Evaluating the Environmental Fate of Short-Chain Chlorinated Paraffins (SCCPs) in the Nordic Environment Using a Dynamic Multimedia Model

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Environmental Impact

Short-chain chlorinated paraffins (SCCPs) are under review for inclusion in the Stockholm Convention for Persistent Organic Pollutants (POPs). However, major uncertainties remain with regard to their environmental fate due to the complexity of the mixture and analytical challenges. In this study, we show that the link between environmental emissions and exposure of SCCPs can be evaluated by comparing simulation results from a dynamic environmental fate and bioaccumulation multimedia model (CoZMoMAN) with existing measurement data. CoZMoMAN was successfully applied to predict SCCPs concentrations in various media in good accordance with the measurements, which increases the confidence in the applied model and facilitates an assessment of key knowledge gaps in the overall understanding of the environmental fate of SCCPs.
Abstract

Short chain chlorinated paraffins (SCCPs) raise concerns due to their potential for persistence, bioaccumulation, long-range transport and adverse effects. An understanding of their environmental fate remains limited, partly due to the complexity of the mixture. The purpose of this study was to evaluate whether a mechanistic, integrated, dynamic environmental fate and bioaccumulation multimedia model (CoZMoMAN) can reconcile what is known about environmental emissions and human exposure of SCCPs in the Nordic environment. Realistic SCCP emission scenarios, resolved by formula group, were estimated and used to predict composition and concentrations of SCCPs in the environment and the human food chain. Emissions at the upper end of the estimated range resulted in predicted total concentrations that were often within a factor of 6 of observations. Similar model performance for a complex group of organic contaminants as for the well-known polychlorinated biphenyls strengthens the confidence in the CoZMoMAN model and implies a relatively good mechanistic understanding of the environmental fate of SCCPs. However, the degree of chlorination predicted for SCCPs in sediments, fish, and humans was higher than observed and poorly established environmental half-lives and biotransformation rate constants contributed to the uncertainties in the predicted composition and ΣSCCPs concentrations. Improving prediction of SCCPs composition will also require better constrained estimates of the composition of SCCP emissions. There is, however, also large uncertainty and lack of coherence in the existing observations, and better model-measurement agreement will require improved analytical methods and more strategic sampling. More measurements of SCCPs levels and composition in samples from background regions are particularly important.
1. Introduction

Short-chain chlorinated paraffins (SCCPs), also known as short-chain polychlorinated alkanes (SPCAs), are alkanes of 10-13 carbon atoms with a chlorination degree of normally 30-70 % (w/w). Produced by free-radical chlorination of n-alkane feedstocks, SCCPs are mainly straight-chain molecules.\(^1\) Multiple chlorine substitution on the same carbon atom is not very likely, and degrees of chlorination exceeding 70 % on a mass basis are difficult to achieve.\(^1\) Nevertheless, the technical mixtures contain a wide range of different formula groups (C\(_{x}H_{2x+2-n}Cl_{n}, 10 \leq x \leq 13, 1 \leq n \leq x\) and positional isomers (Table S1). Produced since the 1930s, SCCPs have mainly found use as cutting fluids in the metal-working industry, and as lubricants, plasticizers, flame-retardants, and additives in paints, sealants, and rubbers in other industries and commercial uses and consumer products.\(^2,3\) While production has declined significantly in western countries since the 1990s, an exponential increase in production volume has made China the largest producer.\(^3,4\) Several reviews have documented the ubiquitous occurrence of SCCPs in the environment.\(^5-10\) Concern about their environmental behavior has prompted a review of SCCPs as potential Persistent Organic Pollutants (POPs) under the Stockholm Convention.\(^11\)

Owing to their complexity, technical SCCPs mixtures are challenging to both model and monitor. Gas chromatography (GC) in combination with mass spectrometry (MS) can separate the formula groups, but not the individual isomers,\(^1\) and concentrations in environmental samples are commonly reported for the bulk mixture (\(\Sigma\)SCCPs). Physical-chemical properties and degradation rates, and hence also environmental behavior, vary considerably among the SCCPs.\(^6-12,13\) The European Union (EU) risk assessment reports (RARs)\(^2,3\) and most modeling studies,\(^8,14-19\) with the exception of a more detailed evaluation by Muir,\(^5\) used a single set of properties to represent the whole group. Recently, SCCPs served as an example in a study on how to assess complex halogenated chemical mixtures with a high number of constituents.\(^20\) Properties (partition coefficients (Ks) and environmental half-lives (HLs) and biotransformation rate constants (k\(_{M}\)s)) of all SCCP isomers with a chlorination degree
of 30–70 % (n = 7750) were predicted with quantitative structure property relationships (QSPRs) and used to display them on chemical partitioning space maps that represent different aspects of environmental behavior, including bioaccumulation and long range transport potential. SCCPs with 12 – 13 carbon atoms and a moderate degree of chlorination were identified as having the highest bioaccumulation potential in humans living in the Arctic. An easy method to simultaneously evaluate all constituents within a complex mixture, the chemical partitioning space approach also demonstrated that randomly selecting one or a few compounds to represent an entire mixture is inadequate if environmental fate differs greatly between constituents, as is the case for SCCPs.

A higher tier evaluation of the environmental risk of SCCPs should include considerations about quantities and modes of emission to the environment to predict realistic exposures, both to the mixture as a whole as well as to individual constituents. Outside the scope of the study by Gawor and Wania, consideration of specific environments in combination with emission information would allow for comparisons to be made with measured environmental levels in order to evaluate the results of model assessments and hence the underlying understanding of the environmental behavior of SCCPs. Also, while Gawor and Wania qualitatively discussed the uncertainties involved in their approach, they did not perform a quantitative uncertainty analysis to identify the most critical parameters.

The purpose of this study was to investigate the environmental fate of SCCPs in a specific region using realistic emission estimates and a dynamic and mechanistic integrated environmental fate and bioaccumulation multimedia model (CoZMoMAN). The western part of the Baltic Sea drainage basin (including Sweden and parts of Norway, Denmark, and Finland) was selected as a case study region, because (i) CoZMoMAN has already been parameterized and evaluated for polychlorinated biphenyls (PCBs) in this region, (ii) the development of realistic emission scenarios for this region is facilitated by the reported use of SCCPs within the Nordic countries, and (iii) the availability of measured environmental levels of SCCPs in the Nordic region allows for a comparison with
predictions and thus an evaluation of the model’s performance. The merits and limitations of using a single property estimate for the whole group of SCCPs, and the variation in environmental fate within the group were also further explored. Sensitivity and uncertainty analyses were carried out to evaluate how the uncertainties of the input parameters affected the results. Our aim is that the model and observations in concert can identify the more critical knowledge gaps with regard to the overall environmental fate of SCCPs.

2. Methods

2.1 General Description of the Model
The mechanistic and dynamic multimedia model CoZMoMAN\textsuperscript{21} applied in this study links the environmental fate model CoZMo-POP 2\textsuperscript{23} and the bioaccumulation model ACC-HUMAN.\textsuperscript{24} The model has been parameterized for the western Baltic Sea and its drainage basin, and was found to predict concentrations of PCBs in key compartments within a factor of 2-4 of observed levels.\textsuperscript{21} The version of the model applied in this study consists of 12 physical compartments: One atmospheric compartment, two water compartments (fresh water and sea water), four sediment compartments (accumulating and transporting sediment in fresh water and sea water), three soil compartments (agricultural, uncultivated, and forest soil), and two forest canopy compartments (deciduous and coniferous canopy). In addition it contains a marine food chain (zooplankton, herring, cod), an agricultural food chain (grass, cow milk, beef), and humans (male and female) who feed from both food chains and breathe outdoor air and drink water from this environment.

2.2 Properties of SCCPs
Theoretically, SCCPs comprise 46 formula groups and 7820 isomers, when the possibility for branched chains and dichlorinated carbon atoms is excluded (Table S1).\textsuperscript{1,25} Some experimental data exist for the properties of SCCPs with specific degrees of chlorination or selected formula groups, including the octanol-water partition coefficient ($K_{OW}$),\textsuperscript{12,26} the air-water partition coefficient ($K_{AW}$),\textsuperscript{27,28} and the $k_{MS}$ in fish.\textsuperscript{13} For consistency and comparability, this study adopted the log $K_s$, atmospheric rate constants ($k_{RA}$), and $k_{MS}$ in fish selected for 7750 SCCP isomers by Gawor and
These isomers belong to 37 formula groups and include all SCCPs with 30 – 70 % chlorination (w/w) (Figure 1, Table S1). Here, we performed model simulations for these 37 formula groups (SCCP$_{37}$), each represented by the mean value of the properties of all isomers within that group. In addition an average SCCP (SCCP$_{\text{average}}$) was included that represents either the mean (molecular weight, log $K$s, and $k_{\text{RA}}$) or the geometric mean ($HL$s and $k_{\text{MS}}$) of all SCCP$_{37}$ properties (Table S2-S4). Calculations were also performed using the properties listed in the EU RARs (SCCP$_{\text{EU-RAR}}$),$^{2,3}$ complimented by the SCCP$_{\text{average}}$ properties ($k_{\text{MS}}$) and assumed values (enthalpies of phase change ($\Delta U$s), feces-blood partition coefficient ($K_{\text{FB}}$), and activation energies ($EA$s)) for properties that were not specified in the EU RARs.

### 2.2.1 Physical-Chemical Properties

Among multiple QSPR predictions, Gawor and Wania$^{20}$ selected those that corresponded best with the available experimental data. $K_{\text{OW}}$ and $K_{\text{AW}}$ had been estimated with ACD/Labs and ACD/Absolv,$^{29}$ respectively.$^{20}$ These values are in the lower range of available experimental$^{12,26}$ and predicted$^{30}$ values for SCCPs. The octanol-air partition coefficient ($K_{\text{OA}}$) had been calculated from the two other partition coefficients by using the pure phase $K_{\text{OW}}$ and a thermodynamic triangle (Table S2, Figure 1).$^{20}$ All three partition coefficients were used as input to the model. Enthalpies of phase change between octanol-water ($\Delta U_{\text{OW}}$), air-water ($\Delta U_{\text{AW}}$) and octanol-air ($\Delta U_{\text{OA}}$) were assigned default values of -20, 60, and -80 kJ mol$^{-1}$, respectively, as these are typical values for POPs$^{31,32}$ and no experimental or estimated values for SCCPs were available.

### 2.2.2 Environmental Half-Lives

AOPWIN$^{33}$ estimates of $k_{\text{RA}}$ for the formula groups were found to be in good agreement with the few experimental data for $\Sigma$SCCPs$^{2}$ (Table S3). Gawor and Wania$^{20}$ had only estimated environmental $HL$s for SCCPs in air, and not in water, soils, or sediments. A method that combines regressions based on four BIOWIN models$^{33-35}$ was used to estimate the $HL$s in water for the 7750 isomers for which SMILES (Simplified Molecular Input Line Entry Specification) codes were available.$^{20}$ The $HL$s in soil
and sediment were assumed to be two and nine times the HLs in water, \(^{34}\) respectively, and the HLs in canopy and grass equal to the HLs in soil (Tables S3 and S4). Different compartments of the same type (e.g. the three soil compartments) were assigned the same values. The EAs in air and in other compartments were assumed to be 10 and 30 kJ mol\(^{-1}\) respectively, as no experimental or estimated values were available.

2.2.3 Biotransformation Rate Constants
The \(k_M\)s had been estimated in BCFBAF for a fish of 10 grams at 15 °C.\(^{33}\) Gawor and Wania\(^{20}\) additionally used \(k_M\)s calculated through an iterative fragment selection (IFS) method.\(^{36}\) However, these were up to an order of magnitude higher than the available experimental values,\(^{13}\) in particular for high chlorinated isomers, and were hence not used in this study. The BCFBAF \(k_M\)s were adjusted to the aquatic and terrestrial species in CoZMoMAN (Table S4) according to the geometric mean of their bodyweight, using the following equation:\(^{37,38}\)

\[
k_{M,X} = k_{M,N} \left( \frac{W_X}{W_N} \right)^{0.25}
\]

Where \(W_X\) and \(W_N\) are the required (x grams) and normalized (10 grams) body weights, respectively, and \(k_{M,X}\) and \(k_{M,N}\) are the biotransformation rate constants (hour\(^{-1}\)) at the required and normalized body weights, respectively. The \(K_{fb}\) was assigned a default value of \(2 \cdot 10^{-8}\) for nonpolar organic molecules.\(^{24,39}\)

2.3 A Note on Analysis of SCCPs
The complexity of the SCCPs mixtures makes accurate quantification difficult and measured concentrations are relatively uncertain.\(^{40}\) Concentrations and formula group composition can vary with instrumentation,\(^{31-44}\) quantification procedure,\(^{7,45}\) and quantification standards.\(^{41,46,47}\) Electron capture negative ionization (ECNI) in low or high resolution MS, following GC separation, is most commonly applied. To increase consistency and comparability between model predictions and observations, data on concentration of SCCPs in environmental samples, and SCCP composition in technical mixtures and environmental samples, were only considered if they had been obtained with
ECNI-MS. This technique is not very sensitive for substances with few halogens and concentrations for SCCPs with less than 5 chlorines are rarely reported, although they are still present in technical mixtures and the environment.\textsuperscript{43,48} The implication is that these formula groups are being ignored. No restrictions were made on the used quantification procedures or quantification standards, as this would substantially reduce the number of measurements that could be included for comparison.

2.4 Emission Estimate

Realistic minimum ($E_{\text{MIN}}$), average ($E_{\text{AVG}}$), and maximum ($E_{\text{MAX}}$) national emissions of ΣSCCPs were estimated applying a previously described high-throughput screening method\textsuperscript{49} to data on SCCP usage in each of the Nordic countries (Sweden, Norway, Denmark, and Finland) for the years 2000 to 2007.\textsuperscript{22} Details are outlined in section 1.1 in the Electronic Supplementary Information (ESI).

Although in this method emission factors can depend on compound water solubility and vapor pressure, the estimated size and mode of entry (MOE) of the ΣSCCPs emissions was independent of the choice of formula group properties. We therefore assumed the formula group composition of the emissions to be identical to that of technical mixtures (ESI Section 1.1, Table S5). While this emission composition is highly uncertain, it is required to explore key knowledge gaps related to the environmental fate of SCCPs. The final national emissions were scaled to the model domain of CoZMoMAN based on the fraction of the population in each Nordic country that lives in side the domain.\textsuperscript{50} Emissions were allocated to different compartments based on the MOE estimated by the high-throughput screening method.\textsuperscript{49} Half of the emissions to water were allocated to fresh and sea water, respectively, while emissions to soil were released entirely to agricultural soil. It was assumed that the model domain is surrounded by equally contaminated regions, and hence, that any inflows of SCCPs by air and water from outside regions are the same as the outflows. However, this is a recognized limitation of the current model strategy, as a similar model for the Baltic Sea area has been shown to be sensitive to the model boundary conditions.\textsuperscript{51,52}

SCCPs have been produced since the 1930s,\textsuperscript{6} and in Europe, including the Nordic countries, production and usage volumes declined in the 1990s,\textsuperscript{2,3} corresponding to a potential emission period
of 60-70 years. Because little information on the temporal variability of production, usage and emissions is available, all simulations were run with constant emissions for 70 years at the levels estimated based on usage from 2000 to 2007, followed by 30 years without emissions to simulate a hypothetical complete emission stop. After 70 years of constant emissions the lower chlorinated formula groups are expected to have approached a steady-state, while concentrations of the higher chlorinated formula groups are expected to still be increasing, especially in soils and sediments. For all modeled compartments the predicted average annual concentrations after 70 years of constant emissions were used for comparison with measured levels. This includes predicted levels in a 29 year old woman, who was born 41 years after the emissions started.

2.5 Model Simulations
Simulations were run for SCCP$_{37}$, SCCP$_{\text{average}}$, and SCCP$_{\text{EU-RAR}}$ using $E_{\text{AVG}}$ for all compounds. Subsequently, as the model is linear for increases in the emissions given constant MOE, the predicted concentrations were multiplied with factors corresponding to the other emission scenarios ($E_{\text{MIN}}$ and $E_{\text{MAX}}$). Additionally, estimated concentrations for the 37 formula groups (SCCP$_{37}$) were multiplied with factors corresponding to the formula group composition of the emission estimate (Table S5), and these concentrations were summarized to calculate the concentration of ΣSCCPs. The simulation time step was 1 hour, and results were stored every 120 hours.

2.6 Monitoring Data Selected for Model Evaluation
To evaluate the model performance, concentrations of ΣSCCPs in the physical environment and biota were collected from the peer-reviewed literature and government reports and databases. To the extent possible, monitoring data for ΣSCCPs in background regions in the Nordic environment for the period 2000-2007 were chosen for comparison. Because the model compartments are well-mixed with uniform concentrations within the model domain, predictions cannot be expected to compare well with elevated levels in areas close to point sources. Median rather than average measured concentrations were used to avoid bias towards highly contaminated hotspots. As reported formula
group profiles of environmental samples are limited, measured formula group profiles from other regions of Europe were also included for comparison.

2.6.1 Physical Compartments

The predicted ΣSCCPs concentrations in air were compared to monthly averages for bulk air (sum gaseous and particulate phases) reported for the Swedish background sites Råå [57°24'N, 11°55'E] and Aspvreten [58°48'N, 17°23'E] for the years 2003 and 2009-2011. The calculated ΣSCCPs concentrations in soil were compared to data for Norwegian background soils sampled in 2008. As most samples (23 out of 32) were below the method detection limit (MDL; 0.8 ng/g dw), these samples were represented by MDL/2 to reduce bias towards the samples above MDL. Predicted concentrations for marine and freshwater sediments (accumulating, not transporting) were compared to measured concentrations in marine and freshwater sediments in populated areas of Norway in 2003. All predicted concentrations in soil and sediment were normalized to particulate organic carbon (POC), and the measured concentrations to soil organic matter (SOM) or total organic carbon (TOC), respectively. In addition, measured concentrations in sediments collected from the Baltic and North Seas in 2003-2004 and the Barents Sea in 2006-2007 in ng/g dry weight were compared to predicted concentrations in marine sediments in ng/g particles.

Measured formula group profiles of SCCPs in air were available for a semi-rural location in England in spring of 1997, from a remote location in the European Arctic in spring of 1999, and for indoor air in Stockholm during the winter of 2006-2007. Formula group composition also existed for marine sediments sampled in the Baltic Sea in 2004. For freshwater sediments, data were available from surface sediments from ponds and rivers in rural and industrial areas of the Czech Republic in 2001-2002, and dated sediment cores from Lake Thun in Switzerland.

2.6.2 Biotic Compartments

All modeled and measured concentrations for biota were normalized to lipid weight. Predicted concentrations for cow milk were compared to results for two butter samples from Denmark and
Ireland reported in 2002. Calculated concentrations in 5-year old cod were compared to measured levels in the livers of cod from the Baltic Sea in 2002. Predicted concentrations for a 29 year old woman were compared to monitoring data for pooled breast milk samples from primipara women in Uppsala County in Sweden from 1996 to 2010.

Measured formula group composition was available for the livers of cod, flounder and North Sea dab sampled in the North and Baltic Seas in 2002, and the livers of cod sampled outside of Iceland and Northern Norway in 2003-2004. Information on formula group composition also existed for human breast milk sampled in 2001-2002 from women living in urban and semi-rural areas of England.

2.7 Sensitivity and Uncertainty Analysis

Model sensitivity can be defined as the relative effect of an input value to the output value, while uncertainty can be defined as the variation in the output value resulting from both the uncertainty in the input parameters in addition to the sensitivity of the output value to the input values. A sensitivity analysis was performed for all SCCP formula groups to identify which compound properties influenced CoZMoMAN output the most. Each property (physical-chemical properties, environmental HIs, and kMs) was varied individually by plus and minus ten percent, respectively. Sensitivity (S) was then calculated as

\[ S = \frac{\Delta O}{O} \times \frac{1}{\Delta I} \]  

where \( \Delta I \) and \( \Delta O \) are the relative changes in the input (I) and output (O) parameters of interest, respectively. The average sensitivity of increasing and decreasing the input parameter was calculated.

An analytical approach for evaluating uncertainty was applied. In this method all input parameters were assigned a confidence factor (Cf) which describes the degree of uncertainty in the parameter. The compound properties were assigned Cs according to the default values recommended by MacLeod et al. for data poor situations, and expert judgment was used for
parameters not included in MacLeod et al. A higher $Cf$ for the log $Ks$ ($Cf = 1.5$) than recommended by MacLeod et al. ($Cf = 1.1$) was chosen as there is considerable uncertainty in the log $Ks$ of SCCPs.

The $\Delta U$s were also assigned $Cfs$ of 1.5. The $EAs$, $K_{FB}$, and $k_{RA}$ were assigned $Cfs$ of 2, and the remaining $HL$s and $k_{RS}$ were assigned $Cfs$ of 3. Based on the assumed $Cfs$ and the calculated sensitivities, the contribution to variance (CV) of each input parameter $I_j$ to each output parameter $O_i$ for formula group X was calculated as

$$CV_{O_i,j, X} = \frac{(\ln Cf_{I_j})^2 s^2_{I_j}}{\sum_{j=1}^{n}(\ln Cf_{I_j})^2 s^2_{I_j}}$$

[3]

The predicted formula group composition in each compartment was subsequently used to weight the various CVs by the importance of a formula group to the contamination of a compartment:

$$CV_{O_i,j} = \sum_X \frac{C_X}{C_{\Sigma SCCPs}} CV_{O_i,j, X}$$

[4]

where $C_X$ and $C_{\Sigma SCCPs}$ are the predicted concentrations of formula group X and of $\Sigma SCCPs$, respectively, in the given compartment. This method rests on the assumptions that the model is linear or near-linear, that the uncertainty in the input parameters is uncorrelated, and that all input parameters are log-normally distributed. To evaluate the assumption of linearity in the model, a Monte Carlo uncertainty analysis was performed for SCCP_{average} (see ESI section 1.2 and Figure S1). Also, to illustrate the relative importance of uncertainty in the emissions relative to uncertainty in the properties of SCCPs an additional uncertainty analysis where the quantities of the emissions were included was also performed (Figure S12).

3. Results and Discussion

3.1 Merits and Limitations of Single vs. Multiple Sets of Properties

Even though the physical-chemical properties for SCCPs vary widely, risk assessments frequently rely on the properties for only a single or a few constituents when evaluating environmental fate. The fit between concentrations predicted for SCCP_{EU-RAR} and $\Sigma SCCPs$ based on the individual formula
groups was good, with $\text{SCCP}_{\text{EU-RAR}}$ concentrations on average $1.2 \pm 0.9$ times higher (range 0.3 to 3.5) than $\Sigma\text{SCCPs}$ concentrations (Figure 2). However, the predicted concentrations for $\text{SCCP}_{\text{average}}$ were only $0.5 \pm 0.3$ times (range 0.1 to 1.1) that of predicted concentrations for $\Sigma\text{SCCPs}$ (Figure S2). This is largely because $\text{SCCP}_{\text{average}}$ has lower predicted concentrations in soils and sediments than $\text{SCCP}_{\text{EU-RAR}}$, due to the long environmental $\text{HLs}$ in these compartments assumed by the EU RARs (Figure S3, Table S3). It should be noted that several of the other properties (the $k_M$s, $\Delta U$s, $K_{FB}$, and $E_A$s) are identical for $\text{SCCP}_{\text{EU-RAR}}$ and $\text{SCCP}_{\text{average}}$. This means that the results for these two SCCPs are not independent of each other, especially not for concentrations in fish and humans where the $k_M$s are the most influential properties (besides emissions) (Section 3.3). Nevertheless, these examples illustrate the difficulty of choosing a representative single set of properties for a complex group of contaminants like the SCCPs. Certainly, the representativeness of the selected properties will vary depending on the context. Variations in the composition of the emissions and the environmental conditions will influence the composition of SCCPs in the environment and thus whether or not the selected properties are representative for $\Sigma\text{SCCPs}$ or not. While it may sometimes be possible to obtain results with a single set of properties that closely resemble those obtained with more sophisticated approaches, caution needs to be applied when this approach is selected.

In addition, using a single set of properties for the SCCPs does not reveal anything about the diversity in environmental fate within the group, and which SCCPs that pose the greatest hazard. The predicted environmental distribution varied considerably between formula groups (Figure S4), which is reflected in the different SCCP composition in different environmental compartments (Section 3.2.3). The various SCCPs also undergo different environmental processes. Gawor and Wania$^{20}$ identified a threshold whereby SCCPs with fewer than 8 chlorine atoms will be mainly present in the atmospheric gaseous phase and undergo dry gaseous deposition, while SCCPs with more than 8 chlorines will be mainly present in the particulate phase and undergo dry and wet particle deposition from the atmosphere.$^{20}$ This phase distribution was reproduced by the present study, where the same threshold of 8 chlorines was identified (Figure S5), although it is acknowledged that higher $K_{OA}$
values for SCCPs as predicted by Glüge et al. would result in a lowering of the threshold to SCCPs with a lower degree of chlorination. Similarly, the potential for long-range atmospheric transport (LRAT) was predicted to be mainly limited by atmospheric degradation in the gaseous phase and deposition to surface media for SCCPs with less and more than 8 chlorines, respectively (Figure S6). Also, estimated hazard criteria for persistence, LRAT, and bioaccumulation of SCCPs varied considerably when using properties of the different formula groups, and were comparable to results for PCBs for the SCCPs that displayed the highest potential for persistence, LRAT, or bioaccumulation (ESI section 1.3, Figure S7).

3.2 Comparison to Monitoring Data in the Nordic Environment

3.2.1 Emission Estimate

The $E_{\text{AVG}}$ estimate for $\Sigma$SCCPs in the Nordic countries was 2.08 tonnes/year (t/y), with $E_{\text{MIN}}$ and $E_{\text{MAX}}$ of 0.71 and 15.35 t/y, respectively. The predicted MOE was 87 % to water, 9 % to the atmosphere, and 4 % to soil. For comparison, previous emission estimates of SCCPs in the EU (EU-RAR), chlorinated paraffins (CPs) in Stockholm, and SCCPs in the individual UNECE (United Nations Economic Commission for Europe) countries were scaled to the model domain of this study based on the population of the respective areas. In addition, the emissions of CPs in Stockholm were adjusted to SCCPs by assuming that the SCCPs constituted 3 - 32 % of the CPs. The population-scaled emission estimate from the EU RAR spanned 1.6 – 7.3 t/y, the estimate based on ref spanned 0.4 - 4.5 t/y, and the estimate based on ref was smallest with 0.2 t/y. Hence, they were all either lower than, or in the lower to middle range of, our estimates. Recently, a report on the major sources and flows of the Baltic Sea Action Plan (BSAP) hazardous substances, including SCCPs and medium chain chlorinated paraffins (MCCPs), was released. This report estimated the total annual input of SCCPs and MCCPs to the Baltic Sea area to be higher than that of any of the other BSAP substances, with annual emissions of 140 – 180 t/y, of which SCCPs constituted about 13 – 16 t/y in accordance with $E_{\text{MAX}}$ in this study. It should be noted that our emission estimate is likely to be underestimated, as
the Nordic product registries only contain information on substances imported in products classified as chemical products, and not substances already incorporated into consumer products.22 In addition, the emission estimate does not take into account the standing stock of SCCPs, which has been shown to be an important contributor to CPs emissions in Stockholm, Sweden, in particular because use of SCCPs was considerably higher in the past and SCCPs are only slowly released from products such as paints and sealants.70

The final formula group composition of the emission estimate (Figure 3, Table S5) had a calculated chlorination degree of 61.4% and included 22 formula groups; C₁₀Cl₅₋₉, C₁₁Cl₅₋₁₀, C₁₂Cl₅₋₁₀, and C₁₃Cl₅₋₉. Whereas the manufacturers provided a range of chlorine content from 51 – 70 % for the technical mixtures that were included in the emission estimate, the calculated degree of chlorination for these mixtures, when calculated from analytical results of their formula group composition, ranged only from 59 – 65 %. This is a consequence of the ECNI-MS method as it is not sensitive to the lower chlorinated formula groups,45,48 and leads to an overestimation of the chlorination degree in the emission estimate. In addition, the assumption that the composition of the emissions equals the composition of technical mixtures is believed to overestimate the fraction of heavy SCCPs in the emissions, as the lighter formula groups are probably more prone to be emitted due to their higher volatilities27 and water solubilities.71

3.2.2 Environmental Levels of ΣSCCPs

The predicted ΣSCCPs concentrations based on $E_{\text{MIN}}$ and $E_{\text{AVG}}$ were all underestimated relative to the median of measured ΣSCCPs concentrations, with ratios of up to three orders of magnitude between measured and predicted levels (Figure S8). A much better fit was achieved when using $E_{\text{MAX}}$, and predictions for all compartments except marine sediments and dairy products were within ± one order of magnitude of the median of the measured concentrations (Figure 4).

More specifically, the ratio of the median of the measurements to predictions (based on $E_{\text{MAX}}$) for the atmosphere was 3.4 (Figure 4), but the measured concentrations ranged over three orders of
magnitude. Similarly, the ratio was 0.2, 0.2, and 1.0 for forest, agricultural, and uncultivated soil, respectively, and 6.0 and 11 for freshwater and marine sediments, respectively (Figure 4). As these measured levels in sediment normalized to organic carbon content were from populated areas in Norway, and likely not representative for background levels, predicted concentrations in sediments were also compared to measured levels not normalized to organic carbon content, but sampled from the North, Baltic, and Barents seas. For these levels, the ratio of measurements to predictions was 1.6 instead of 11, possibly reflecting the more remote character of the sampling sites included in these data. The same measured ΣSCCPs concentrations were used for comparison to predictions for all three soil compartments. Higher predicted concentrations in agricultural and forest soil, relative to uncultivated soil, were due to the release of SCCPs emissions in agricultural soil and transfer of SCCPs to soil via the canopy for forest soil, respectively. Overestimation of concentrations in forest soil compared to observed levels was also observed for PCBs in the previous evaluation of CoZMoMAN, and could indicate that the transfer of SCCPs to soil via the canopy, i.e. by uptake from air to the canopy and subsequent deposition to soil through falling leaves, might be overestimated by the model. However, the measured levels are uncertain as many of the samples were below detection limits. There were no suitable measurement data available for water. SCCPs have been measured in water in Sweden as part of the implementation of the European water framework directive, but ΣSCCPs were below the reporting limit of 0.2 µg/L which is one to two orders of magnitude higher than the model predicted ΣSCCPs concentrations in fresh and sea water, respectively, based on $E_{MAX}$.

For biota, the ratio of measurements to predictions (based on $E_{MAX}$) was 4.4 for human breast milk, 0.2 for cod, and 193 for dairy products (Figure 4). The reason for the large discrepancy for the dairy products is not known, but the measured levels only consist of two single butter samples from Denmark and Ireland that are industrially processed, and are hence not completely comparable.
Overall, for $E_{\text{MAX}}$, there was a good consistency between measurements and predictions across a range of compartments. This means that the model succeeded in reproducing the concentration ratios in the different environmental media. Predictions for $\Sigma$SCCPs concentrations in air, the three soil compartments, freshwater sediments, cod, and human breast milk were all within a factor of 6 compared to measured levels, which is small when put in a larger context. The measured concentrations of $\Sigma$SCCPs in different media span ten orders of magnitude, with median concentrations of 190 pg/m$^3$ in air$^{53,54}$ and 1950 ng/g lipid in the butter samples.$^{63}$ Also, concentrations of $\Sigma$SCCPs in analytical standards and environmental samples measured with ECNI-MS have been shown to vary often within a factor of 2 to 6 between laboratories,$^{47,74,75}$ and within a factor of 20 when quantified with the commonly used method by Tomy et al.$^1$ and different quantification standards.$^{41,45}$ In the original CoZMoMAN study where the model was evaluated for PCBs, predicted concentrations were typically within a factor of 2 to 4 of measured values.$^{21}$ The fact that CoZMoMAN performs nearly similarly well for a complex group of organic contaminants as for the well-known PCBs, strengthens the confidence in the model. In addition to the greater analytical uncertainty for SCCPs than for PCBs, this is especially the case as the properties of SCCPs were derived from QSPRs, while the properties for PCBs had been substantiated in numerous experimental studies. Hence, it is likely that CoZMoMAN will also work well for other compound groups that are similar in nature to PCBs and SCCPs.

### 3.2.3 Environmental Formula Group Profiles

In the atmosphere, SCCPs with medium carbon chain lengths (C11-12) and chlorination degrees (Cl6-7) were predicted to dominate (Figure S9). This is quite similar to the composition measured in the UK$^{58}$ and in the European Arctic$^{59}$ where C12 with 6-7 chlorines, and C11 with 6 chlorines were prevalent, respectively. Although the measurements are from outside the model domain, the relatively good match is still encouraging. Lighter formula groups, especially the C10 homologue, were more prevalent in indoor air in Stockholm,$^{60}$ which could illustrate that the lighter formula groups are more prone to being emitted.
SCCPs with long chain lengths (C12, followed by C11 and C13) and high chlorination degrees (Cl8-9) were predicted to be dominant in the sediment compartments (Figure 5 and S9). While SCCPs with 12 and 13 carbons dominated in Baltic Sea sediments, the predicted chlorine content was higher than what had been measured (Figure 5). In addition, both chain lengths and chlorination degree were high compared to what had been measured in sediments from other regions in Europe.\textsuperscript{62,63}

SCCPs with 11-12 carbons and 7-8 chlorines were predicted to be dominant in the agricultural food-chain, while those with long chain-lengths and high chlorination degrees were predicted to be more prevalent in the aquatic food-chain (Figure S10). Both chlorination degree and chain length of SCCPs in fish were predicted to be higher than measured in fish from the Baltic and North seas (Figure 5).\textsuperscript{64,66} This trend was even more pronounced for humans compared to the observed SCCPs composition in breast milk from the UK (Figure 5).\textsuperscript{67}

The overestimation of heavier SCCPs in sediments, fish, and humans (Figure 5) can either be explained by the emission estimate, the predicted properties of the SCCPs, or a combination of both. As already discussed, the emission estimate is probably biased towards the heavier formula groups (Section 3.2.1). Also, the molecular fragment-based QSPRs predict the environmental $HLs$ and $k_{M}$s to increase considerably with carbon chain length and degree of chlorination (Table S3-S4). It is a well-known limitation of fragment based QSPRs that they assume linear additivity of fragments, and hence, incorrect predictions are expected to be more probable for molecules with high numbers of the same fragments, such as the SCCPs.\textsuperscript{76} $HLs$ and $k_{M}$s that do not increase as rapidly with chain length and chlorine substitutions as predicted, could also lead to overestimation of the fraction of the heavy formula groups.

The predicted SCCP composition in humans generally resembled the predicted composition in the marine food-chain, which indicated that fish might make a more important contribution to human exposure than agricultural food (Figure S10). However, formula groups with 6-7 chlorines were enriched in humans relative to in fish, possibly through an agricultural contribution to exposure.
When the fraction of human intake of SCCPs originating from the various sources (dairy products, beef, fish, air, and water) was calculated, exposure from the aquatic food-chain indeed contributed between 80 and 100%, depending on the formula group, and exposure through agricultural food was highest for SCCPs with 6-7 chlorine atoms (Figure S11). The predicted profiles also indicated that the formula groups with longer chain lengths and higher chlorination degree (i.e. slower elimination and biotransformation rates) have a higher bioaccumulation potential, which is in agreement both with estimated environmental bioaccumulation potential (EBAP)\textsuperscript{20} and observations in laboratory experiments\textsuperscript{13,77-79} and in the field\textsuperscript{19,80} However, although this overall trend was consistent with observations, the relative increase in bioaccumulation potential with increasing chain length and chlorination degree might be overestimated based on the overestimation of heavy SCCPs in fish and humans as discussed above.

3.3 Sensitivity and Uncertainty Analysis

The sensitivity and uncertainty analysis only investigated the impact of chemical properties (physical-chemical properties, environmental and metabolic HILs) on the predicted SCCPs concentrations after 70 years of emissions, as well as for persistence and LRAT. In general, the quantities of emissions are often recognized to be the main source of uncertainty,\textsuperscript{34,49} and if included in the uncertainty analysis, the emissions would dominate (Figure S12).Tables S6-S8 provide the absolute sensitivities as the average of the sensitivities for all SCCP formula groups. Most of the results are relatively intuitive, and can be explained by the important transport pathways for SCCPs in the model environment. For example, while uncultivated soil was less sensitive to \(K_{OA}\) and its temperature dependence than to the two other partition coefficients, it was the other way around for forest soil. This reflects the additional pathway for SCCPs input to forest soil via the canopy and the high sensitivity of SCCPs concentration in canopy to \(K_{OA}\) and its temperature dependence. Indeed, the highest observed sensitivities overall were those of the concentrations in the canopies and in the agricultural food-chain to \(\Delta U_{OA}\) (Table S6). The concentrations in humans showed the highest sensitivities to the \(k_M\) in humans, and then to the \(k_M\) in herring, \(k_{BA}\), and the partitioning parameters (Table S6-S8). Also, the
concentrations in humans were hardly sensitive to any of the $k_{Ms}$ in the agricultural food-chain, in accordance with the result that human exposure of SCCPs mainly occurs through the aquatic food-chain. Interestingly, none of the biotic concentrations were sensitive to $K_{FB}$, which means that accurate parameterization of this property is probably not necessary for SCCPs.

The contribution of each input parameter’s uncertainty to the variance of the concentration of $\Sigma$SCCPs in various compartments was, as previously explained, calculated by weighing the contribution for each input parameter by the predicted formula group composition in a given compartment. This implies that any differences between the results from the sensitivity and uncertainty analyses are a result of either the $Cfs$ assigned to an input parameter or the weighing based on the formula group composition. Overall, for the physical environment, the main contributors to uncertainty in the results were both the degradation parameters as well as the partition coefficients and their temperature dependence (Figure 6). More specifically, for both the atmosphere and the soil compartments the largest contributors to variance in the results were parameters that control degradation in air and soil, respectively. For canopy, both parameters that control atmospheric degradation as well as uptake in canopy ($\log Ks$ and $\Delta U$s) contributed to the variance in the results. An interesting feature is that $k_{Ra}$ and $HL$ in water contributed to the variance in predicted concentrations in sea water and marine sediments, but not in fresh water or freshwater sediments. Similarly, $HL$ in sediment contributed to the variance in predicted concentration in freshwater sediments, but not in marine sediments. This is in accordance with the results from the sensitivity analysis, and hence must have a mechanistic explanation, for example the different ratios between the emissions that were emitted to fresh and sea water relative to the volumes of the compartments.

Overall, for the biotic compartments, a distinction was seen between humans and fish where the $k_{Ms}$ were the main contributors to variation in the predicted concentrations, and zooplankton, grass, and cattle where other parameters contributed more (Figure 6). This was in accordance with the results
from the sensitivity analysis (Table S6-S8). Specifically, the main contributors to variance for the
collection in zooplankton were the partitioning parameters and HL in water, rationalized by the
fact that zooplankton is assumed to be in equilibrium with water. For grass, milk cow, and beef cow,
$k_{RA}$ was the largest contributor to variance, which illustrates the importance of the concentrations of
SCCPs in air for the concentrations in the agricultural food-chain. In line with the sensitivity analysis,
the main contributors to variance in the predicted human concentrations of SCCPs were the $k_M$ for
humans, followed by the $k_M$ for herring, and $k_{RA}$.

### 3.4 Further Research Needs

This model exercise supported the predicted large variation in environmental fates within the group
of SCCPs, and great caution is advised if a single set of properties is used for the whole group. In
future studies, composition of SCCPs emissions and properties of the formula groups such as those
applied here, could be used to make more sophisticated model predictions either independently or
to evaluate the simplifying assumptions inherent in a single set of properties. There is considerable
uncertainty in the estimated formula group composition of the emissions, and better information is
needed on the composition and the relative quantities of the technical mixtures used both presently
and in the past. Moreover, the comparison of formula group compositions in both the physical
environment and in biota additionally identified the need for better information on $k_M$s in fish and
humans and environmental HLs for the individual formula groups to facilitate explanation of the
observed patterns. This knowledge gap was confirmed by the sensitivity- and uncertainty analysis,
and is in accordance with the main sources of uncertainty (in addition to emissions) identified also
for other compounds and other multimedia models,e.g.\textsuperscript{17,34}

Overall, a good agreement between the model results and measurements was obtained for
concentrations of \( \Sigma \)SCCPs. In particular, predictions and observations were fairly consistent across
different compartments, which indicate that we have a reasonably good mechanistic understanding
of the environmental fate of SCCPs, despite any remaining uncertainties already identified and
discussed. To facilitate a more thorough comparison, there is a need for more monitoring data from
background regions, as the currently available data for SCCPs in the literature is dominated by samples collected from populated regions and areas close to point sources. There is no data on ΣSCCPs levels in water from Nordic background regions, but this would probably require development of analytical techniques with lower detection and quantification limits as the limits are currently above the predicted concentrations in this study. Also, the set of reported measured formula group profiles of SCCPs in environmental samples from Europe are characterized by randomness and inconsistency. A coherent set of measured formula group profiles that span a range of media, including biota, obtained from the same geographic region and the same time period, as has started to emerge from the area around Beijing in China, would have been invaluable to further evaluate the understanding of the environmental fate of SCCPs e.g. in the Nordic region. Moreover, the uncertainty in measured ΣSCCPs concentrations and formula group patterns is high due to the analytical challenges and the differences between results obtained through different analytical techniques and quantification procedures. Improved methods and improved consistency between methods would not only reduce the uncertainty in the measured results, but also facilitate improved model evaluations for SCCPs in the future. Also, to better understand the observed environmental levels in the Nordic environment and the link between sources and exposure, alternative modeling strategies are needed to elucidate the importance of emissions within the model region, relative to LRAT, in controlling environmental burdens. Finally, this study illustrates the substantial value of combining models and monitoring data to identify the key knowledge gaps in understanding the environmental behavior of organic contaminants.

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Electronic Supplementary Information (ESI)
Additional information on the emission estimation method, Monte Carlo uncertainty analysis, hazard evaluation and benchmarking against PCBs, detailed input parameters, comparison of all emission
scenarios to measured data, and more detailed model output for environmental distribution, predicted formula group profiles, LRAT, human exposure pathways, and model sensitivities is available.
Figure 1: Chemical space plot of SCCP isomers and formula groups (FGs) with 30-70% Cl (w/w), the properties used for SCCPs in EU RAR (SCCP_{EU-RAR}), and seven selected polychlorinated biphenyls (PCB7). The average set of properties of all formula groups (SCCP_{average}) overlaps with SCCP_{EU-RAR}. See Table S2 for details.

Figure 2: Comparison of the logarithm of the predicted ΣSCCPs concentrations based on all formula groups in the emission estimate against the logarithm of the predicted concentrations based on the single set of properties used for SCCPs in EU RAR (SCCP_{EU-RAR}). Both predictions are based on E_{EMAS}. The solid line is the one-to-one line, while the dotted lines mark deviations of ± one order of magnitude.
Figure 3: Estimated formula group composition of emissions. Detailed numbers are provided in Table S5.

Figure 4: The logarithm of the predicted ΣSCCPs concentrations based on $E_{\text{MAX}}$ against the logarithm of the measured ΣSCCPs concentrations. The error bars display the ranges in measured concentrations. The solid line is the one-to-one line, while the dotted lines mark deviations of ± one order of magnitude. $dw =$ dryweight.
Figure 5: Measured SCCP composition in sediment\textsuperscript{42} and cod\textsuperscript{64} from the Baltic Sea and in human breast milk from the United Kingdom,\textsuperscript{67} as well as predicted SCCP composition in accumulating marine sediments, 5 year old cod, and 29 year old human female.

Figure 6: Contribution to variance for all physical-chemical and reactivity input parameters to the predicted concentration of SCCPs in a given compartment, weighted by the predicted formula group distribution in the compartment. Acc = accumulating, trans = transporting, and numbers in parentheses for the biotic compartments specify the age of the model organism in years.
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