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 ($C_xH_{2x+2-n}Cl_n$, $10 \leq x \leq 13$, $1 \leq n \leq x$) 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 (ΣSCCPs). Physical-chemical properties and degradation rates, and hence also environmental behavior, vary considerably among the SCCPs.[e.g.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_Ms)) of all SCCP isomers with a chlorination degree

70   of 30-70 % (n = 7750) were predicted with quantitative structure property relationships (QSPRs) and

71   used to display them on chemical partitioning space maps that represent different aspects of

72   environmental behavior, including bioaccumulation and long range transport potential.[20] SCCPs with

73   12 – 13 carbon atoms and a moderate degree of chlorination were identified as having the highest

74   bioaccumulation potential in humans living in the Arctic.[20] An easy method to simultaneously

75   evaluate all constituents within a complex mixture, the chemical partitioning space approach also

76   demonstrated that randomly selecting one or a few compounds to represent an entire mixture is

77   inadequate if environmental fate differs greatly between constituents, as is the case for SCCPs.[20]

78   A higher tier evaluation of the environmental risk of SCCPs should include considerations about

79   quantities and modes of emission to the environment to predict realistic exposures, both to the

80   mixture as a whole as well as to individual constituents. Outside the scope of the study by Gawor and

81   Wania,[20] consideration of specific environments in combination with emission information would

82   allow for comparisons to be made with measured environmental levels in order to evaluate the

83   results of model assessments and hence the underlying understanding of the environmental

84   behavior of SCCPs. Also, while Gawor and Wania[20] qualitatively discussed the uncertainties involved

85   in their approach, they did not perform a quantitative uncertainty analysis to identify the most

86   critical parameters.

87   The purpose of this study was to investigate the environmental fate of SCCPs in a specific region

88   using realistic emission estimates and a dynamic and mechanistic integrated environmental fate and

89   bioaccumulation multimedia model (CoZMoMAN).[21] The western part of the Baltic Sea drainage

90   basin (including Sweden and parts of Norway, Denmark, and Finland) was selected as a case study

91   region, because (i) CoZMoMAN has already been parameterized and evaluated for polychlorinated

92   biphenyls (PCBs) in this region,[21] (ii) the development of realistic emission scenarios for this region is

93   facilitated by the reported use of SCCPs within the Nordic countries,[22] and (iii) the availability of

94   measured environmental levels of SCCPs in the Nordic region allows for a comparison with

95   predictions and thus an evaluation of the model's performance. The merits and limitations of using a

96   single property estimate for the whole group of SCCPs, and the variation in environmental fate within

97   the group were also further explored. Sensitivity and uncertainty analyses were carried out to

98   evaluate how the uncertainties of the input parameters affected the results. Our aim is that the

99   model and observations in concert can identify the more critical knowledge gaps with regard to the

100   overall environmental fate of SCCPs.

2. Methods

101

2.1 General Description of the Model

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103   The mechanistic and dynamic multimedia model CoZMoMAN[21] applied in this study links the

104   environmental fate model CoZMo-POP 2[23] and the bioaccumulation model ACC-HUMAN.[24] The

105   model has been parameterized for the western Baltic Sea and its drainage basin, and was found to

106   predict concentrations of PCBs in key compartments within a factor of 2-4 of observed levels.[21] The

107   version of the model applied in this study consists of 12 physical compartments: One atmospheric

108   compartment, two water compartments (fresh water and sea water), four sediment compartments

109   (accumulating and transporting sediment in fresh water and sea water), three soil compartments

110   (agricultural, uncultivated, and forest soil), and two forest canopy compartments (deciduous and

111   coniferous canopy). In addition it contains a marine food chain (zooplankton, herring, cod), an

112   agricultural food chain (grass, cow milk, beef), and humans (male and female) who feed from both

113   food chains and breathe outdoor air and drink water from this environment.

2.2 Properties of SCCPs

114

115   Theoretically, SCCPs comprise 46 formula groups and 7820 isomers, when the possibility for

116   branched chains and dichlorinated carbon atoms is excluded (Table S1).[1,25] Some experimental data

117   exist for the properties of SCCPs with specific degrees of chlorination or selected formula groups,

118   including the octanol-water partition coefficient (K_{OW}),[12,26] the air-water partition coefficient

119   (K_{AW}),[27,28] and the k_Ms in fish.[13] For consistency and comparability, this study adopted the log Ks,

120   atmospheric rate constants (k_{RA}), and k_Ms in fish selected for 7750 SCCP isomers by Gawor and

121   Wania.[20] These isomers belong to 37 formula groups and include all SCCPs with 30 − 70 %

122   chlorination (w/w) (Figure 1, Table S1).[20] Here, we performed model simulations for these 37 formula

123   groups ($SCCP_{37}$), each represented by the mean value of the properties of all isomers within that

124   group. In addition an average SCCP ($SCCP_{average}$) was included that represents either the mean

125   (molecular weight, log Ks, and k_{RA}) or the geometric mean (HLs and k_Ms) of all $SCCP_{37}$ properties

126   (Table S2-S4). Calculations were also performed using the properties listed in the EU RARs ($SCCP_{EU-}$

127      $_{RAR}$),[2,3] complimented by the $SCCP_{average}$ properties (k_Ms) and assumed values (enthalpies of phase

128   change (ΔUs), feces-blood partition coefficient (K_{FB}), and activation energies (EAs)) for properties that

129   were not specified in the EU RARs.

2.2.1 Physical-Chemical Properties

131   Among multiple QSPR predictions, Gawor and Wania[20] selected those that corresponded best with

132   the available experimental data. K_{OW} and K_{AW} had been estimated with ACD/Labs and ACD/Absolv,[29]

133   respectively.[20] These values are in the lower range of available experimental[12,26] and predicted[30]

134   values for SCCPs. The octanol-air partition coefficient (K_{OA}) had been calculated from the two other

135   partition coefficients by using the pure phase K_{OW} and a thermodynamic triangle (Table S2, Figure

136   1).[20] All three partition coefficients were used as input to the model. Enthalpies of phase change

137   between octanol-water (ΔU_{OW}), air-water (ΔU_{AW}) and octanol-air (ΔU_{OA}) were assigned default values

138   of -20, 60, and -80 kJ mol^{-1}, respectively, as these are typical values for POPs[31,32] and no experimental

139   or estimated values for SCCPs were available.

2.2.2 Environmental Half-Lives

141   AOPWIN[33] estimates of k_{RA} for the formula groups were found to be in good agreement with the few

142   experimental data for ΣSCCPs[2] (Table S3). Gawor and Wania[20] had only estimated environmental HLs

143   for SCCPs in air, and not in water, soils, or sediments. A method that combines regressions based on

144   four BIOWIN models[33-35] was used to estimate the HLs in water for the 7750 isomers for which

145   SMILES (Simplified Molecular Input Line Entry Specification) codes were available.[20] The HLs in soil

146 and sediment were assumed to be two and nine times the *HL*s in water,[34] respectively, and the *HL*s in

147 canopy and grass equal to the *HL*s in soil (Tables S3 and S4). Different compartments of the same

148 type (e.g. the three soil compartments) were assigned the same values. The *EA*s in air and in other

149 compartments were assumed to be 10 and 30 kJ mol^{-1}, respectively, as no experimental or estimated

150 values were available.

151 ### *2.2.3 Biotransformation Rate Constants*

152 The k_Ms had been estimated in BCFBAF for a fish of 10 grams at 15 °C.[33] Gawor and Wania[20]

153 additionally used k_Ms calculated through an iterative fragment selection (IFS) method.[36] However,

154 these were up to an order of magnitude higher than the available experimental values,[13] in particular

155 for high chlorinated isomers, and were hence not used in this study. The BCFBAF k_Ms were adjusted

156 to the aquatic and terrestrial species in CoZMoMAN (Table S4) according to the geometric mean of

157 their bodyweight, using the following equation:[37,38]

158 $$k_{M,X} = k_{M,N} \, (W_X/W_N)^{-0.25} \hspace{3cm} [1]$$

159 Where W_X and W_N are the required (x grams) and normalized (10 grams) body weights, respectively,

160 and $k_{M,X}$ and $k_{M,N}$ are the biotransformation rate constants (hour^{-1}) at the required and normalized

161 body weights, respectively. The K_{FB} was assigned a default value of $2 \cdot 10^{-8}$ for nonpolar organic

162 molecules.[24,39]

163 ## 2.3 A Note on Analysis of SCCPs

164 The complexity of the SCCPs mixtures makes accurate quantification difficult and measured

165 concentrations are relatively uncertain.[40] Concentrations and formula group composition can vary

166 with instrumentation,[41-44] quantification procedure,[1,45] and quantification standards.[41,46,47] Electron

167 capture negative ionization (ECNI) in low or high resolution MS, following GC separation, is most

168 commonly applied. To increase consistency and comparability between model predictions and

169 observations, data on concentration of SCCPs in environmental samples, and SCCP composition in

170 technical mixtures and environmental samples, were only considered if they had been obtained with

7

171 ECNI-MS. This technique is not very sensitive for substances with few halogens and concentrations

172 for SCCPs with less than 5 chlorines are rarely reported, although they are still present in technical

173 mixtures and the environment.[43,48] The implication is that these formula groups are being ignored.

174 No restrictions were made on the used quantification procedures or quantification standards, as this

175 would substantially reduce the number of measurements that could be included for comparison.

176 **2.4 Emission Estimate**

177 Realistic minimum (E_{MIN}), average (E_{AVG}), and maximum (E_{MAX}) national emissions of ΣSCCPs were

178 estimated applying a previously described high-througput screening method[49] to data on SCCP usage

179 in each of the Nordic countries (Sweden, Norway, Denmark, and Finland) for the years 2000 to

180 2007.[22] Details are outlined in section 1.1 in the Electronic Supplementary Information (ESI).

181 Although in this method emission factors can depend on compound water solubility and vapor

182 pressure, the estimated size and mode of entry (MOE) of the ΣSCCPs emissions was independent of

183 the choice of formula group properties. We therefore assumed the formula group composition of the

184 emissions to be identical to that of technical mixtures (ESI Section 1.1, Table S5). While this emission

185 composition is highly uncertain, it is required to explore key knowledge gaps related to the

186 environmental fate of SCCPs. The final national emissions were scaled to the model domain of

187 CoZMoMAN based on the fraction of the population in each Nordic country that lives in side the

188 domain.[50] Emissions were allocated to different compartments based on the MOE estimated by the

189 high-throughput screening method.[49] Half of the emissions to water were allocated to fresh and sea

190 water, respectively, while emissions to soil were released entirely to agricultural soil. It was assumed

191 that the model domain is surrounded by equally contaminated regions, and hence, that any inflows

192 of SCCPs by air and water from outside regions are the same as the outflows. However, this is a

193 recognized limitation of the current model strategy, as a similar model for the Baltic Sea area has

194 been shown to be sensitive to the model boundary conditions.[51,52]

195 SCCPs have been produced since the 1930s,[6] and in Europe, including the Nordic countries,

196 production and usage volumes declined in the 1990s,[2,3] corresponding to a potential emission period

197   of 60-70 years. Because little information on the temporal variability of production, usage and

198   emissions is available, all simulations were run with constant emissions for 70 years at the levels

199   estimated based on usage from 2000 to 2007, followed by 30 years without emissions to simulate a

200   hypothetical complete emission stop. After 70 years of constant emissions the lower chlorinated

201   formula groups are expected to have approached a steady-state, while concentrations of the higher

202   chlorinated formula groups are expected to still be increasing, especially in soils and sediments. For

203   all modeled compartments the predicted average annual concentrations after 70 years of constant

204   emissions were used for comparison with measured levels. This includes predicted levels in a 29 year

205   old woman, who was born 41 years after the emissions started.

2.5 Model Simulations

207   Simulations were run for $SCCP_{37}$, $SCCP_{average}$, and $SCCP_{EU-RAR}$ using E_{AVG} for all compounds.

208   Subsequently, as the model is linear for increases in the emissions given constant MOE, the predicted

209   concentrations were multiplied with factors corresponding to the other emission scenarios (E_{MIN} and

210   E_{MAX}). Additionally, estimated concentrations for the 37 formula groups ($SCCP_{37}$) were multiplied with

211   factors corresponding to the formula group composition of the emission estimate (Table S5), and

212   these concentrations were summarized to calculate the concentration of ΣSCCPs. The simulation

213   time step was 1 hour, and results were stored every 120 hours.

2.6 Monitoring Data Selected for Model Evaluation

215   To evaluate the model performance, concentrations of ΣSCCPs in the physical environment and biota

216   were collected from the peer-reviewed literature and government reports and databases. To the

217   extent possible, monitoring data for ΣSCCPs in background regions in the Nordic environment for the

218   period 2000-2007 were chosen for comparison. Because the model compartments are well-mixed

219   with uniform concentrations within the model domain, predictions cannot be expected to compare

220   well with elevated levels in areas close to point sources.[21] Median rather than average measured

221   concentrations were used to avoid bias towards highly contaminated hotspots. As reported formula

222   group profiles of environmental samples are limited, measured formula group profiles from other

223   regions of Europe were also included for comparison.

224   *2.6.1 Physical Compartments*

225   The predicted ΣSCCPs concentrations in air were compared to monthly averages for bulk air (sum

226   gaseous and particulate phases) reported for the Swedish background sites Råö [57°24'N, 11°55'E]

227   and Aspvreten [58°48'N, 17°23'E] for the years 2003 and 2009-2011.[53,54] The calculated ΣSCCPs

228   concentrations in soil were compared to data for Norwegian background soils sampled in 2008.[55] As

229   most samples (23 out of 32) were below the method detection limit (MDL; 0.8 ng/g dw), these

230   samples were represented by MDL/2 to reduce bias towards the samples above MDL. Predicted

231   concentrations for marine and freshwater sediments (accumulating, not transporting) were

232   compared to measured concentrations in marine and freshwater sediments in populated areas of

233   Norway in 2003.[56] All predicted concentrations in soil and sediment were normalized to particulate

234   organic carbon (POC), and the measured concentrations to soil organic matter (SOM) or total organic

235   carbon (TOC), respectively. In addition, measured concentrations in sediments collected from the

236   Baltic and North Seas in 2003-2004[42] and the Barents Sea in 2006-2007[57] in ng/g dry weight were

237   compared to predicted concentrations in marine sediments in ng/g particles.

238   Measured formula group profiles of SCCPs in air were available for a semi-rural location in England in

239   spring of 1997,[58] from a remote location in the European Arctic in spring of 1999,[59] and for indoor air

240   in Stockholm during the winter of 2006-2007.[60] Formula group composition also existed for marine

241   sediments sampled in the Baltic Sea in 2004.[42] For freshwater sediments, data were available from

242   surface sediments from ponds and rivers in rural and industrial areas of the Czech Republic in 2001-

243   2002,[61] and dated sediment cores from Lake Thun in Switzerland.[62]

244   *2.6.2 Biotic Compartments*

245   All modeled and measured concentrations for biota were normalized to lipid weight. Predicted

246   concentrations for cow milk were compared to results for two butter samples from Denmark and

247 Ireland reported in 2002.[63] Calculated concentrations in 5-year old cod were compared to measured

248 levels in the livers of cod from the Baltic Sea in 2002.[64] Predicted concentrations for a 29 year old

249 woman were compared to monitoring data for pooled breast milk samples from primipara women in

250 Uppsala County in Sweden from 1996 to 2010.[65]

251 Measured formula group composition was available for the livers of cod, flounder and North Sea dab

252 sampled in the North and Baltic Seas in 2002,[64] and the livers of cod sampled outside of Iceland and

253 Northern Norway in 2003-2004.[66] Information on formula group composition also existed for human

254 breast milk sampled in 2001-2002 from women living in urban and semi-rural areas of England.[67]

255 **2.7 Sensitivity and Uncertainty Analysis**

256 Model sensitivity can be defined as the relative effect of an input value to the output value, while

257 uncertainty can be defined as the variation in the output value resulting from both the uncertainty in

258 the input parameters in addition to the sensitivity of the output value to the input values.[68] A

259 sensitivity analysis was performed for all SCCP formula groups to identify which compound

260 properties influenced CoZMoMAN output the most. Each property (physical-chemical properties,

261 environmental HLs, and k_Ms) was varied individually by plus and minus ten percent, respectively.

262 Sensitivity (S) was then calculated as

263 $S = \frac{\Delta O}{O} \times \frac{I}{\Delta I}$ [2]

264 where ΔI and ΔO are the relative changes in the input (I) and output (O) parameters of interest,

265 respectively.[68] The average sensitivity of increasing and decreasing the input parameter was

266 calculated.

267 An analytical approach for evaluating uncertainty was applied.[68,69] In this method all input

268 parameters were assigned a confidence factor (Cf) which describes the degree of uncertainty in the

269 parameter. The compound properties were assigned Cfs according to the default values

270 recommended by MacLeod et al.[68] for data poor situations, and expert judgment was used for

271   parameters not included in MacLeod et al.[68] A higher Cf for the log Ks (Cf = 1.5) than recommended

272   by MacLeod et al.[68] (Cf = 1.1) was chosen as there is considerable uncertainty in the log Ks of SCCPs,[30]

273   The ΔUs were also assigned Cfs of 1.5. The EAs, K_{FB}, and k_{RA} were assigned Cfs of 2, and the remaining

274   HLs and k_Ms were assigned Cfs of 3. Based on the assumed Cfs and the calculated sensitivities, the

275   contribution to variance (CV) of each input parameter I_j to each output parameter O_i for formula

276   group X was calculated as[68]

277     $$CV_{O_i I_j X} = \frac{\left(\ln Cf_{I_j}\right)^2 S_{I_j}^2}{\sum_{j=1}^{n}\left(\ln Cf_{I_j}\right)^2 S_{I_j}^2} \qquad [3]$$

278   The predicted formula group composition in each compartment was subsequently used to weight the

279   various CVs by the importance of a formula group to the contamination of a compartment:

280     $$CV_{O_i I_j} = \sum_X \frac{C_X}{C_{\Sigma SCCPs}} CV_{O_i I_j X} \qquad [4]$$

281   where C_X and $C_{\Sigma SCCPs}$ are the predicted concentrations of formula group X and of ΣSCCPs, respectively,

282   in the given compartment. This method rests on the assumptions that the model is linear or near-

283   linear, that the uncertainty in the input parameters is uncorrelated, and that all input parameters are

284   log-normally distributed.[68] To evaluate the assumption of linearity in the model, a Monte Carlo

285   uncertainty analysis was performed for SCCP$_{average}$ (see ESI section 1.2 and Figure S1). Also, to

286   illustrate the relative importance of uncertainty in the emissions relative to uncertainty in the

287   properties of SCCPs an additional uncertainty analysis where the quantities of the emissions were

288   included was also performed (Figure S12).

289   **3. Results and Discussion**

290   **3.1 Merits and Limitations of Single vs. Multiple Sets of Properties**

291   Even though the physical-chemical properties for SCCPs vary widely, risk assessments frequently rely

292   on the properties for only a single or a few constituents when evaluating environmental fate.[20] The

293   fit between concentrations predicted for SCCP$_{EU-RAR}$ and ΣSCCPs based on the individual formula

294   groups was good, with SCCP$_{EU-RAR}$ concentrations on average 1.2 ± 0.9 times higher (range 0.3 to 3.5)

295   than ΣSCCPs concentrations (Figure 2). However, the predicted concentrations for SCCP$_{average}$ were

296   only 0.5 ± 0.3 times (range 0.1 to 1.1) that of predicted concentrations for ΣSCCPs (Figure S2). This is

297   largely because SCCP$_{average}$ has lower predicted concentrations in soils and sediments than SCCP$_{EU-RAR}$,

298   due to the long environmental HLs in these compartments assumed by the EU RARs (Figure S3, Table

299   S3). It should be noted that several of the other properties (the k_Ms, ΔUs, K_{FB}, and EAs) are identical

300   for SCCP$_{EU-RAR}$ and SCCP$_{average}$. This means that the results for these two SCCPs are not independent of

301   each other, especially not for concentrations in fish and humans where the k_Ms are the most

302   influential properties (besides emissions) (Section 3.3). Nevertheless, these examples illustrate the

303   difficulty of choosing a representative single set of properties for a complex group of contaminants

304   like the SCCPs. Certainly, the representativeness of the selected properties will vary depending on

305   the context. Variations in the composition of the emissions and the environmental conditions will

306   influence the composition of SCCPs in the environment and thus whether or not the selected

307   properties are representative for ΣSCCPs or not. While it may sometimes be possible to obtain results

308   with a single set of properties that closely resemble those obtained with more sophisticated

309   approaches, caution needs to be applied when this approach is selected.

310   In addition, using a single set of properties for the SCCPs does not reveal anything about the diversity

311   in environmental fate within the group, and which SCCPs that pose the greatest hazard. The

312   predicted environmental distribution varied considerably between formula groups (Figure S4), which

313   is reflected in the different SCCP composition in different environmental compartments (Section

314   3.2.3). The various SCCPs also undergo different environmental processes. Gawor and Wania[20]

315   identified a threshold whereby SCCPs with fewer than 8 chlorine atoms will be mainly present in the

316   atmospheric gaseous phase and undergo dry gaseous deposition, while SCCPs with more than 8

317   chlorines will be mainly present in the particulate phase and undergo dry and wet particle deposition

318   from the atmosphere.[20] This phase distribution was reproduced by the present study, where the

319   same threshold of 8 chlorines was identified (Figure S5), although it is acknowledged that higher K_{OA}

320 values for SCCPs as predicted by Glüge et al.[30] would result in a lowering of the threshold to SCCPs

321 with a lower degree of chlorination. Similarly, the potential for long-range atmospheric transport

322 (LRAT) was predicted to be mainly limited by atmospheric degradation in the gaseous phase and

323 deposition to surface media for SCCPs with less and more than 8 chlorines, respectively (Figure S6).

324 Also, estimated hazard criteria for persistence, LRAT, and bioaccumulation of SCCPs varied

325 considerably when using properties of the different formula groups, and were comparable to results

326 for PCBs for the SCCPs that displayed the highest potential for persistence, LRAT, or bioaccumulation

327 (ESI section 1.3, Figure S7).

328 **3.2 Comparison to Monitoring Data in the Nordic Environment**

329 *3.2.1 Emission Estimate*

330 The E_{AVG} estimate for ΣSCCPs in the Nordic countries was 2.08 tonnes/year (t/y), with E_{MIN} and E_{MAX} of

331 0.71 and 15.35 t/y, respectively. The predicted MOE was 87 % to water, 9 % to the atmosphere, and

332 4 % to soil. For comparison, previous emission estimates of SCCPs in the EU (EU-RAR),[3] chlorinated

333 paraffins (CPs) in Stockholm,[70] and SCCPs in the individual UNECE (United Nations Economic

334 Commission for Europe) countries[71] were scaled to the model domain of this study based on the

335 population of the respective areas. In addition, the emissions of CPs in Stockholm were adjusted to

336 SCCPs by assuming that the SCCPs constituted 3 - 32 % of the CPs.[70] The population-scaled emission

337 estimate from the EU RAR spanned 1.6 – 7.3 t/y,[3] the estimate based on ref[70] spanned 0.4 - 4.5 t/y,

338 and the estimate based on ref[71] was smallest with 0.2 t/y. Hence, they were all either lower than, or

339 in the lower to middle range of, our estimates. Recently, a report on the major sources and flows of

340 the Baltic Sea Action Plan (BSAP) hazardous substances, including SCCPs and medium chain

341 chlorinated paraffins (MCCPs), was released.[72] This report estimated the total annual input of SCCPs

342 and MCCPs to the Baltic Sea area to be higher than that of any of the other BSAP substances, with

343 annual emissions of 140 – 180 t/y, of which SCCPs constituted about 13 – 16 t/y in accordance with

344 E_{MAX} in this study.[72] It should be noted that our emission estimate is likely to be underestimated, as

345   the Nordic product registries only contain information on substances imported in products classified

346   as chemical products, and not substances already incorporated into consumer products.[22] In

347   addition, the emission estimate does not take into account the standing stock of SCCPs, which has

348   been shown to be an important contributor to CPs emissions in Stockholm, Sweden, in particular

349   because use of SCCPs was considerably higher in the past and SCCPs are only slowly released from

350   products such as paints and sealants.[70]

351   The final formula group composition of the emission estimate (Figure 3, Table S5) had a calculated

352   chlorination degree of 61.4% and included 22 formula groups; $C_{10}Cl_{5-9}$, $C_{11}Cl_{5-10}$, $C_{12}Cl_{5-10}$, and $C_{13}Cl_{5-9}$.

353   Whereas the manufacturers provided a range of chlorine content from 51 – 70 % for the technical

354   mixtures that were included in the emission estimate, the calculated degree of chlorination for these

355   mixtures, when calculated from analytical results of their formula group composition, ranged only

356   from 59 – 65 %. This is a consequence of the ECNI-MS method as it is not sensitive to the lower

357   chlorinated formula groups,[45,48] and leads to an overestimation of the chlorination degree in the

358   emission estimate. In addition, the assumption that the composition of the emissions equals the

359   composition of technical mixtures is believed to overestimate the fraction of heavy SCCPs in the

360   emissions, as the lighter formula groups are probably more prone to be emitted due to their higher

361   volatilities[27] and water solubitilies.[73]

362   *3.2.2 Environmental Levels of ΣSCCPs*

363   The predicted ΣSCCPs concentrations based on E_{MIN} and E_{AVG} were all underestimated relative to the

364   median of measured ΣSCCPs concentrations, with ratios of up to three orders of magnitude between

365   measured and predicted levels (Figure S8). A much better fit was achieved when using E_{MAX}, and

366   predictions for all compartments except marine sediments and dairy products were within ± one

367   order of magnitude of the median of the measured concentrations (Figure 4).

368   More specifically, the ratio of the median of the measurements to predictions (based on E_{MAX}) for the

369   atmosphere was 3.4 (Figure 4), but the measured concentrations ranged over three orders of

370   magnitude. Similarly, the ratio was 0.2, 0.2, and 1.0 for forest, agricultural, and uncultivated soil,

371   respectively, and 6.0 and 11 for freshwater and marine sediments, respectively (Figure 4). As these

372   measured levels in sediment normalized to organic carbon content were from populated areas in

373   Norway, and likely not representative for background levels, predicted concentrations in sediments

374   were also compared to measured levels not normalized to organic carbon content, but sampled from

375   the North, Baltic, and Barents seas. For these levels, the ratio of measurements to predictions was

376   1.6 instead of 11, possibly reflecting the more remote character of the sampling sites included in

377   these data.[42,57] The same measured ΣSCCPs concentrations were used for comparison to predictions

378   for all three soil compartments.[55] Higher predicted concentrations in agricultural and forest soil,

379   relative to uncultivated soil, were due to the release of SCCPs emissions in agricultural soil and

380   transfer of SCCPs to soil via the canopy for forest soil, respectively. Overestimation of concentrations

381   in forest soil compared to observed levels was also observed for PCBs in the previous evaluation of

382   CoZMoMAN,[21] and could indicate that the transfer of SCCPs to soil via the canopy, i.e. by uptake from

383   air to the canopy and subsequent deposition to soil through falling leaves, might be overestimated by

384   the model. However, the measured levels are uncertain as many of the samples were below

385   detection limits.[55] There were no suitable measurement data available for water. SCCPs have been

386   measured in water in Sweden as part of the implementation of the European water framework

387   directive,[54] but ΣSCCPs were below the reporting limit of 0.2 µg/L which is one to two orders of

388   magnitude higher than the model predicted ΣSCCPs concentrations in fresh and sea water,

389   respectively, based on E_{MAX}.

390   For biota, the ratio of measurements to predictions (based on E_{MAX}) was 4.4 for human breast milk,

391   0.2 for cod, and 193 for dairy products (Figure 4). The reason for the large discrepancy for the dairy

392   products is not known, but the measured levels only consist of two single butter samples from

393   Denmark and Ireland that are industrially processed,[63] and are hence not completely comparable.

394   Overall, for E_{MAX}, there was a good consistency between measurements and predictions across a

395   range of compartments. This means that the model succeeded in reproducing the concentration

396   ratios in the different environmental media. Predictions for ΣSCCPs concentrations in air, the three

397   soil compartments, freshwater sediments, cod, and human breast milk were all within a factor of 6

398   compared to measured levels, which is small when put in a larger context. The measured

399   concentrations of ΣSCCPs in different media span ten orders of magnitude, with median

400   concentrations of 190 pg/m^3 in air[53,54] and 1950 ng/g lipid in the butter samples.[63] Also,

401   concentrations of ΣSCCPs in analytical standards and environmental samples measured with ECNI-MS

402   have been shown to vary often within a factor of 2 to 6 between laboratories,[47,74,75] and within a

403   factor of 20 when quantified with the commonly used method by Tomy et al.[1] and different

404   quantification standards.[41,45] In the original CoZMoMAN study where the model was evaluated for

405   PCBs, predicted concentrations were typically within a factor of 2 to 4 of measured values.[21] The fact

406   that CoZMoMAN performs nearly similarly well for a complex group of organic contaminants as for

407   the well-known PCBs, strengthens the confidence in the model. In addition to the greater analytical

408   uncertainty for SCCPs than for PCBs, this is especially the case as the properties of SCCPs were

409   derived from QSPRs, while the properties for PCBs had been substantiated in numerous experimental

410   studies. Hence, it is likely that CoZMoMAN will also work well for other compound groups that are

411   similar in nature to PCBs and SCCPs.

412   *3.2.3 Environmental Formula Group Profiles*
413   In the atmosphere, SCCPs with medium carbon chain lengths (C11-12) and chlorination degrees (Cl6-

414   7) were predicted to dominate (Figure S9). This is quite similar to the composition measured in the

415   UK[58] and in the European Arctic[59] where C12 with 6-7 chlorines, and C11 with 6 chlorines were

416   prevalent, respectively. Although the measurements are from outside the model domain, the

417   relatively good match is still encouraging. Lighter formula groups, especially the C10 homologue,

418   were more prevalent in indoor air in Stockholm,[60] which could illustrate that the lighter formula

419   groups are more prone to being emitted.

17

420   SCCPs with long chain lengths (C12, followed by C11 and C13) and high chlorination degrees (Cl8-9)

421   were predicted to be dominant in the sediment compartments (Figure 5 and S9). While SCCPs with

422   12 and 13 carbons dominated in Baltic Sea sediments,[42] the predicted chlorine content was higher

423   than what had been measured (Figure 5).[42] In addition, both chain lengths and chlorination degree

424   were high compared to what had been measured in sediments from other regions in Europe.[62,63]

425   SCCPs with 11-12 carbons and 7-8 chlorines were predicted to be dominant in the agricultural food-

426   chain, while those with long chain-lengths and high chlorination degrees were predicted to be more

427   prevalent in the aquatic food-chain (Figure S10). Both chlorination degree and chain length of SCCPs

428   in fish were predicted to be higher than measured in fish from the Baltic and North seas (Figure

429   5).[64,66] This trend was even more pronounced for humans compared to the observed SCCPs

430   composition in breast milk from the UK (Figure 5).[67]

431   The overestimation of heavier SCCPs in sediments, fish, and humans (Figure 5) can either be

432   explained by the emission estimate, the predicted properties of the SCCPs, or a combination of both.

433   As already discussed, the emission estimate is probably biased towards the heavier formula groups

434   (Section 3.2.1). Also, the molecular fragment-based QSPRs predict the environmental HLs and k_Ms to

435   increase considerably with carbon chain length and degree of chlorination (Table S3-S4). It is a well-

436   known limitation of fragment based QSPRs that they assume linear additivity of fragments, and

437   hence, incorrect predictions are expected to be more probable for molecules with high numbers of

438   the same fragments, such as the SCCPs.[76] HLs and k_Ms that do not increase as rapidly with chain

439   length and chlorine substitutions as predicted, could also lead to overestimation of the fraction of

440   the heavy formula groups.

441   The predicted SCCP composition in humans generally resembled the predicted composition in the

442   marine food-chain, which indicated that fish might make a more important contribution to human

443   exposure than agricultural food (Figure S10). However, formula groups with 6-7 chlorines were

444   enriched in humans relative to in fish, possibly through an agricultural contribution to exposure.

445   When the fraction of human intake of SCCPs originating from the various sources (dairy products,

446   beef, fish, air, and water) was calculated, exposure from the aquatic food-chain indeed contributed

447   between 80 and 100 %, depending on the formula group, and exposure through agricultural food was

448   highest for SCCPs with 6-7 chlorine atoms (Figure S11). The predicted profiles also indicated that the

449   formula groups with longer chain lengths and higher chlorination degree (i.e. slower elimination and

450   biotransformation rates) have a higher bioaccumulation potential, which is in agreement both with

451   estimated environmental bioaccumulation potential (EBAP)[20] and observations in laboratory

452   experiments[13,77-79] and in the field.[19,80] However, although this overall trend was consistent with

453   observations, the relative increase in bioaccumulation potential with increasing chain length and

454   chlorination degree might be overestimated based on the overestimation of heavy SCCPs in fish and

455   humans as discussed above.

456   **3.3 Sensitivity and Uncertainty Analysis**
457   The sensitivity and uncertainty analysis only investigated the impact of chemical properties (physical-

458   chemical properties, environmental and metabolic HLs) on the predicted SCCPs concentrations after

459   70 years of emissions, as well as for persistence and LRAT. In general, the quantities of emissions are

460   often recognized to be the main source of uncertainty,[34,49] and if included in the uncertainty analysis,

461   the emissions would dominate (Figure S12).Tables S6-S8 provide the absolute sensitivities as the

462   average of the sensitivities for all SCCP formula groups. Most of the results are relatively intuitive,

463   and can be explained by the important transport pathways for SCCPs in the model environment. For

464   example, while uncultivated soil was less sensitive to K_{OA} and its temperature dependence than to

465   the two other partition coefficients, it was the other way around for forest soil. This reflects the

466   additional pathway for SCCPs input to forest soil via the canopy and the high sensitivity of SCCPs

467   concentration in canopy to K_{OA} and its temperature dependence. Indeed, the highest observed

468   sensitivities overall were those of the concentrations in the canopies and in the agricultural food-

469   chain to ΔU_{OA} (Table S6). The concentrations in humans showed the highest sensitivities to the k_M in

470   humans, and then to the k_M in herring, k_{RA}, and the partitioning parameters (Table S6-S8). Also, the

471   concentrations in humans were hardly sensitive to any of the k_Ms in the agricultural food-chain, in

472   accordance with the result that human exposure of SCCPs mainly occurs through the aquatic food-

473   chain. Interestingly, none of the biotic concentrations were sensitive to K_{FB}, which means that

474   accurate parameterization of this property is probably not necessary for SCCPs.

475   The contribution of each input parameter's uncertainty to the variance of the concentration of

476   ΣSCCPs in various compartments was, as previously explained, calculated by weighing the

477   contribution for each input parameter by the predicted formula group composition in a given

478   compartment. This implies that any differences between the results from the sensitivity and

479   uncertainty analyses are a result of either the Cfs assigned to an input parameter or the weighing

480   based on the formula group composition. Overall, for the physical environment, the main

481   contributors to uncertainty in the results were both the degradation parameters as well as the

482   partition coefficients and their temperature dependence (Figure 6). More specifically, for both the

483   atmosphere and the soil compartments the largest contributors to variance in the results were

484   parameters that control degradation in air and soil, respectively. For canopy, both parameters that

485   control atmospheric degradation as well as uptake in canopy (log Ks and ΔUs) contributed to the

486   variance in the results. An interesting feature is that k_{RA} and HL in water contributed to the variance

487   in predicted concentrations in sea water and marine sediments, but not in fresh water or freshwater

488   sediments. Similarly, HL in sediment contributed to the variance in predicted concentration in

489   freshwater sediments, but not in marine sediments. This is in accordance with the results from the

490   sensitivity analysis, and hence must have a mechanistic explanation, for example the different ratios

491   between the emissions that were emitted to fresh and sea water relative to the volumes of the

492   compartments.

493   Overall, for the biotic compartments, a distinction was seen between humans and fish where the k_Ms

494   were the main contributors to variation in the predicted concentrations, and zooplankton, grass, and

495   cattle where other parameters contributed more (Figure 6). This was in accordance with the results

20

496   from the sensitivity analysis (Table S6-S8). Specifically, the main contributors to variance for the

497   concentration in zooplankton were the partitioning parameters and HL in water, rationalized by the

498   fact that zooplankton is assumed to be in equilibrium with water. For grass, milk cow, and beef cow,

499   k_{RA} was the largest contributor to variance, which illustrates the importance of the concentrations of

500   SCCPs in air for the concentrations in the agricultural food-chain. In line with the sensitivity analysis,

501   the main contributors to variance in the predicted human concentrations of SCCPs were the k_M for

502   humans, followed by the k_M for herring, and k_{RA}.

3.4 Further Research Needs

503
504   This model exercise supported the predicted large variation in environmental fates within the group

505   of SCCPs,[20] and great caution is advised if a single set of properties is used for the whole group. In

506   future studies, composition of SCCPs emissions and properties of the formula groups such as those

507   applied here, could be used to make more sophisticated model predictions either independently or

508   to evaluate the simplifying assumptions inherent in a single set of properties. There is considerable

509   uncertainty in the estimated formula group composition of the emissions, and better information is

510   needed on the composition and the relative quantities of the technical mixtures used both presently

511   and in the past. Moreover, the comparison of formula group compositions in both the physical

512   environment and in biota additionally identified the need for better information on k_Ms in fish and

513   humans and environmental HLs for the individual formula groups to facilitate explanation of the

514   observed patterns. This knowledge gap was confirmed by the sensitivity- and uncertainty analysis,

515   and is in accordance with the main sources of uncertainty (in addition to emissions) identified also

516   for other compounds and other multimedia models.[e.g 17,34]

517   Overall, a good agreement between the model results and measurements was obtained for

518   concentrations of ΣSCCPs. In particular, predictions and observations were fairly consistent across

519   different compartments, which indicate that we have a reasonably good mechanistic understanding

520   of the environmental fate of SCCPs, despite any remaining uncertainties already identified and

521   discussed. To facilitate a more thorough comparison, there is a need for more monitoring data from

522   background regions, as the currently available data for SCCPs in the literature is dominated by

523   samples collected from populated regions and areas close to point sources. There is no data on

524   ΣSCCPs levels in water from Nordic background regions, but this would probably require

525   development of analytical techniques with lower detection and quantification limits as the limits are

526   currently above the predicted concentrations in this study.[75,81] Also, the set of reported measured

527   formula group profiles of SCCPs in environmental samples from Europe are characterized by

528   randomness and inconsistency. A coherent set of measured formula group profiles that span a range

529   of media, including biota, obtained from the same geographic region and the same time period, as

530   has started to emerge from the area around Beijing in China,[80,82-86] would have been invaluable to

531   further evaluate the understanding of the environmental fate of SCCPs e.g. in the Nordic region.

532   Moreover, the uncertainty in measured ΣSCCPs concentrations and formula group patterns is high

533   due to the analytical challenges and the differences between results obtained through different

534   analytical techniques and quantification procedures. Improved methods and improved consistency

535   between methods would not only reduce the uncertainty in the measured results,[40] but also facilitate

536   improved model evaluations for SCCPs in the future. Also, to better understand the observed

537   environmental levels in the Nordic environment and the link between sources and exposure,

538   alternative modeling strategies are needed to elucidate the importance of emissions within the

539   model region, relative to LRAT, in controlling environmental burdens. Finally, this study illustrates the

540   substantial value of combining models and monitoring data to identify the key knowledge gaps in

541   understanding the environmental behavior of organic contaminants.

## Electronic Supplementary Information (ESI)
546   Additional information on the emission estimation method, Monte Carlo uncertainty analysis, hazard

547   evaluation and benchmarking against PCBs, detailed input parameters, comparison of all emission

548 scenarios to measured data, and more detailed model output for environmental distribution,

549 predicted formula group profiles, LRAT, human exposure pathways, and model sensitivities is
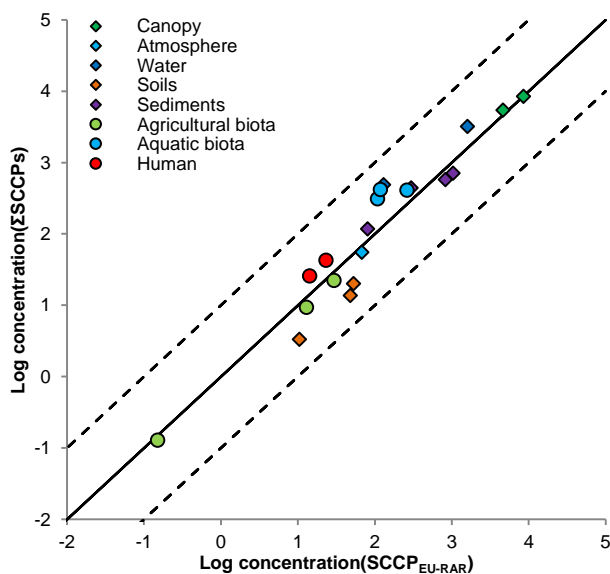
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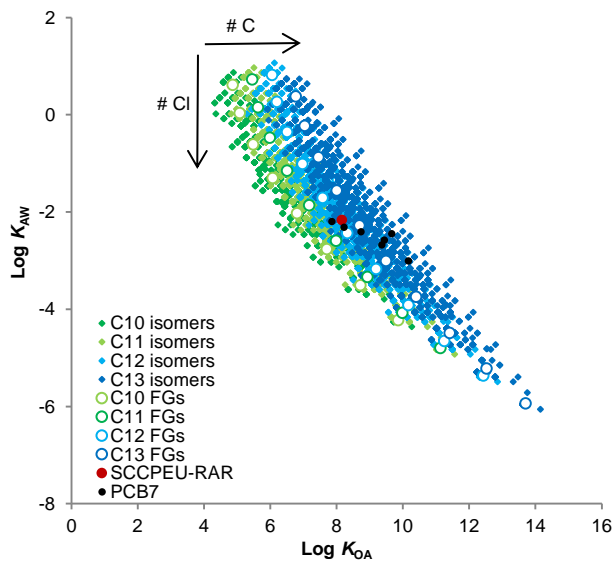
Figure 1: Chemical space plot of SCCP isomers and formula groups (FGs) with 30-70 % Cl (w/w), the properties used for SCCPs in EU RAR (SCCP$_{\text{EU-RAR}}$), and seven selected polychlorinated biphenyls (PCB7). The average set of properties of all formula groups (SCCP$_{\text{average}}$) overlaps with SCCP$_{\text{EU-RAR}}$. See Table S2 for details.

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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$_{\text{EU-RAR}}$). Both predictions are based on E_{MAX}. The solid line is the one-to-one line, while the dotted lines mark deviations of ± one order of magnitude.
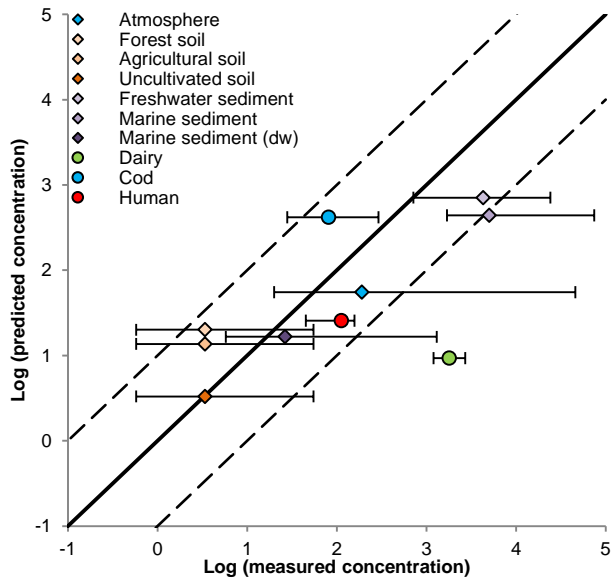
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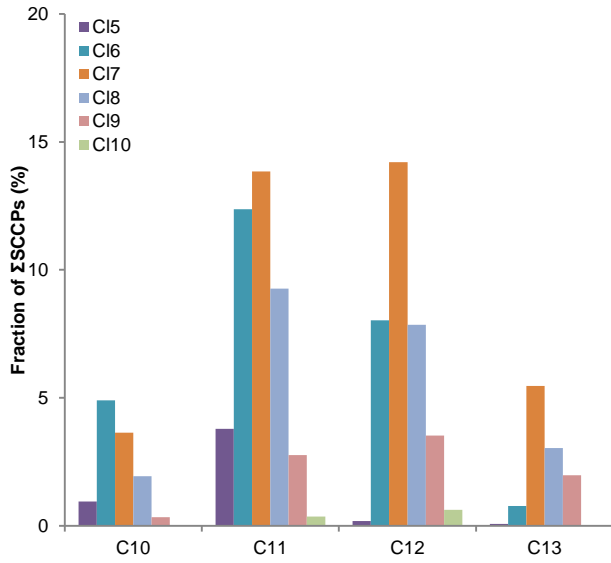
Figure 3: Estimated formula group composition of emissions. Detailed numbers are provided in Table S5.

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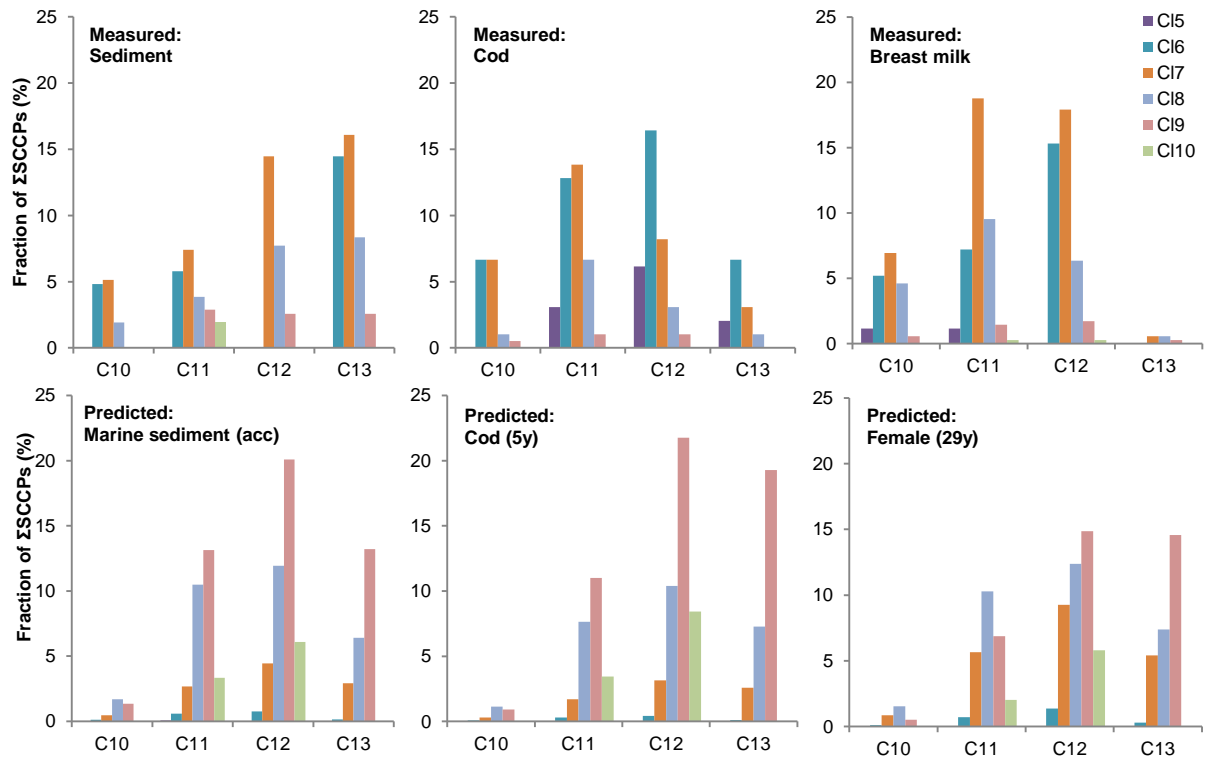570

571 **Figure 4: The logarithm of the predicted ΣSCCPs concentrations based on E_{MAX} against the logarithm of the measured**
572 **ΣSCCPs concentrations. The error bars display the ranges in measured concentrations. The solid line is the one-to-one**
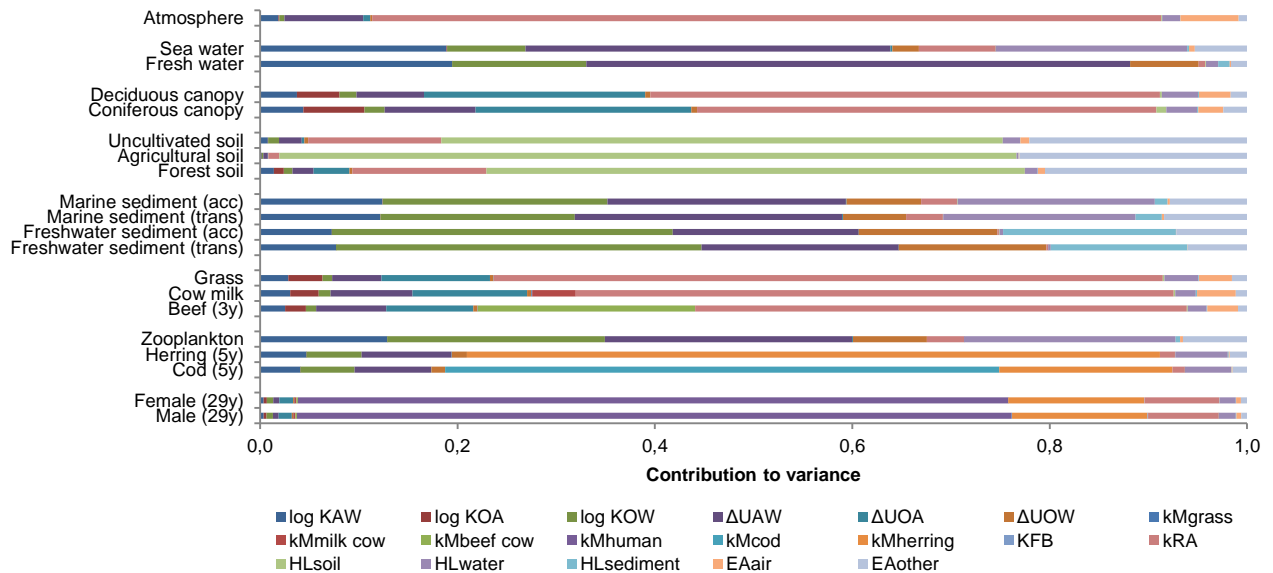573 **line, while the dotted lines mark deviations of ± one order of magnitude. dw = dryweight.**

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575

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Figure 5: Measured SCCP composition in sediment[42] and cod[64] from the Baltic Sea and in human breast milk from the United Kingdom,[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 ΣSCCPs 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.

References

1. G. T. Tomy, G. A. Stern, D. C. G. Muir, A. T. Fisk, C. D. Cymbalisty and J. B. Westmore, *Anal. Chem.*, 1997, **69**, 2762-2771.
2. European Chemicals Bureau, *European Union Risk Assessment Report: Alkanes, C10-13, chloro-,* EUR 19010 EN, European Chemicals Bureau, Luxembourg, 2000.
3. European Chemicals Bureau, *Updated Risk Assessment of Alkanes, C10-13, chloro-,* EUR 23396 EN, European Chemicals Bureau, Luxembourg, 2008.
4. H. Fiedler, in *The handbook of environmental chemistry: Chlorinated Paraffins*, ed. J. De Boer, Springer, Heidelberg, 1st edn., 2010, vol. 10, pp. 1-40.
5. D. C. G. Muir, in *The handbook of environmental chemistry: Chlorinated paraffins*, ed. J. De Boer, Springer, Heidelberg, 1st edn., 2010, vol. 10, pp. 107-133.
6. S. Bayen, J. P. Obbard and G. O. Thomas, *Environ. Int.*, 2006, **32**, 915-929.
7. M. L. Feo, E. Eljarrat and D. Barceló, *TrAC, Trends Anal. Chem.*, 2009, **28**, 778-791.
8. D. C. G. Muir, in *New Types of Persistent Halogenated Compounds*, ed. J. Paasivirta, Springer-Verlag, Berlin Heidelberg, 2000, vol. 3, Part K, pp. 203-236.
9. F. J. Santos, J. Parera and M. T. Galceran, *Anal. Bioanal. Chem.*, 2006, **386**, 837-857.
10. Z. Zencak and M. Oehme, *TrAC, Trends Anal. Chem.*, 2006, **25**, 310-317.
11. Persistent Organic Pollutants Review Committee (POPRC), *Revised draft risk profile: short-chain chlorinated paraffins,* UNEP/POPS/POPRC.6/11/Rev.1, United Nations Environment Programme (UNEP), Geneva, 2011.
12. B. Hilger, H. Fromme, W. Völkel and M. Coelhan, *Environ. Sci. Technol.*, 2011, **45**, 2842-2849.
13. A. T. Fisk, G. T. Tomy, C. D. Cymbalisty and D. C. G. Muir, *Environ. Toxicol. Chem.*, 2000, **19**, 1508-1516.
14. K. Tsunemi and A. Tokai, *J. Risk Res.*, 2007, **10**, 747-757.
15. T. Gouin, *Environ. Sci. Policy*, 2010, **13**, 175-184.
16. National Industrial Chemicals Notifications and Assessment Scheme (NICNAS), *Environmental exposure assessment of short chain chlorinated paraffins (SCCPs) in Australia, A follow up report to the National Industrial Chemicals Notifications and Assessment Scheme (NICNAS) short chain chlorinated paraffins (SCCPs) priority existing chemical assessment report no. 16*, Australian Government, Department of Health and Ageing, Canberra, 2004.
17. C. E. Cowan-Ellsberry, M. S. McLachlan, J. A. Arnot, M. MacLeod, T. E. McKone and F. Wania, *Integrated Environ. Assess. Manag.*, 2009, **5**, 662-679.
18. Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE), *Opinion of the scientific committee on toxicity, ecotoxicity and the environment (CSTEE) on the scientific basis of the national provisions on short chain chlorinated paraffins (SCCPs) being more restrictive than those laid down in directive 2002/45/EC that the Netherlands intends to maintain in accordance with Article 95(4) of the EC Treaty,* C7/GF/csteeop/SCCPs/031003 D(03), European Commission, Brussels, 2003.
19. M. Houde, D. C. G. Muir, G. T. Tomy, D. M. Whittle, C. Teixeira and S. Moore, *Environ. Sci. Technol.*, 2008, **42**, 3893-3899.
20. A. Gawor and F. Wania, *Environmental Science: Processes & Impacts*, 2013, **15**, 1671-1684.
21. K. Breivik, G. Czub, M. S. McLachlan and F. Wania, *Environ. Int.*, 2010, **36**, 85-91.
22. *SPIN - Substances in Preparations in Nordic Countries*, www.spin2000.net, Accessed September, 2012.
23. F. Wania, K. Breivik, N. J. Persson and M. S. McLachlan, *Environ. Modell. Softw.*, 2006, **21**, 868-884.
24. G. Czub and M. S. McLachlan, *Environ. Toxicol. Chem.*, 2004, **23**, 2356-2366.
25. S. Shojania, *Chemosphere*, 1999, **38**, 2125-2141.
26. D. Sijm and T. L. Sinnige, *Chemosphere*, 1995, **31**, 4427-4435.

638   27.   K. G. Drouillard, G. T. Tomy, D. C. G. Muir and K. J. Friesen, *Environ. Toxicol. Chem.*, 1998, **17**,
639   1252-1260.

640   28.   K. J. Friesen, T. Hlebert, K. Drouillard, A. T. Fisk, Å. Bergman, G. T. Tomy, S. A. Tittlemeier, J. B.
641   Westmore and D. C. G. Muir, *Organohalogen Compd.*, 1995, **24**, 5.

642   29.   ACD/ADME Suite 5.0, version 12.0, *Advanced Chemistry Development, Inc.*, Toronto,
643   www.acdlabs.com, 2012

644   30.   J. Glüge, C. Bogdal, M. Scheringer, A. M. Buser and K. Hungerbühler, *J. Phys. Chem. Ref. Data*,
645   2013, **42**, 023103-023112.

646   31.   F. Wania, *Environ. Sci. Technol.*, 2003, **37**, 1344-1351.

647   32.   A. Beyer, F. Wania, T. Gouin, D. Mackay and M. Matthies, *Environ. Toxicol. Chem.*, 2002, **21**,
648   941-953.

649   33.   U. S. EPA, *Estimation Programs Interface Suite(TM) for Microsoft Windows, v 4.1*,
650   http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm.

651   34.   J. A. Arnot, T. N. Brown, F. Wania, K. Breivik and M. S. McLachlan, *Environ. Health Perspect.*,
652   2012, **120**, 1565-1570.

653   35.   J. A. Arnot, T. Gouin and D. Mackay, *Development and application of models of chemical fate
654   in Canada. Practical methods for estimating environmental biodegradation rates. Report to
655   Environment Canada.* CEMN Report No. 200503, Canadian Environmental Modelling Network
656   (CEMN), Trent University, Peterborough, 2005.

657   36.   T. N. Brown, J. A. Arnot and F. Wania, *Environ. Sci. Technol.*, 2012, **46**, 8253-8260.

658   37.   J. A. Arnot, D. Mackay, T. F. Parkerton and M. Bonnell, *Environ. Toxicol. Chem.*, 2008, **27**,
659   2263-2270.

660   38.   J. A. Arnot, W. Meylan, J. Tunkel, P. H. Howard, D. Mackay, M. Bonnell and R. S. Boethling,
661   *Environ. Toxicol. Chem.*, 2009, **28**, 1168-1177.

662   39.   G. A. Moser and M. S. McLachlan, *Environ. Sci. Technol.*, 2002, **36**, 3318-3325.

663   40.   E. Sverko, G. T. Tomy, C. H. Marvin and D. C. G. Muir, *Environ. Sci. Technol.*, 2012, **46**, 4697-
664   4698.

665   41.   Z. Zencak, A. Borgen, M. Reth and M. Oehme, *J. Chromatogr. A*, 2005, **1067**, 295-301.

666   42.   J. Hüttig and M. Oehme, *Chemosphere*, 2006, **64**, 1573-1581.

667   43.   S. Moore, L. Vromet and B. Rondeau, *Chemosphere*, 2004, **54**, 453-459.

668   44.   M. Reth and M. Oehme, *Anal. Bioanal. Chem.*, 2004, **378**, 1741-1747.

669   45.   M. Reth, Z. Zencak and M. Oehme, *J. Chromatogr. A*, 2005, **1081**, 225-231.

670   46.   M. Coelhan, M. Saraci and H. Parlar, *Chemosphere*, 2000, **40**, 685-689.

671   47.   G. T. Tomy, J. B. Westmore, G. A. Stern, D. C. G. Muir and A. T. Fisk, *Anal. Chem.*, 1999, **71**,
672   446-451.

673   48.   Z. Zencak, M. Reth and M. Oehme, *Anal. Chem.*, 2003, **75**, 2487-2492.

674   49.   K. Breivik, J. A. Arnot, T. N. Brown, M. S. McLachlan and F. Wania, *J. Environ. Monit.*, 2012,
675   **14**, 2028-2037.

676   50.   F. Wania, J. Persson, A. Di Guardo and M. S. McLachlan, *The POPCYCLING-Baltic model. A
677   non-steady state multicompartment mass balance model of the fate of persistent organic
678   pollutants in the Baltic Sea environment.* NILU: OR 10/2000, Norwegian Institute for Air
679   Research, Kjeller, 2000.

680   51.   K. Breivik and F. Wania, *Environ. Sci. Technol.*, 2002, **36**, 1014-1023.

681   52.   K. Breivik and F. Wania, *Environ. Sci. Technol.*, 2002, **36**, 1024-1032.

682   53.   IVL Svenska Miljöinstitutet, *POP i luft*, http://www3.ivl.se/db/plsql/dvspopluft$.startup,
683   Accessed Jan. 31st, 2013.

684   54.   IVL Svenska Miljöinstitutet, *Miljöövervakningsdata: Screening av miljögifter*,
685   http://dvss.ivl.se/DataSelect.aspx, Accessed Jan. 31st, 2013.

686   55.   A. K. Halse, M. Schlabach, J. K. Schuster, K. C. Jones, E. Steinnes and K. Breivik, Unpublished
687   work.

688   56.   E. Fjeld, M. Schlabach, J. A. Berge, E. T., P. Snilsberg, G. Källberg, S. Rognerud, E. K. Enge, A.
689   Borgen and H. Gundersen, *Screening of selected new organic contaminants - brominated*

690   *flame retardants, chlorinated paraffins, bisphenol-A and trichlosan* TA-2006/2004, Norwegian
691   Institute for Water Research, Oslo, 2004.

692 57. T. Bakke, S. Boitsov, E. M. Brevik, G. W. Gabrielsen, N. Green, L. B. Helgason, J. Klungsøyr, H.
693   Leknes, C. Miljeteig, A. Måge, B. E. Rolfsnes, T. Savinova, M. Schlabach, B. B. Skaare and S.
694   Valdersnes, *Mapping selected organic contaminants in the Barents Sea 2007*, TA-2400/2008,
695   Norwegian Pollution Control Authority, Oslo, 2008.

696 58. A. J. Peters, G. T. Tomy, K. C. Jones, P. Coleman and G. A. Stern, *Atmos. Environ.*, 2000, **34**,
697   3085-3090.

698 59. A. Borgen, M. Schlabach and H. Gundersen, *Organohalogen Compd.*, 2000, **47**, 272 - 275.

699 60. U. E. Fridén, M. S. McLachlan and U. Berger, *Environ. Int.*, 2011, **37**, 1169-1174.

700 61. P. Stejnarova, M. Coelhan, R. Kostrhounova, H. Parlar and I. Holoubek, *Chemosphere*, 2005,
701   **58**, 253-262.

702 62. S. Iozza, C. E. Müller, P. Schmid, C. Bogdal and M. Oehme, *Environ. Sci. Technol.*, 2008, **42**,
703   1045-1050.

704 63. G. O. Thomas and K. C. Jones, *Chlorinated paraffins in human and bovine milk-fat. A report on
705   a research project funded by the Eurochlor chlorinated paraffin sector group*, Department of
706   Environmental Sciences, Lancaster University, Lancaster, 2002 [cited in ref. 3].

707 64. M. Reth, Z. Zencak and M. Oehme, *Chemosphere*, 2005, **58**, 847-854.

708 65. P. O. Darnerud, M. Aune, A. Glynn and A. Borgen, *Chlorinated paraffins in Swedish breast
709   milk*, PM 18/12 (order no. 511 080), Swedish Chemicals Agency, Sundbyberg, 2012.

710 66. M. Reth, A. Ciric, G. N. Christensen, E. S. Heimstad and M. Oehme, *Sci. Total Environ.*, 2006,
711   **367**, 252-260.

712 67. G. O. Thomas, D. Farrar, E. Braekevelt, G. Stern, O. I. Kalantzi, F. L. Martin and K. C. Jones,
713   *Environ. Int.*, 2006, **32**, 34-40.

714 68. M. MacLeod, A. J. Fraser and D. Mackay, *Environ. Toxicol. Chem.*, 2002, **21**, 700-709.

715 69. W. Slob, *Risk Anal.*, 1994, **14**, 571-576.

716 70. U. Fridén and M. S. McLachlan, *Substansflödanalys av klorparaffiner i Stockholms stad 2004*,
717   Stockholm Stad Miljöforvaltningen, Stockholm, Sweden, 2007.

718 71. H. D. van der Gon, M. van het Bolscher, A. Visschedijk and P. Zandveld, *Atmos. Environ.*,
719   2007, **41**, 9245-9261.

720 72. H. Andersson, A. P. Cousins, J. Westerdahl, H. Braun, L. Bergfors, E. Brorström-Lundén, M.
721   Pettersson, T. Wickman, A. Jamtrot, H. Parkman, J. Krupanek, J. Fridmanis, V. Toropovs, M.
722   Verta and U. Nielsen, *Major sources and flows of the Baltic Sea action plan hazardous
723   substances, WP4 final report*, IVL Swedish Environmental Research Institute, Stockholm,
724   Sweden, 2012.

725 73. K. G. Drouillard, T. Hiebert, P. Tran, G. T. Tomy, D. C. G. Muir and K. J. Friesen, *Environ.
726   Toxicol. Chem.*, 1998, **17**, 1261-1267.

727 74. F. Pellizzato, M. Ricci, A. Held, H. Emons, W. Böhmer, S. Geiss, S. Iozza, S. Mais, M. Petersen
728   and P. Lepom, *TrAC, Trends Anal. Chem.*, 2009, **28**, 1029-1035.

729 75. S. Geiss, M. Schneider, G. Donnevert, J. W. Einax, N. Lettmann, A. Rey, H. Lepper, B. Körner,
730   T. Prey, B. Hilger, M. Engelke, M. P. Strub, H. Adrien, G. Sawal, D. Löffler, T. Schillings, I.
731   Hussy, P. Steinbichl, S. Scharf, A. Ruderisch, J. E. Olmos, F. J. Santos, A. Bartolome and J.
732   Caixach, *Accreditation and Quality Assurance*, 2012, **17**, 15-25.

733 76. W. Meylan, R. Boethling, D. Aronson, P. Howard and J. Tunkeli, *Environ. Toxicol. Chem.*, 2007,
734   **26**, 1785-1792.

735 77. A. T. Fisk, C. D. Cymbalisty, A. Bergman and D. C. G. Muir, *Environ. Toxicol. Chem.*, 1996, **15**,
736   1775-1782.

737 78. A. T. Fisk, C. D. Cymbalisty, G. T. Tomy and D. C. G. Muir, *Aquat. Toxicol.*, 1998, **43**, 209-221.

738 79. A. T. Fisk, S. C. Wiens, G. R. B. Webster, W. Bergman and D. C. G. Muir, *Environ. Toxicol.
739   Chem.*, 1998, **17**, 2019-2026.

740 80. L. X. Zeng, T. Wang, P. Wang, Q. Liu, S. L. Han, B. Yuan, N. L. Zhu, Y. W. Wang and G. B. Jiang,
741   *Environ. Sci. Technol.*, 2011, **45**, 5529-5535.

742   81.   S. Geiss, N. Lettmann, A. Rey, H. Lepper, B. Körner, S. Mais, T. Prey, B. Hilger, M. Engelke, S.
743   Lebertz, C. Chatellier, G. Sawal, D. Löffler and T. Schillings, *Clean-Soil Air Water*, 2011, **39**,
744   537-542.
745   82.   Q. L. Li, J. Li, Y. Wang, Y. Xu, X. H. Pan, G. Zhang, C. L. Luo, Y. Kobara, J. J. Nam and K. C. Jones,
746   *Environ. Sci. Technol.*, 2012, **46**, 11948-11954.
747   83.   T. Wang, S. L. Han, B. Yuan, L. X. Zeng, Y. M. Li, Y. W. Wang and G. B. Jiang, *Environ. Pollut.*,
748   2012, **171**, 38-45.
749   84.   B. Yuan, T. Wang, N. L. Zhu, K. G. Zhang, L. X. Zeng, J. J. Fu, Y. W. Wang and G. B. Jiang,
750   *Environ. Sci. Technol.*, 2012, **46**, 6489-6496.
751   85.   L. X. Zeng, T. Wang, W. Y. Han, B. Yuan, Q. A. Liu, Y. W. Wang and G. B. Jiang, *Environ. Sci.
752   Technol.*, 2011, **45**, 2100-2106.
753   86.   L. Zeng, H. Li, T. Wang, Y. Gao, K. Xiao, Y. Du, Y. Wang and G. Jiang, *Environ. Sci. Technol.*,
754   2012, **47**, 732-740.

755