected to adsorb strongly to particulates. Given the relatively high gaseous fraction predicted for the C₁₄ constituents in the OECD Screening Tool, it is not clear how well the adsorption of the constituents is actually modelled. Several lines of evidence from other models and experimental data suggest that the fraction adsorbed to aerosols could be higher. Using COSMOtherm predicted physico-chemical properties, the LRET potential modelled by the OECD Screening Tool is greater, due to a greater proportion adsorbed to aerosols. The atmospheric transport of airborne particulates provides a potential route for long-range transport, and this is supported by the detection of "MCCPs" at low levels in air samples taken in remote locations. These include 5 years' monitoring in the Arctic and Antarctica, and sampling at the Tibetan Plateau. "MCCPs" monitoring at both Svalbard and the Tibetan Plateau suggests levels in air are increasing at these remote locations. The ratio of "MCCPs" to SCCPs is also observed to be increasing in Antarctic air. The levels of "MCCPs" observed in the Polar locations was noted to be higher than some listed POPs such as PBDEs.
- 129. The modelled comparability to SCCPs is further supported by the detection of "MCCPs" in environmental samples from remote regions, including in top predators. In some instances, the levels of "MCCPs" were indicated to be around or above SCCPs concentrations.
- 130. As discussed in document UNEP/POPS/POPRC.18/INF/10, the OECD Screening Tool predictions for the LRET of "MCCPs" via water are significantly lower than the values predicted for transport via air (CTD_{air} values are ~5 to 20 times greater than CTD_{water}). Nevertheless, monitoring data indicate the presence of "MCCPs" in seawater (both in the dissolved and particulate phase), and sediment in the Arctic environment. These data suggest that transport via ocean currents is a complementary pathway for "MCCPs" to reach remote regions.
- 131. Overall, the evidence demonstrates that long-range environmental transport occurs. Limited biota monitoring data indicate detection of "MCCPs" in remote areas, with similar concentrations to SCCPs suggested in some studies. Air sampling data are also limited to specific locations, but the available information confirms the potential for transport via this medium. The predicted atmospheric half-life of a range of "MCCP" constituents is around 2 days with values above and below the threshold. It remains unclear how accurate these predictions are, and to what degree the gaseous transport of CPs with C_{14-17} chain lengths is relevant compared to adsorption to particles.
- 132. In conclusion, the limited data indicate that there is both a pathway and delivery of CPs with C_{14-17} chain lengths to remote locations. The characteristics of these constituents, while slightly less efficiently transported over long distances than SCCPs, appear to be similar to that of this listed POP.

2.3 Exposure

2.3.1 Environmental monitoring data

133. A summary of all cited environmental monitoring data, based on Environment Agency (2019a) and more recent studies can be found in document UNEP/POPS/POPRC.18/INF/10. This also includes details of number and species sampled, as well information on carbon chain length and chlorination where this was included in the analysis. Several studies are described in sections 2.2.2.2.3, 2.2.3.4, 2.2.4.3 and 2.2.4.4 rather than this section.

2.3.1.1 Ambient air

2.3.1.1.1 Remote

134. Section 2.2.4.3 details studies where "MCCPs" were detected in the air of remote regions such as polar areas and the Tibetan plateau. These provide evidence of long-range transport (Wu *et al.*, 2019; Ma *et al.*, 2014; Bohlin-Nizzetto *et al.*, 2014, 2015, 2017, 2018, 2019, 2020; Bohlin-Nizzetto & Aas, 2016; Jiang *et al.*, 2021; Schlabach *et al.*, 2022). It is also notable that for all three locations, concentrations of "MCCPs" are reported to be rising over time.

2.3.1.1.2 Other

135. "MCCPs" have been detected in China, Iceland, India, Norway, Pakistan, Sweden, Tanzania and the UK. "MCCPs" can be detected in air sampled in urban areas at concentrations up to around 12 ng/m³. Since 2012, no significant trends over time for "MCCPs" have been observed in the Swedish national monitoring program for air and deposition (Sweden, Annex E information).

2.3.1.2 Water

2.3.1.2.1 Remote

136. No remote water monitoring data have been located.

2.3.1.2.2 Other

137. The available European monitoring data generally show widespread occurrence of "MCCPs" in water (at concentrations typically up to a few μ g/L).

2.3.1.3 Wastewater and landfill leachate

- 138. Several studies have analysed Norwegian wastewater treatment plant (WWTP) sludge for "MCCPs", reporting concentrations up to 17 mg/kg (Thomas *et al.*, 2011; Norsk Vann, 2018; Fjeld, 2005; Ruus *et al.*, 2018). Several other authors have detected "MCCPs" in UK, Chinese, Swedish and Swiss sewage sludge at similar concentration ranges (Stevens *et al.*, 2003; Wang H *et al.*, 2019; Olofsson *et al.*, 2012; Bogdal *et al.*, 2015). There has been no clear change in the concentrations of "MCCPs" measured in the Swedish national monitoring programme since 2004 (Sweden Annex E information).
- 139. Brandsma *et al.*, (2017) found that "MCCPs" were the dominant CPs in sludge samples collected from 15 different WWTPs in Australia. "MCCPs" were detected in all studied sludge samples with concentrations ranging from 0.54 to 3.65 mg/kg dw, using APCI-QToF-MS. All four chain lengths were detected although the predominant congeners in all samples were $C_{14-15}Cl_{5-9}$.

2.3.1.4 Sediment

2.3.1.4.1 Remote

- 140. The MAREANO (Marine AREA database for Norwegian waters) program has analysed for a number of contaminants including CPs (using ECNI-HRMS) in surface marine sediment collected from several locations within the MAREANO area. In a pilot study between 2009 and 2015, concentrations of SCCPs and "MCCPs" in the 10 marine sediment samples could be detected but were all below their limits of quantification (1 393 and 19 μ g/kg dw) (Boitsov *et al.*, 2016). Based on these findings, Boitsov *et al.*, (2019) sampled marine sediment from 8 locations in 3 areas near Svalbard and analysed for CPs. Levels of SCCPs and "MCCPs" were mostly below their LOQs (although, the LOQs were higher than the previous study 96 and 334 μ g/kg). "MCCPs" were quantified at two locations (410 and 536 μ g/kg dw). Boitsov and Sanden (2020) did not detect either SCCPs or "MCCPs" in sediment samples from 7 locations near Bjørnøya and Svalbard in 2019 (LOQ = 20 and 6.9 μ g/kg dw). More recent sampling from 7 locations in the Norwegian Sea in 2020 detected "MCCPs" at all sites, with concentrations between 25 and 529 μ g/kg dw (Boitsov & Sanden, 2021).
- 141. Bakke *et al.*, (2008) collected surface marine sediment samples from the Barents Sea in 2006 and 2007, and analysed for CPs using ECNI-HRGC-HRMS. "MCCPs" was detected in one sample at 4.8 μ g/kg dw. Further marine sediment sampling for "MCCPs" from the eastern Barents Sea in 2017 detected "MCCPs" at one location (2.8 mg/kg dw), however the LOQ of 655 μ g/kg was relatively high (Boitsov and Klungsøyr, 2018).

2.3.1.4.2 Other

- 142. "MCCPs" have been widely detected in river and marine sediment at concentrations typically up to around 2 mg/kg dw, although up to 65 mg/kg dw has been reported near industrial areas. Sampling locations include Australia, Canada, China, Czech Republic, Germany, Japan, Netherlands, Norway, Sweden, Switzerland, UK, Irish Sea and the Baltic Sea. Several studies reviewing sediment cores are described in section 2.2.2.2.3 where all "MCCPs" chain lengths could be detected (Iozza *et al.*, 2008; Yuan *et al.*, 2017; Chen *et al.*, 2011; Zeng *et al.*, 2017a; Zhang *et al.*, 2019).
- 143. Guida *et al.*, (2020) report measured contamination of sediment at "MCCPs" manufacturing sites in China and the USA at up to 50 mg/kg dw.

2.3.1.5 Soil

144. Soil monitoring data are available for China, Germany and Switzerland. "MCCP" concentrations in soil measured using GC-ECNI-HRMS show an increase from 1989 to 2014 from 6 sampling sites in Switzerland with "MCCP" concentrations (up to 160 μg/kg) exceeding SCCPs in the most recent samples (Bogdal *et al.*, 2017). In Germany, the concentrations were up to 49 μg/kg dw (Yuan *et al.*, 2022). Levels in Chinese soil vary, but concentrations up to 2 mg/kg dw have been detected in agricultural soils based on a survey performed by Aamir *et al.*, (2019). All chain lengths were detected in Chinese soil where this level of analysis was performed (Aamir *et al.*, 2019; Wang *et al.*, 2017; Xu *et al.*, 2016). Aamir *et al.*, (2019) found that C₁₄₋₁₅Cl₅₋₇ were the predominant congeners. Concentrations in soil sampled around a non-ferrous metal recycling park in China detected concentrations of "MCCPs" up to 6 mg/kg, with the major "MCCPs" congener groups noted to be C₁₅₋₁₆Cl₅ (Weng *et al.*, 2022). In the more remote agricultural Chinese soils sampled by Aamir *et al.*, (2019), the authors also noted the possibility of a mountain cold-trapping effect for atmospheric CPs resulting in increasing levels of "MCCPs" compared to SCCPs in soils at higher elevation. This is similar to the suggestion of Zhang *et al.*, (2019) regarding high altitude lake sediment.

2.3.1.6 Biota

2.3.1.6.1 Remote

- 145. Reth $\it et\,al.$, (2006) detected "MCCPs" in liver and muscle samples from Arctic Char, Little Auk and Blacklegged Kittiwake collected from the Arctic using HRGC-ECNI-LRMS. The highest concentration was 0.37 mg/kg (in auk liver tissue). The authors reported that the C_{14}/C_{15} ratios detected in the study were similar to that found in commercially supplied "MCCPs" products. "MCCP" and SCCP concentrations in the bird muscle and liver tissue were also comparable. The very small sample size used in this study means that limited weight should be placed on the findings. Glüge $\it et\,al.$, (2018) noted that the "MCCP" concentrations from the fish in the study were in the upper 50th percentile of the observed concentrations in fish sampled from the Canadian Arctic and Europe (principally Norway), and concentrations in the bird eggs were comparable between the Canadian Arctic and Norway. Analytical standards used appear to range from 49% to 57% chlorine "MCCPs" in the Reth $\it et\,al.$, (2006) study (and indeed in the majority of monitoring studies).
- 146. Schlabach *et al.*, (2018) detected "MCCPs" using GC-MS in biota collected in 2017 from Svalbard and the Norwegian island of Røst. Tissue was sampled from Common Eider, European Shag, Kittiwake, Glaucous Gull and Polar Bear (n = 5 to 10). The detection frequency of "MCCPs" was 100% with the exception of Polar Bears (60%). "MCCP" concentrations were generally lower than SCCPs but within the same order of magnitude, apart from Polar Bears. The authors estimated the total measurement uncertainty to be 40-50%.
- 147. Green *et al.*, (2018, 2019 & 2020) have analysed for SCCPs and "MCCPs" in remote biota as part of the *Contaminants in coastal waters of Norway* programme in Atlantic Cod (liver) and Common Eider (blood and egg) sampled from Svalbard in 2017, 2018 and 2019 (n=15 for all samples, except eider blood in 2019). Analyses were performed using GC-MS, GC-HRMS or GC-QTOf-MS. In 2018 the median concentrations of "MCCPs" were 35 μ g/kg ww and 14 μ g/kg ww in eider blood and eggs, which were higher than the 2017 samples, but similar to those reported in Schlabach *et al.*, (2018). Green *et al.*, (2019) notes that the median concentration of "MCCPs" detected in cod liver samples originating from Svalbard (56 μ g/kg ww) in 2018 were similar to those from urban areas of coastal Norway. "MCCP" concentrations were broadly similar to SCCPs. In 2019, the median "MCCP" concentration in cod liver was slightly higher (110 μ g/kg ww), with the levels in eider eggs and blood slightly lower (31 and 9 μ g/kg ww). SCCPs concentrations were slightly lower than 2018, although of a similar order of magnitude (Green *et al.*, 2020). The authors estimated the analytical uncertainty to be around 50%.
- 148. Casa *et al.*, (2019) detected "MCCPs" in blubber samples obtained from Humpback Whales stranded between 2007 and 2015 in western and eastern Australia. Genetic testing indicated that the whales were associated with two Antarctic Management Areas, and principally feed on Antarctic Krill. The authors expect the chemical profiles of this population to reflect their krill diet. Unsatisfactory analytical recoveries were obtained for the "MCCP" congeners, but "MCCPs" were detected in three of the nine samples.
- 149. Further detection of "MCCPs" in Arctic biota (Ringed Seal plasma, Polar Bear plasma, Black-legged Kittiwake eggs, Common Eider eggs, Glaucous Gull plasma and Atlantic Cod liver and whole Polar Cod) were noted by Harju *et al.*, (2013) (see section 2.2.3.4).

2.3.1.6.2 Other

150. Huber *et al.*, (2015) collected eggs of 3 species of seabird from 2 remote Norwegian coastal islands, and analysed for several contaminants including SCCPs and "MCCPs". Analyses were performed using GC-MS. Concentrations of "MCCPs" in bird eggs were <0.76–17.5 μg/kg ww and it was found at a much higher frequency (80%) compared to SCCPs (40%). Concentrations of "MCCPs" in this study were in the same order of magnitude as the sea bird eggs sampled from Svalbard (Harju *et al.*, 2013).

- 151. Green *et al.*, (2022) analysed for SCCPs and "MCCPs" in whole Blue Mussels and Atlantic Cod liver at a number of monitoring stations along the Norwegian coast. This was part of the *Contaminants in coastal waters of Norway* programme which has been in place since 2012. The stations include areas with possible point and diffuse pollution sources (local airports were noted) as well as more remote areas. Analyses were performed using GC-MS. "MCCPs" were detected in all samples: median concentrations were 13 to 62 μg/kg ww in mussel and between 98 and 320 μg/kg ww in cod liver. Earlier results from the programme are provided in document UNEP/POPS/POPRC.18/INF/10. Green *et al.*, (2022) also assessed long-term trends in the monitoring for SCCPs and "MCCPs" at 8 of monitoring stations where there was sufficient data. No trend in levels was seen at any station for "MCCPs". In a review article by Vorkamp *et al.*, (2019) considered CPs monitoring data including an earlier part of the *Contaminants in coastal waters of Norway* monitoring programme. The authors noted that "MCCP" concentrations exceeded that of SCCPs in mussels and Atlantic Cod liver sampled in one Northern Norway location (Lofoten) but trends were less clear at two other locations (Tromsø, Cod; Bodø, mussels) in the period monitored (2012–2016).
- 152. Ruus *et al.*, (2018 and 2019) and Grun *et al.*, (2021) reported concentrations of "MCCPs" in Atlantic Cod liver, and Herring Gull blood and eggs in the Inner and Outer Oslofjord areas as part of the *Norwegian Environment Agency Urban Fjord Monitoring Programme*. Analyses were performed using GC-MS with mean concentrations detected between 3.57 and 231.9 μg/kg ww. Higher concentrations were seen in the cod liver and gull blood in the Inner Oslo Fjord in 2017 and 2018 compared to 2020, although the gull egg concentrations were similar. Herring Gull samples from the Outer Oslo Fjord area were of the same order of magnitude as the Inner Fjord in 2017 (these were not sampled in 2018 and 2020). In a related study, Knudtzon *et al.*, (2021) analysed for a number of contaminants including C_{14–17} congeners (degree of chlorination not stated) in 30 paired whole blood and egg samples from female urban Herring Gulls from the Inner and Outer Oslofjord in May 2017. Measurements were performed using GC-MS, with C_{14–17} congeners detected above the LOD in all samples. Concentrations were between 6 and 200 μg/kg ww in blood and 3–630 μg/kg ww in eggs for the Outer Oslofjord samples. The Inner Oslofjord concentrations ranged from 8.0–76.0 μg/kg ww in blood and 6.0–68.0 μg/kg ww in eggs.
- 153. Schlabach *et al.*, (2018) detected "MCCPs" in all Common Gulls' eggs (range: 9.4 Common Eider 87, average: 40 μ g/kg ww) collected in 2017 from Tromsø, Norway (urban). Furthermore, the detection frequency was also 100% in biota samples from the Norwegian Arctic, with concentrations ranging from 1.1 to 366 μ g/kg ww. Concentrations of "MCCPs" in these urban eggs were comparable to the other bird species (Svalbard, Common Eider: 13 Common Eider 9, average: 31 μ g/kg ww; Black-legged Kittiwake: 9.3 Common Eider 96, average: 40 μ g/kg ww; Glaucous Gull: 8.6 Common Eider 49, average 36 μ g/kg ww) sampled from the remote Arctic in the same study. "MCCPs" were also detected in European Mink from Sommarøy (1.1–32, average: 13 μ g/kg ww), Polar Bear from Svalbard (5.1–93, average: 41 μ g/kg ww) and European Shag from Røst (7.8–366, average: 150 μ g/kg ww). Analysis was performed by GC-MS.
- 154. Herzke *et al.*, (2019) analysed liver samples from Herring Gulls collected in Skulsfjord in Troms, northern Norway in 2017 using GC-HRMS. CPs were noted to dominate the analytical results with mean concentrations in the livers of 210 μ g/kg ww for SCCPs and 87.8 μ g/kg ww for "MCCPs".
- 155. De Wit *et al.*, (2020) reported the sampling and analysis of Blue Mussel and Viviparous Eelpout collected from several locations in the Baltic Sea in 2015 (which was additional to the sampling described in section 2.2.3.4). CP analyses were performed using a modified method following Yuan *et al.*, (2020). Average total "MCCPs" and SCCPs concentrations in the mussels were 210 μ g/kg lw and 72 μ g/kg lw, respectively. Average total "MCCPs" and SCCPs concentrations in the fish muscle were 130 μ g/kg lw and 52 μ g/kg lw, respectively. The homologue and congener pattern of the mussels (only) are presented graphically in the paper which indicates all "MCCP" chain lengths could be detected. In this study SCCPs, "MCCPs" and LCCPs were detected in both species. The distribution pattern was similar across species with "MCCP" (48–54%) > SCCP (31–38%) > LCCP (13–15%). A graphical presentation of the detected CPs and their congener pattern indicate the detection of Cl₃₋₁₀ "MCCPs" with Cl₅₋₈ the most prevalent.
- 156. Yuan *et al.*, (2021) analysed biota from marine waters around Greenland, Iceland and the Swedish west coast between 2001 and 2020 for CPs using UPLC-APCI-Orbitrap-MS. "MCCPs" were detected above their MDL in 54% of samples (see UNEP/POPS/POPRC.18/INF/10). These include mussel, scallop, Minke Whale muscle, Killer Whale muscle, Pilot Whale muscle and blubber, Greenland Shark liver and Harbour Porpoise blubber (in most instances these were single samples). "MCCP" concentrations were $14-270~\mu g/kg$ lw. The homologue and congener pattern are presented graphically in the paper which indicates all "MCCP" chain lengths could be detected, with C_{14} and C_{15-7} dominating in most samples. The authors noted higher CP concentrations in the cetacean muscle tissue compared to blubber (by a ratio of 3.6 for "MCCPs").
- 157. Schlabach *et al.*, (2022) analysed for CPs in biota from different Nordic locations (including remote and urban sites) using GC-QtoF-HRMS. "MCCP" concentrations were noted to be usually higher than SCCPs. In birds' eggs "MCCPs" were detected in 100% of samples at 2.46–22.3 µg/kg ww. In freshwater fish, "MCCPs" were detected in 67%, 100%, and 83% of samples from remote Brown Trout, 'perch' and 'urban perch', respectively (up to 138

 $\mu g/kg$ ww in the latter). In marine fish, "MCCPs" were detected in all samples, ranging between 22 and 106 $\mu g/kg$ ww. In seal blubber, "MCCPs" were detected in 1 of 2 samples at a concentration of 48.8 $\mu g/kg$ ww. In terrestrial mammals (Moose, Red Deer and Reindeer) SCCPs and "MCCPs" were detected in all samples with "MCCPs" between 2.55 and 14.5 $\mu g/kg$ ww.

- 158. Yuan *et al.*, (2022) determined the concentrations of CPs in 72 pooled biota samples from the German Environmental Specimen bank using UPLC-APCI-orbitrap-MS analysis. The samples were from multiple sites across coastal, terrestrial and freshwater ecosystems and collected in 2017 and 2018. "MCCPs" were detected in 99% of samples and noted to be the predominant CP in nearly all sample types. Additional Bream samples collected downstream from a CP production site were used to establish a temporal trend in CPs, and indicated relatively steady "MCCP" concentrations over the period 1995–2019 (with C₁₄ and C₁₅ chain lengths predominating, but all four detected).
- 159. Labadie *et al.*, (2019) detected all four "MCCPs" chain lengths (with Cl_{7-9} congeners) in Common Barbel sampled from 4 rivers and a canal from the Rhone River basin in France in 2019. Using GC-ECNI-ToF HRMS analysis, concentrations of "MCCPs" were up to 72.7 μ g/kg ww (11,300 μ g/kg lw).
- 160. Basconcillo *et al.*, (2015) measured "MCCPs" in top predatory freshwater fish (Lake Trout, Walleye and Brook Trout) from across Canada in 2010–2011 using GC-HRMS analysis. "MCCPs" were detected in all fish, with the highest concentration in Lake Trout from industrialised and populated areas (11–12 μ g/kg ww). Concentrations of "MCCPs" in fish in less populated locations ranged from 4 to 6 μ g/kg ww, while those in remote locations were 1 μ g/kg ww. The C₁₄ chain length was the most abundant from all sites ranging from 60 to 85%, followed by C₁₅ and C₁₆. C₁₇ chain lengths were not detected. The authors also noted that concentrations of SCCPs in Lake Ontario Lake Trout collected in 2011 had decreased compared to 2001 (reported by Houde *et al.*, 2008; see also UNEP/POPS/POPRC.18/INF/10), but no significant change had occurred for "MCCPs". Furthermore, the ratio of SCCPs/"MCCPs" decreased from 2001 to 2011 showing a shift towards "MCCPs".
- 161. Choo *et al.*, (2022) analysed for "MCCPs" congeners in egg samples from Black-tailed Gulls from two South Korean islands, collected from 2012 to 2018. Analysis was performed using GC-MS and quantified based on correlation with known "MCCPs" mixtures. Pooled samples from both sites showed increasing "MCCP" concentrations with time (the highest detected concentration was 4 898 μ g/kg lw). The predominant homologue grouping, irrespective of the chlorination degree, was C_{14-15} (55%). The proportion of longer chain length (C_{16-17}) homologues increased at a rate of 5% over the time span of the study.
- 162. Du *et al.*, (2018) investigated the occurrence of CPs in wildlife (2 fish, 3 reptiles, 1 mammal and 3 birds) from paddy fields in the Yangtze River Delta, China. The highest values were found in snakes, weasel and predatory birds (up to 33 mg/kg lw or 4.7 mg/kg dw). The authors found that the average concentrations were in the order "MCCPs" > SCCPs > LCCPs, except in birds where SCCPs were found to be more abundant. "MCCPs" appears to be widely dispersed in wildlife at the sampling locations. For "MCCPs", dominant chain lengths were reported to be C_{14} (43.8%), C_{15} (25.7%) and C_{16} (18.2%) (and hence C_{17} 12.3%) with an average chlorination degree of 56.6–57.5% Cl wt. (Cl₇ congeners made up 25.7% and Cl₈ congeners 22.5% of the detected "MCCPs").
- 163. In a related study to Du *et al.*, (2018) by the same research group, Zhou *et al.*, (2019) investigated the occurrence of CPs in aquatic wildlife (9 species: 7 fish, one snail and one clam) from Lake Dianshan in the Yangtze River Delta, China. "MCCP" concentrations in fish were up to 3.1 mg/kg lw, which is similar to concentrations in the fish (up to 4 mg/kg lw) sampled in the paddy fields by Du *et al.*, (2018). It should be noted that a limited number of fish were sampled in the lake (a single individual per species, aside from anchovy). Concentrations in clams and snails were at a similar order of magnitude to the fish. Detected "MCCPs" had an average chlorination of 52–58% Cl wt.
- 164. Zeng *et al.*, (2015) detected all four chain lengths (with Cl_{6-8} congeners) in the blubber samples of Finless Porpoises, and C_{14} and C_{15} chain lengths (with Cl_{6-8} congeners) in Indo-Pacific Humpback Dolphins in waters around Hong Kong SAR from samples collected between 2004 and 2014. A statistically significant temporal increasing trend for Σ "MCCPs" was observed in both species. Concentrations detected were between 0.32 and 56 mg/kg lw.
- 165. Wang *et al.*, (2021 Abstr.) collected 3 species of mollusc from the Chinese Bohai Sea between 2011 and 2018 and analysed these for SCCPs and "MCCPs". "MCCP" concentrations ranged between not detected and 4.34 mg/kg dw. The authors noted no obvious temporal or spatial trends of CPs, but did record homologue profile changes which were thought to reflect compositional changes of CP industrial products. Oysters were reported to contain the highest CP concentrations of the species sampled.
- 166. Chen *et al.*, (2021) determined the concentrations of SCCPs and "MCCPs" in 10 species of coastal coral at two locations in the South China Sea. Using GC-QToFMS analysis, the median concentrations of "MCCPs" median (204 μ g/kg dw) were higher than SCCPs (103 μ g/kg dw). All 4 "MCCPs" chain lengths were detected, and the dominant chlorine pattern was noted to be similar to CP-52.
- 167. Yuan and De Wit (2018) and Yuan *et al.*, (2019) analysed biota samples from Sweden for CPs with a chain length up to C_{30} using APCI-QTOF-MS. In the terrestrial food web, Bank Voles were found to contain the lowest

amounts of "MCCPs" among the studied species. The detected concentrations of "MCCP" in muscle were comparable in Eurasian Lynx and Grey Wolf (0.75–0.83 mg/kg lw), whilst Moose muscle contained the highest concentrations (1.6 mg/kg lw). "MCCPs" were also detected in muscle or eggs of terrestrial birds of prey (Tawny Owl, Eagle Owl, Marsh Harrier, Golden Eagle and Peregrine Falcon) up to 0.72 mg/kg lw. "MCCPs" were reported as summed congeners, and the authors detected all four "MCCPs" chain lengths (chlorination levels detected varied Cl_{4–7} up to Cl_{8–10}), including in top predators.

- 168. The *Environmental Pollutants in the Terrestrial and Urban Environment Monitoring Programme* in Norway has detected "MCCPs" in several terrestrial biota living in the Oslo area, including Tawny Owl eggs (50% detection, <LOD–26 μg/kg ww, (544 μg/kg lw)), Fieldfare eggs (100% detection, 21–132 μg/kg ww (4218 μg/kg lw)), Brown Rat liver (60% detection, <LOD–66 μg/kg ww) and Red Fox liver (50% detection, <LOD–9 μg/kg ww) from sampling performed in 2020. Concentrations in the Tawny Owl eggs were noted to be in a similar range to perfluoroalkyl substances (PFAS) and PCB, with Fieldfare egg concentrations much higher (Heimstad *et al.*, 2020).
- 169. Glüge *et al.*, (2018) summarised monitoring data in a literature review of measured concentrations of "MCCPs" in environmental matrices, biota and humans worldwide, including remote regions. The researchers concluded 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."

2.3.2 Humans

- 170. The European Food Safety Authority recently summarised the available information on levels of CPs in human samples collected in Europe, Asia (mainly China) and Australia (EFSA, 2020). "MCCPs" have been detected in human milk samples, with levels generally lower in the few European studies than in samples collected in Asia. EFSA (2020) quotes levels of "MCCPs" between < 5.5 to $112~\mu g/kg$ lw in human breast milk across 11 European countries.
- 171. The United Nations Environment Programme conducted a global survey of CPs in pooled human breast milk samples from individual countries collected from 2012–2019 (Krätschmer *et al.*, 2021). A total of 57 pooled milk samples were obtained from 53 countries on five continents (Africa, Central/South America, Asia, Europe and Australia/Oceania). Eligible donors were identified by application of standardised screening questionnaires. Analysis was conducted at the UNEP Reference Laboratories, Germany. "MCCPs" were present in all pooled samples, from 23–700 μg/kg lw, with the highest ranges noted in Africa (47–370 μg/kg lw) and Asia (38–540 μg/kg lw). As the study used pooled samples, so individual levels (very high or very low) were not taken into account in the review. CPs comprised 18–46% of the total POPs in human milk, while "MCCP" concentrations equalled or exceeded SCCPs in 43 of 57 pooled samples. It was noted that "higher MCCP concentrations suggest that accumulated SCCP exposures in the mothers were lower than accumulated exposures to MCCPs, even though the ban on SCCPs only came into effect in 2017."
- 172. Xu *et al.*, (2022) determined the concentrations of "MCCPs" in human serum samples, using uPLC-qToF-ENCI-MS, collected from 2 cohorts (2007–2009; 3 days postpartum n=62; and 2019 pregnant n=28 and non-pregnant n=10). Mean concentrations were 0.02 μ g/L ww during 2007-2009 and 0.07 μ g/L in 2019, with an increasing trend between 2007-2009 and 2019 (p=0.019). In addition, detection frequency of "MCCPs" increased in the 2019 samples, and in two thirds of the samples "MCCP" levels were higher than SCCP levels (the "MCCP":SCCP ratio across all samples was 1.60). The majority of "MCCPs" were $C_{14}Cl_{7-8}$ and $C_{15}Cl_7$ congener groups.
- 173. Xia *et al.*, (2017a) found "MCCP" concentrations in pooled samples of human breast milk collected from rural China ranged from 9.05 to 139 μ g/kg lw (median 35.7 μ g/kg lw) in 2007, and between 9.51 and 146 μ g/kg lw (median 45.4 μ g/kg lw) for samples taken in 2011. Analysis was performed using GC-ECNI-HR-ToFMS, which indicated that the C₁₄ homologues comprised 82% of the total "MCCP" content, with Cl_{7–8} the most abundant congeners. In a further study of samples of human breast milk from urban locations in China at the same time points, Xia *et al.*, (2017b) found "MCCP" concentrations ranged from 18.7 to 350 μ g/kg lw (median 60.4 μ g/kg lw) in 2007, and between 22.3 and 1501 μ g/kg lw (median 137 μ g/kg lw) for samples taken in 2011. Good correlation in the urban study was noted between areas with higher CP breast milk concentrations and areas of higher CP production (Xia *et al.*, 2017b).
- 174. Zhou *et al.*, (2020) detected CPs using APCI-QToF-HRMS in human breast milk sampled from three cities in the Yangtze Delta of China, a city in Sweden and one in Norway. "MCCPs" were found in most samples, with concentrations ranging <LOD-1,260 μ g/kg lw (median 78.8 μ g/kg lw) for the Chinese samples, and <LOD-311 μ g/kg lw (median 29.6 μ g/kg lw) for the Scandinavian samples. "MCCPs" were detected in all samples from the Chinese sites (36 individuals), in 18 of 19 samples from the Swedish site and 7 of 8 from the Norwegian site. "MCCPs" was found to be the most abundant CP group in all locations and samples, with the exception of one Chinese city (Jiaxing) where the proportion of SCCPs (50%) was slightly higher than "MCCPs" (48%).
- 175. Li *et al.*, (2017) determined the concentration of CPs in all 50 human blood samples taken from the general population in Shenzhen, China. The "MCCP" concentrations were reported as being between 130 and 3,200 μg/kg lw.

The relative exposure of the participants is unknown. "MCCPs" were also detected in human placenta samples from China by Wang *et al.*, (2018), with concentrations ranging from 80.8 to 954 μ g/kg lw.

176. Document UNEP/POPS/POPRC.18/INF/10 includes details of all studies reporting the presence of CPs in human tissue and fluid samples. Several older studies are also summarised in document UNEP/POPS/POPRC.18/INF/10.

2.3.3 Food, Food-Related Exposures, and Consumer Products

- 177. Numerous studies detecting "MCCPs" in food are summarised in EFSA (2020). That report notes that the majority of these are from China, where concentrations were in the order of tens of $\mu g/kg$, which were higher than in other Asian countries (a few ng/kg). Levels detected varied across different regions, and with the level of local contamination and food types. Higher concentrations were found in fish and marine mammals, and then fatty and liver tissues of terrestrial mammals. EFSA (2020) considered that the impact of the uncertainties on the risk assessment of exposure to CPs in food was substantial, and due to the limited data on occurrence of CPs in food the dietary exposure was considered to be underestimated.
- 178. Perkons *et al.*, (2022) analysed 86 baby food samples from 22 countries grouped into 8 food-type categories for SCCPs and "MCCPs" using uHPLC-ESI-FT-ICR-MS. In 6 out of 8 sample categories, concentrations of "MCCPs" significantly exceeded SCCPs. "MCCP" concentrations ranged from <LOD-118 μ g/kg ww (<LOD-3 765 μ g/kg lw) with a median of 1.6 μ g/kg ww (64 μ g/kg lw). "MCCPs" were detected in 94% of the samples and C₁₄₋₁₅Cl₆₋₇ congener groups were the dominant constituents. The estimated "MCCP" intake per portion of baby food in infants (3–6 months), infants (6–12 months), toddlers (1–3 years) and children (3–10 years) ranged from 0.8–23.7 ng/kg bw, being highest for infants.
- 179. Chen *et al.*, (2021) analysed "MCCPs" in mature maize plants near to a Chinese CP production plant using GC-qTOF-NCI-HRMS. They found ranges of "MCCPs" of $<1.51-188 \mu g/kg$ dw in the soil and 77.6–52,930 $\mu g/kg$ dw in maize leaves (the median concentration in leaves was 448 $\mu g/kg$ dw, which reflects the inclusion of two extremely high values). The tissues that were directly exposed to airborne CPs had the highest concentrations.
- 180. Y Liu *et al.*, (2022) reported levels of MCCP of 4–306 µg/kg in a range of foodstuff from across China, as part of the sixth China Total Diet Study, conducted between 2016 and 2019. No information was provided on degree of chlorination or specific congener.
- 181. EFSA (2020) also considered the detection of "MCCPs" in animal feed, but as only very limited data were available, no general conclusions were drawn.
- 182. Several studies have detected "MCCPs" in house dust in Norway, South Africa, Germany and Sweden (Yuan et al., 2021; Brits et al., 2020; Hilger et al., 2013; Fridén et al., 2011). Concentrations in samples ranged from a few mg/kg up to 700 mg/kg. EFSA (2020) note that the concentrations of CPs in dust cover several orders of magnitude. "MCCPs" have been detected in domestic indoor air in Norway at concentrations between <0.35 and 13 ng/m³ with a detection frequency of 95% (Yuan et al., 2021). EFSA (2020) note that in addition to dietary exposure, CPs in house dust can be an important additional source of exposure. For children, crawling and hand-to-mouth habits should be considered as possibly increasing the ingestion of dust. EFSA (2020) noted that only a very crude estimate of the exposure via dust could be made, which had a large associated uncertainty, but it shows that for toddlers exposure from dust could be in the same order of magnitude as the dietary exposure estimated from fish. For adults, the exposure from dust was lower than for toddlers both in absolute terms and when compared with the exposure estimated from fish consumption, but could nevertheless still be an important source of exposure to CPs.
- 183. EFSA (2020) describe several studies assessing the effects of food processing on the concentrations of "MCCPs", including when it is found in some common kitchen equipment. This suggests that food could become more contaminated at the preparation stage as a result of transfer during contact (direct or secondary), and this is an important consideration when making exposure estimates. CPs have also been found in domestic plastic and food packaging, and the possibility of migration into food has been studied. Based on the studies available, migration from plastic and kitchen equipment can contribute to the total CP exposure. However, because of the limited available information EFSA (2020) concluded that exposure levels cannot be estimated. The studies include Yuan *et al.*, (2017), who detected SCCPs and "MCCPs" in hand-blenders; Gallistl *et al.*, (2017) who detected "MCCPs" in dishcloths following normal kitchen use; Gallistl *et al.*, (2018) who detected CPs in household oven components; and Wang *et al.*, (2018) who measured "MCCPs" in plastics, rubber and food packaging, finding mean values ranging from 10s to 1,000s of μg/kg with C₁₄Cl₆₋₈ congener groups dominant. More recently Guida *et al.*, (2020) investigated "MCCPs" in consumer products and found that "MCCPs" can constitute up to 22% of adhesives, 15% of PVC and 16% of rubber by weight. EFSA (2020) concluded that it was not possible to make estimates for intake of CPs from these other non-dietary sources, meaning that total non-dietary exposure will be underestimated.

2.3.4 Exposure Synthesis

- 184. CPs with C_{14-17} chain lengths are not routinely included in many environmental monitoring programmes. However, the available data generally show widespread occurrence of "MCCPs" in water (at concentrations typically up to a few μ g/L), sediment (at concentrations typically up to around 2 mg/kg dw, but up to 65 mg/kg dw near an industrial area) and soils (more limited information, but at concentrations up to around 2 mg/kg dw, and slightly higher near an industrial area). "MCCPs" is also found in sewage sludge up to 17 mg/kg dw, and in air at a few ng/m³. Levels in dust are reported to be in the low mg/kg range.
- 185. Monitoring studies demonstrate widespread contamination of wildlife by CPs with C_{14-17} chain lengths at all trophic levels (including predatory species and sensitive life stages such as birds' eggs). Typically, concentrations are below 1 mg/kg ww. Samples from relatively uncontaminated regions have maximum detected levels of 540 μ g/kg lw (Grey Seal liver), 720 μ g/kg lw (Eagle Owl muscle), 1,600 μ g/kg lw (Moose muscle), 830 μ g/kg lw (Grey Wolf muscle) and 5 390 μ g/kg ww (Atlantic Cod liver). In cetaceans, several studies record levels in blubber of up to 23 mg/kg lw (South China Sea), and up to 80 mg/kg ww (Canada). In more locally contaminated areas, biota tissue concentrations can exceed 1 mg/kg dw.
- 186. Environmental monitoring data show the detection of "MCCPs" in different matrices at locations in the following countries: Australia, Belgium, Canada, China, Czech Republic, Denmark, France, Germany, India, Ireland, Japan, Norway, Pakistan, Sweden, Switzerland, UK and the USA, various marine locations such as the Baltic Sea, Irish Sea and North Sea in Europe and Chinese Bohai Sea, as well as remote locations such as the Arctic, Antarctic and Tibetan Plateau.
- 187. Numerous studies detect "MCCPs" in food for human consumption indicating dietary exposure. Several monitoring studies also indicate the presence of "MCCPs" in household dust, a number of household products and appliances, rubber granulates used in playing fields and other sources that may represent exposure pathways to humans.
- 188. Human monitoring data shows that "MCCPs" are widely detected in breast milk, and in some instances maximum concentrations were 1–3 mg/kg lw. Some studies indicate that levels of "MCCPs" in breast milk equal or exceed SCCPs. "MCCPs" can also be detected in other human tissue such as blood and placenta. (Greenpeace 1995; Thomas and Jones 2002; Darnerud *et al.*, 2012; Xia *et al.*, 2017a and b; Zhou *et al.*, 2020; Li *et al.*, 2017; Wang *et al.*, 2018; EFSA 2020; Krätschmer *et al.*, 2021; Chen *et al.*, 2020; see also UNEP/POPS/POPRC.18/INF/10).
- 189. The most recent biota monitoring studies have usually provided chain length and congener level information (Labadie *et al.*, 2019; Yuan *et al.*, 2017, 2019 & 2021 & 2022; Du *et al.*, 2018 & 2019 & 2020; Liu *et al.*, 2020; Zeng *et al.*, 2017; Chen *et al.*, 2021; Niu *et al.*, 2022; Xu *et al.*, 2021; Dan Xia *et al.*, 2022; Wang *et al.*, 2019; Li *et al.*, 2018a; Pan *et al.*, 2018 & 2021; Wu *et al.*, 2020; Huang *et al.*, 2020; Aamir *et al.*, 2019; Xu *et al.*, 2016; Zhang *et al.*, 2019; Xu *et al.*, 2019; Zeng *et al.*, 2015; Huang *et al.*, 2017). In these cases, all chain lengths of "MCCPs" are routinely detected.
- 190. Several studies provide information about increasing temporal trends in "MCCP" levels. These include both environmental matrices such as air and sediment, and biota including predators such as porpoises and dolphins. These increases in concentration match the increasing use and production of "MCCPs" globally. Increasing trends are also seen in "MCCPs" measured in air in all remote locations where data are available.
- 191. Overall, the available monitoring data are consistent with the findings of the available measured laboratory data for persistence and bioaccumulation, and modelling of long-range environmental transport potential. Extensive detection in wildlife, human tissue, food sources, and detection in consumer products also indicate the bioavailability and potential exposure pathways of "MCCPs".

2.4 Hazard assessment for endpoints of concern

2.4.1 Ecotoxicity

- 192. Ecotoxicity data are available covering aquatic, benthic, and terrestrial organisms. The data have been extensively reviewed in EC (2005 & 2007), EA (2019) and ECHA (2021a). Since CPs with C_{14-17} chain lengths contain thousands of constituents, the reported toxicity endpoints effectively reflect an average of the contributions that individual constituents make. The influence of varying degrees of chlorination and chain length on toxicity is not known. It is therefore assumed that if toxicity is demonstrated for one type of product, it will be applicable for all, although this is an area of uncertainty.
- 193. Two aquatic toxicity studies have been performed with *Daphnia magna* using a C_{14-17} chlorinated n-alkane, 52% Cl wt. The first is an acute test performed according to OECD TG 202 and GLP that is considered to be reliable without restriction. This determined a 48-h EC₅₀ value of 5.9 μ g/L, based on (arithmetic) mean measured concentrations (Thompson *et al.*, 1996). The second is a long-term test performed according to OECD TG 202 (later superseded by OECD TG 211) and GLP that is also considered to be reliable without restriction (Thompson *et al.*,

- 1997a). The study met the validity criteria of the later test guideline as well as OECD TG 202. Based on the chemical analysis, results were calculated as time-weighted mean values, with the 21-day NOEC for reproduction and length being 8.7 μ g/L. The lower EC₅₀ value might be explained by the absence of food compared to the longer test (leading to greater availability of the substance and differences in elimination efficiency of the organisms).
- 194. A further long-term invertebrate toxicity study was summarised in EC (2005). This reported a 60-d NOEC of 0.22 mg/L for a C_{14-17} , 52% Cl wt. substance with Blue Mussel (*Mytilus edulis*) (Madeley and Thompson, 1983).
- 195. The available acute and chronic data for fish and algae cited in EA (2019) and EC (2005) suggest that these taxa are less sensitive to "MCCPs" than *D. magna*. Long-term fish data are limited, but a GLP 60-d study using Rainbow Trout (*O. mykiss*) exposed to C_{14-17} CP, 52% Cl wt. found no effects on mortality, growth or behaviour at 4.5 mg/L (Madeley *et al.*, 1983). In an algal toxicity study performed with a C_{14-17} CP, 52% Cl wt. substance according to OECD TG 201 and GLP (Thompson *et al.*, 1997b), a 72-hour EC₅₀ >3.2 mg/L was determined, as little or no effect on the growth of the green alga *Selenastrum capricornutum* occurred at concentrations up to 3.2 mg/L.
- 196. Three reliable prolonged sediment toxicity studies for "MCCPs" conducted in accordance with GLP using three taxa (*Hyalella azteca*, *Lumbriculus variegatus* and *Chironomus riparius*) are summarised in EC (2005). These used sediments spiked with a C_{14-17} , 52% Cl wt. substance. The lowest 28-d NOEC was 130 mg/kg dw (~50 mg/kg ww), obtained in the studies with *L. variegatus* for the mortality/reproduction endpoint and *H. azteca* for growth. The LOEC was 410 mg/kg sediment dw. EC (2005 & 2007) also report three reliable long-term terrestrial toxicity studies conducted in accordance with GLP with the same chemical using earthworms (OECD TG 222), terrestrial plants (OECD TG 208) and soil microorganisms (OECD TG 216). Earthworms (*Eisenia fetida*) were the most sensitive species, with a 56-d NOEC of 280 mg/kg dw (~250 mg/kg ww).
- 197. Acute oral 1-day LD_{50} values of "MCCPs" (Cereclor S52, C_{14-17} , 52% Cl wt.) were reported to be > 24 606 mg/kg bw/day for Ring-necked Pheasant and > 10 280 mg/kg bw/day for Mallard. After dietary treatment, the 5-day LC_{50} values of "MCCPs" (C_{14-17} , 52% Cl wt.) were reported to be > 24,603 mg/kg diet for both Ring-necked Pheasant and Mallard (Madeley and Birtley, 1980). No long-term avian toxicity data are available.
- 198. Reflecting the toxicity to *Daphnia magna*, "MCCPs" has a harmonised EU environmental classification of Aquatic Acute 1, Aquatic Chronic 1 (H400, H410) in accordance with the UN Globally Harmonised System. More recent self-classification by the lead EU REACH Registrants includes an M-factor for acute and chronic aquatic hazards of 100 and 10, respectively. The significant levels of toxicity observed have also resulted in the substance being concluded to meet the "T" criterion for the EU PBT assessment (EA, 2019; ECHA, 2021a).

2.4.2 Human health toxicity

- 199. An EU human health risk assessment report (HSE, 2008) provides a summary of the available laboratory mammalian testing, which used one commercial product type (a C_{14-17} , 52% Cl wt. substance) for the majority of regulatory studies. A more recent review performed by the European Food Safety Authority (EFSA, 2020) relies on the same key hazard data. The outline below summarises a more comprehensive assessment completed in 2021 and provided in document UNEP/POPS/POPRC.18/INF/10. In addition, two more recent *in vitro* studies and an epidemiology study are also briefly reported.
- 200. The potential of "MCCPs" to perturb thyroxine (T4) binding to the transport protein transthyretin (TTR) has been investigated using a non-standard *in vitro* assay (Sprengel *et al.*, 2021b). "MCCPs" and purified "MCCPs" demonstrated some capacity to interfere with T4 binding to TRR in this specific *in vitro* system. A second *in vitro* study (Zhou *et al.*, 2021) was conducted to determine if 17 technical CPs demonstrate aryl hydrocarbon receptor (AhR)-agonist activity. No information is available on chain length or percentage chlorination of the technical CP samples. Overall, it appears that in this assay system, "MCCPs" do not bind to the AhR.
- 201. Ren et al., (2019) compared effects of SCCPs, "MCCPs" and LCCPs on cell viability and HepG2 cells were treated with 10, 100 and 1000 μg/L of SCCPs, "MCCPs" and LCCPs for 24 h. Overall, the results on cell viability "suggested that three kinds of CPs with comparable chlorine contents induced similar cytotoxicity. Effects on ATP, ROS and MDA were only investigated at 100 μg/L. The results showed a decrease in ATP levels, with the highest decrease seen in samples exposed to "MCCPs". "MCCPs" also lead to the highest increase (46.9%. compared to control) in reactive oxygen species.
- 202. Ding *et al.*, (2020) measured the occurrence and homologue profiles of SCCPs and "MCCPs" in serum of 145 people aged 50-84 living in Jinan, Shandong Province of China and assessed associations with haematologic parameters. Median serum "MCCP" levels were 134 μ g/kg ww (15 200 μ g/kg lw). The study also reported C₁₄-CPs as the most abundant "MCCP" groups. "MCCPs" were inversely associated with haemoglobin (HGB) and haematocrit (HCT) and positively associated with HGB in males, while significant negative associations of blood "MCCP" concentrations with mean corpuscular haemoglobin concentration (MCHC) were observed in females.
- 203. The target organs for repeated oral dose toxicity are liver, thyroid and kidney. EFSA (2020) identified changes in kidney weights as the critical effect of "MCCPs" of relevance to humans. Eight relevant repeated dose

toxicity studies were reviewed in HSE (2008). The assessment determined the lowest No Observed Adverse Effects Level (NOAEL) of toxicological significance to be 23 mg/kg bw/day from a 90-d study with F344 rats *Rattus norvegicus* (CXR Biosciences Ltd, 2005b), based on increased relative kidney weights (HSE, 2008). A second 90-day study also using F344 rats recorded a NOAEL of 10 mg/kg bw/day for the same endpoint (IRDC, 1984). EFSA (2020) has derived a BMDL $_{10}^{24}$ of 36 mg/kg bw/day from this second study the BMDU $_{25}$ /BMDL ratio of 6 indicates some uncertainty in the value). The BMDL $_{10}$ for CXR Biosciences Ltd (2005b) was 68 mg/kg bw/day (BMDU/BMDL ratio 2.7).

- 204. Liu *et al.*, (2020) evaluated associations between SCCP and "MCCP" serum concentrations and six liver enzyme biomarkers in 197 people living in Jinan, China. The study found an association between "MCCP" serum concentrations and liver enzyme biomarkers.
- 205. No carcinogenicity studies have been conducted, therefore there is no IARC classification for carcinogenity. "MCCPs" is not known to be mutagenic. The carcinogenic potential of "MCCPs" is expected to be similar at least in qualitative terms to that of SCCPs, although direct read across is not appropriate. SCCPs induce liver and thyroid adenomas and carcinomas and kidney tubular cell adenomas and carcinomas in animal studies. The liver and thyroid tumours are considered to be of little or no relevance to human health (further information is provided in document UNEP/POPS/POPRC.18/INF/10). It cannot be completely ruled out that the kidney toxicity observed for "MCCPs" might lead to kidney cancer in rats through a non-genotoxic mode of action. However, "MCCPs" is not classified for this endpoint in the EU under Regulation (EC) No. 1272/2008.
- 206. "MCCPs" has no apparent effect upon fertility in rats up to approximately 400 mg/kg/day in the diet. No adverse developmental effects occurred during gestation in rats or rabbits in two conventional developmental studies using maternal doses up to 5,000 and 100 mg/kg/day, respectively. In contrast, exposure of Wistar rats R. norvegicus to a C₁₄₋₁₇ CP, 52% Cl wt. substance at a maternal dietary dose of 74 mg/kg/day (1,000 ppm) up to approximately 400 mg/kg/day (6,250 ppm) produced internal haemorrhaging and deaths in the pups (IRDC, 1985). Follow-up studies with Sprague Dawley rats (CXR Biosciences Ltd, 2003, 2004 & 2006) demonstrated that "MCCPs" can perturb blood clotting. In adult females that had been treated for 7 to 8 weeks including pregnancy and lactation, decreased levels of vitamin K and of the clotting factors VII and X were found, and 5 out of 32 dams showed signs of haemorrhaging during parturition. However, these decreases did not affect their prothrombin times, indicating that the functional reserve in the majority of these adult animals was sufficient. The foetus in utero apparently receives sufficient vitamin K via the placenta, but after birth becomes severely deficient in vitamin K and related clotting factors and relies on the mothers' milk to receive them. Exposure to "MCCPs" in the milk may also further reduce their vitamin K levels. This in turn leads to a severe vitamin K deficiency in the neonates and consequently to haemorrhaging. This is the basis for the harmonised EU classification for effects via lactation (H362 – May cause harm to breast-fed children) according to Regulation (EC) No. 1272/2008.
- 207. From the studies available, an overall NOAEL of 47 mg/kg/day (600 ppm) as a maternal dose was identified for these effects mediated via lactation (EC, 2005). However, it should be noted that the effects (11% reduction in pup survival and related haemorrhaging) observed at the LOAEL (74 mg/kg/day; 1 000 ppm) were not statistically significant. Haemorrhaging was also seen in one study at the time of parturition in 16% of dams given 538 mg/kg/day (6,250 ppm), but not up to 100 mg/kg/day (1 200 ppm) in other studies. The NOAEL of 100 mg/kg/day (1,200 ppm) was therefore selected for the risk characterisation of haemorrhaging effects potentially occurring in pregnant women at the time of parturition. EFSA (2020) estimated the BMDL₅ values of 48.5 mg/kg bw/day (BMDU/BMDL ratio of 1.3) for the combined incidence of subcutaneous haematoma/haemorrhage in rats and 53 mg/kg bw/day (BMDU/BMDL ratio of 1.8) for rat pup deaths (EFSA, 2020).
- 208. The potential association of perturbation of kidney function with "MCCPs" exposure was investigated in a cross-sectional study (Zhao *et al.*, 2021). Information on educational attainment, smoking and drinking habits and history of kidney disease of the volunteers (n=387) was obtained by employing a standardised questionnaire. BMI (body mass index), blood glucose and blood pressure of volunteers were also recorded. After adjustment for multiple variables, in males only, elevated "MCCPs" levels (above median) were associated with an elevated odds ratio (OR) for glomerular hyperfiltration (estimated Glomerular Filtration Rate, eGFR) of \geq 135 mL/min/1.73 m²) ("MCCPs": OR = 3.25; 95% Confidence Interval (CI): 1.20–5.29; p=0.009). It is possible that the elevated eGFR could reflect glomerular damage, indicative of early impaired kidney function. However, the study only noted an association between "MCCPs" and elevated eGFR in males, and it is not possible to infer causation from this study.
- 209. "MCCPs" is not classified with respect to carcinogenicity (category 1A or 1B) (no data available). The substance is not classified for germ cell mutagenicity (category 1A or 1B), or toxicity for reproduction (category 1A, 1B, or 2) in Europe according to Regulation (EC) No. 1272/2008. It is not considered to be classified for specific target organ toxicity after repeated exposure (STOT RE category 1 or 2).

²⁴ Benchmark Dose Level associated with a 10% response adjusted for background.

²⁵ Benchmark dose upper confidence limit.

2.4.3 Adverse effects synthesis

- 210. Ecotoxicity data for "MCCPs" are available covering aquatic, benthic and terrestrial organisms. These indicate that the substance causes adverse effects in aquatic and benthic invertebrates. Terrestrial organisms, fish and algae were less sensitive to "MCCPs", although the fish data are limited. Short-term avian data do not indicate significant effects, but long-term data are not available. From the available information, the most sensitive organism was *D. magna* as the 48-h EC₅₀ for a C₁₄₋₁₇ chlorinated n-alkane, 52% Cl wt. was 0.0059 mg/L and the 21-day NOEC for the same species and substance was 0.0087 mg/L. Effects at higher concentrations were also seen in *H. azteca* and *L. variegatus* (28-d NOEC mortality and reproduction of around 50 mg/kg sediment ww). The *D. magna* results indicate that CPs with C₁₄₋₁₇ chain lengths are very toxic to aquatic invertebrates in the environment. Furthermore, in the EU REACH registration and CLP inventory, these data are used by the companies involved to cover all "MCCPs" products supplied in the EU (the chlorine content of the commercially available product types is generally within the range 40% to 63% by weight). This indicates that all of the products were assessed to be equally toxic. "MCCPs" has a harmonised EU environmental hazard classification of Aquatic Acute 1, Aquatic Chronic 1 (H400, H410) which are the most stringent classifications for acute and chronic environmental hazard under the United Nations Globally Harmonised System. The significant level of toxicity observed has also resulted in the substance being concluded to meet the "T" criterion for PBT evaluation within the EU.
- 211. The concern for adverse effects is supported by the internal haemorrhaging and death observed in rodent offspring in a mammalian reproduction study (EFSA, 2020) resulting in a harmonised EU classification for "MCCPs" as H362 (May cause harm to breast-fed children). Potential adverse effects could therefore occur in mammalian wildlife.

3. Synthesis of information

- 212. "MCCPs" is a widely used industrial chemical which is estimated to be supplied in the order of 800 000 tonnes per year globally. It has a broad range of uses, primarily as a flame retardant and secondary plasticiser in polymers such as PVC, and in metal working fluids. The C_{14} constituents are a major congener group in commercial "MCCP" products currently being supplied in Europe and the US, with the C_{15-17} constituents present in lower proportions. Chain lengths in CP products manufactured in China are broader, and the proportion of "MCCP" components appears to be more variable, although in a number of instances C_{14} is suggested to be the dominant constituent. CPs with C_{14-17} chain lengths are hydrophobic with a low water solubility (up to 27 μ g/L) and high log K_{OW} values above 5.
- 213. CPs with C_{14-17} chain lengths (at or exceeding 45% chlorine by weight) meet the persistence criteria of the Convention. The C_{14} (50% Cl wt.) chain length is considered to have a half-life exceeding 180 days in two types of aerobic sediment based on a laboratory test. Assessment of the persistence screening data indicates that "MCCP" constituents with chlorination levels at or exceeding 45% chlorine by weight would also be expected to be persistent in sediment. Persistence in sediment is supported by sediment core monitoring data, where "MCCPs" can be detected at similar orders of magnitude across horizons spanning the last 8 years (and longer) in the same core. The persistence conclusion for the C_{14} chain length can be applied to the C_{15-17} chain lengths because they will be more adsorptive based on the measured and predicted trends for water solubility and log K_{OW} . This is supported by the detection of these chain lengths in sediment, and notably, where data are available, the congener profile detected reflects that in commercial substances (i.e., there appears to be no preferential degradation of one chain length compared to the others).
- CPs with C_{14-17} chain lengths meet the bioaccumulation criteria of the Convention. All constituents have log K_{OW} values exceeding 5. The values tested for C_{15-17} chlorinated paraffins with chlorination >45% are considered to be reliable with restrictions and this does not prevent a conclusion being drawn from the tests. Two recent laboratory fish bioaccumulation studies using C₁₄ chain lengths show measured or estimated BCF values well above 5,000 L/kg. The available fish bioaccumulation laboratory studies for the C₁₅, C₁₆ and C₁₈ chain lengths were not performed to current test guidelines nor to such a high standard as the modern tests for the C₁₄ substance. Nevertheless, they indicate a high bioaccumulation potential for all three chain lengths (although C₁₇ was not tested, its bioaccumulation potential can be inferred to lie between that of C_{16} and C_{18}). A non-guideline invertebrate bioaccumulation study using a C_{14-17} 45% Cl wt. substance measured a BCF value well in excess of 5,000 L/kg for Daphnia magna. Field monitoring studies indicate that all chain lengths are bioavailable and can be detected in biota, including in top predators as well as in sensitive life stages (such as birds' eggs). Where data are available, the congener profile in organisms is similar to the congener profile in environmental matrices such as soil and sediment, and wastewater treatment plant sludge, suggesting congener uptake reflects exposure. Overall, the bioaccumulation behaviour of the longer chain lengths appears to be broadly similar to C₁₄. A number of field biomagnification studies are available, where BMFs or TMFs both above and below 1 were calculated. Each field study has limitations, but the data indicate that the possibility of biomagnification of "MCCPs" cannot be excluded.
- 215. CPs with C_{14-17} chain lengths are shown to meet the long-range environmental transport potential criteria of the Convention. The predicted atmospheric half-life values are between 37 and 140 hours, principally dependent on

the degree of chlorination: more highly chlorinated constituents will be more photolytically stable and more adsorptive to particulates. There are uncertainties regarding both the model training set, and the effect of the fraction adsorbed to aerosols (which is reliant on the predicted log K_{OA}). Modelling using the OECD Screening tool indicates LRET comparable to, but slightly below, that for SCCPs, which is a listed POP. The "MCCPs" LRET also falls within the range of other listed POPs. The modelling is also affected by the fraction adsorbed to aerosols, which could be higher than the OECD tool predicts, and would result in greater LRET potential. Monitoring data support the modelling conclusion. Detection of "MCCPs" in air (gaseous and particulate) and water (dissolved and particulate) suggests a number of pathways exist to deliver "MCCPs" to remote locations. While "MCCPs" are rarely included in monitoring campaigns in remote regions, they have been detected in the Arctic (air, sediment, and biota including predators), Antarctic (air) and Tibetan Plateau (air and biota). In some instances, the monitoring data indicate levels of "MCCPs" comparable to or exceeding levels of SCCPs and some other listed POPs in remote regions.

- 216. CPs with C_{14-17} chain lengths are shown to meet the adverse effects criteria of the Convention. A C_{14-17} chlorinated n-alkane, 52% Cl wt. is very toxic to *D. magna* in both acute and long-term studies. This indicates significant toxicity to aquatic invertebrates which are an important part of aquatic food chains. Effects on organisms at this trophic level may reduce food availability at higher levels of the food chain with potential population-level effects. Regulatory testing is designed to protect all organisms living in the environment, and is limited in scope for practical and ethical reasons. Therefore, high toxicity observed in one organism within a trophic level means that it cannot be excluded that others are equally or more affected (this is a general principal of regulatory ecotoxicology). For chemicals that are also shown to be persistent and bioaccumulative, the concern is also for unpredictable effects within the food chain. Internal haemorrhaging and death have been observed in rodent offspring in a mammalian reproduction study (EFSA, 2020). This observation suggests that potential adverse effects could occur in wild mammals exposed to "MCCPs" via their diet. As the (eco)toxicity tests used a substance containing C_{14-17} chain lengths, all chain lengths are considered to contribute to the observed effects. The tests are also used to support regulatory submissions by suppliers covering all "MCCPs" products on the market (not just 52% Cl wt.) indicating the applicability of the studies to a broad range of chlorination levels.
- 217. The available monitoring data generally show widespread occurrence of "MCCPs" in surface water, sediment, soil, biota, sludge and air, in multiple regions of the world, including remote regions. The substance can be widely detected in wildlife including predators, as well as human tissues. In some instances, tissue concentrations up to 23 mg/kg lw have been detected. Increasing detections in local biota have been observed where trend information is available. "MCCPs" has also been detected in a range of market foods, household dust, household products and appliances, playing fields and other sources that may represent important human exposure pathways.
- 218. The most recent wildlife monitoring studies (section 2.3.4 and UNEP/POPS/POPRC.18/INF/10) usually provide chain length and congener level information, which indicates the bioavailability of all chain lengths. Where data are available, "MCCPs" chain length / congener profiles detected in biota are consistent with those detected in environmental matrices and wastewater treatment plant sludge.
- 219. Following national and international restrictions on the use of SCCPs, the supply of "MCCPs" has increased significantly as the main drop-in replacement. The increase in supply (with consequent environmental emission) is reflected in environmental monitoring trends: increasing levels of "MCCPs" are detected where multi-year sampling has been undertaken. Sediment core data also indicate a decline in SCCPs with a concurrent increase in "MCCPs" in layers representing more recent years. As the switch from SCCPs to "MCCPs" has only occurred in recent years, "MCCPs" detection can be expected to increase in the absence of risk management.
- 220. The concentrations detected in wildlife in more contaminated areas show that high levels can be attained in organisms. If environmental exposure of "MCCPs" is increasing in more remote areas as suggested by the limited trend data available, increasing levels in the wildlife of those regions can be expected.
- 221. The concern for "MCCPs" is its demonstrated persistence, bioaccumulation and toxicity, together with a similar long-range environmental transport potential to SCCPs. The underlying concern is that "MCCPs" poses similar types of risk to SCCPs. While the two substances are not identical, they are sufficiently similar to warrant action to address the potential risk from "MCCPs". The very high levels of estimated emissions to the environment are reflected in widespread detection, together with indications that these levels are increasing, including in remote areas. Given the bioavailability and increasing trend in the detection of a known persistent, bioaccumulative and toxic substance, it can be expected that levels in remote environments will continue to increase, and levels in biota will also continue to increase with consequent risk of unpredictable impacts unless risk management measures are implemented.
- 222. As a result of its persistence, bioaccumulative and toxic properties, "MCCPs" is concluded to be of high concern by regulators in Australia, Canada, the EU, Switzerland and UK.

4. Concluding statement

- 223. Chlorinated paraffins with carbon chain lengths in the range $C_{14\text{--}17}$ and levels at or exceeding 45 per cent chlorine by weight are considered to fulfil the criteria for persistence, bioaccumulation, long-range environmental transport and adverse effects under the Convention. The different applications and ongoing use of CPs with $C_{14\text{--}17}$ chain lengths and levels at or exceeding 45 per cent chlorine by weight globally is conservatively estimated to result in the potential environmental release of around 2 400 to 24 000 tonnes each year. Due to the hazardous properties of "MCCPs", and the annual estimated level of environmental emissions, together with evidence of long-range transport potential, extensive environmental contamination and an indication that levels in the environment are increasing and spreading, global action is required to manage the risks to human health and the environment from chlorinated paraffins with carbon chain lengths in the range $C_{14\text{--}17}$ and chlorination levels \geq 45% chlorine by weight.
- 224. Based on evidence of its persistence, bioaccumulation and adverse effects, widespread occurrence in environmental compartments and frequent detection in biota in remote regions, it is concluded that chlorinated paraffins with carbon chain lengths in the range C_{14-17} and levels at or exceeding 45 per cent chlorine by weight are likely, as a result of long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted.

Abbreviations

AOPWIN Atmospheric Oxidation Program

APCI-QToF-HRMS Atmospheric-Pressure Chemical Ionization Quantitative Time of Flight High Resolution

Mass Spectrometry

BAF Bioaccumulation Factor
BCF Bioconcentration Factor

BCFSS Steady State BCF

BMDL Benchmark dose (lower confidence limit)
BMDU Benchmark dose (upper confidence limit)

BMF Biomagnification Factor

BMFKgL Growth-corrected and lipid-normalised kinetic biomagnification factor

BSAF Biota-sediment accumulation factor

bw Bodyweight

Ca. Circa ("approximately")

CAS number Chemical Abstracts Service number

Cl wt. Chlorine content by weight

CLP Classification, Labelling and Packaging

CPs Chlorinated paraffins

CTD Characteristic Travel Distance

CXx Carbon chain with x Carbon atoms

dw Dry weight

EC50 Half maximal effective concentration

EC number European Community Number

EC (reg) European Union council (regulation)

ECHA European Chemicals Agency
EFSA European Food Safety Authority

EU European Union

GC-ECNI-LRMS Gas Chromatography Electron Capture Negative Ionisation Low Resolution Mass

Spectrometry

GCxGC-ECD Two Dimensional Gas Chromatography with Electron Capture Detector

GHS Globally Harmonised System
GLP Good Laboratory Practise

HCB Hexachlorobenzene

HPLC High Performance Liquid Chromatography

HRMS High Resolution Mass Spectrometry

HSE Health & Safety Executive

KAW Air-water partition coefficient

KOC Organic carbon-water partition coefficient

KOW Octanol-water partition coefficient

KOA Octanol/air partition coefficient

LCCP(s) Long-chain chlorinated paraffin(s)

LOD Limit of Detection

LOQ Limit of Quantification

LRET Long-Range Environmental Transport

LRTP Long-Range Transport Potential

lw Lipid weight

MCCP(s) Medium-chain chlorinated paraffin(s)

M-factors Multiplication Factors
MDL Method Detection Limit

NICNAS National Industrial Chemicals Notification and Assessment Scheme

NOAEL No Observed Adverse Effect Level
NOEC No Observed Effect Concentration

OECD Organisation for Economic Co-operation and Development

PBDEs Polybromodiphenyl ethers

PBPK Physiologically-based pharmacokinetic modelling

POV Overall persistence

PBT Persistent, Bioaccumulative and Toxic

PCB Polychlorinated biphenyls
POP Persistent Organic Pollutant

PVC Polyvinyl Chloride

REACH Registration, Evaluation and Authorisation of Chemicals

RMOA Regulatory Management Option Analysis

RP-HPTLC Reversed-phase high performance thin layer chromatography

RSD Relative Standard Deviation

SCCP(s) Short-chain chlorinated paraffin(s)

SMILES Simplified Molecular Input Line Entry System

SVHC Substance of very high concern

TE Transfer Efficiency
TG Test Guideline

ThOD Theoretical Oxygen Demand
TMF Trophic Magnification Factor

TOC total organic carbon
UN United Nations

UNEP United Nations Environment Programme

USEPA United States Environmental Protection Agency
UVCB Unknown Variable Concentration or Biological

WHO World Health Organisation

ww Wet weight

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