Determination of chlorinated paraffins in sediments from the Firth of Clyde by gas chromatography with electron capture negative ionisation mass spectrometry and carbon skeleton analysis by gas chromatography with flame ionisation detection

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Abstract

Short chain chlorinated paraffins (SCCPs) are a group of persistent organic pollutants (POPs) of increasing concern, but are to date not widely investigated in the environment, largely due to the challenges involved in their quantification. Here, SCCPs were quantified in marine sediments from the Firth of Clyde, Scotland, by gas chromatography with electron capture negative ionisation mass spectrometry (GC–ECNIMS) and through carbon skeleton analysis by gas chromatography with flame ionisation detection (GC–FID), and the analytical challenges encountered are discussed. Concentrations in the sediments ranged from 0.4 to 69 μg kg \(^{-1}\) when determined by GC–ECNIMS, and from 5.6 to 379 μg kg \(^{-1}\) when determined by GC–FID. For 8 out of 11 samples, analysis by GC–FID gave higher results than analysis by GC–ECNIMS. Unexpected aspects of the analysis, such as the presence of high concentrations of longer chain chlorinated paraffins in the samples, are also presented.

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1. Introduction

Short chain chlorinated paraffins (SCCPs) have been listed on the OSPAR List of Chemicals for Priority Action and are classified under the European Community Water Framework Directive (WFD) as Priority Hazardous Substances, because of their toxicity, persistence and tendency to bioaccumulate and biomagnify (OSPAR, 2001). SCCPs have been produced on a large scale since the 1930s, initially as high pressure lubricants, then also for use as plasticisers and flame retardants in adhesives, paints, rubber and sealants (Muir et al., 2000). SCCPs have been detected in remote areas, for example in Arctic biota (Reth et al., 2006), indicating that they can undergo long range transport and are already ubiquitous in the environment. Toxicity studies have shown that SCCPs are carcinogenic to rats and mice (Hallgren and Darnerud, 1998) and there is also evidence of toxic effects on fish and shellfish (Haux et al., 1982; Cooley et al., 2001). For example, freshwater daphnids showed 50% mortality after 5 days exposure at 10 μg L \(^{-1}\) (UNEP, 2009). Therefore steps are now being undertaken to restrict the use of SCCPs in the EU under REACH (Registration, Evaluation and Authorization of Chemical Substances; European Chemicals Agency, 2009).

Chlorinated paraffins (CPs) are formed by the chlorination of \(n\)-paraffins, with carbon chain lengths of 10–30 carbon atoms and with a chlorine content of 30–70% by weight (WHO, 1996; OSPAR, 2001). CP formulations are therefore highly complex mixtures that contain a large number of structural isomers, theoretically more than 10,000 diastereoisomers and enantiomers. SCCPs are defined as \(C_{10-13}\) paraffins with greater than 48% chlorination by weight. \(C_{14-17}\) CPs are defined as medium chain chlorinated paraffins (MCCPs), and \(C_{18-20}\) CPs as long chain chlorinated paraffins (LCCPs). To date the main environmental and health concerns – in particular concerns about toxicity to aquatic biota – with chlorinated paraffins lie with the short chains, as they are the most toxic, water soluble and bioavailable of the CPs. However, there are increasing concerns about the toxic effects of the longer chained paraffins, as they have also been shown to bioaccumulate and biomagnify in the food chain. For example, the government of Canada concluded in 2009 that all CPs up to \(C_{20}\) are toxic (USEPA, 2009).

Limited environmental data are available to date, largely due to the complexity of CP analysis. Extraction of all CPs of various chain-lengths and degrees of chlorination from environmental samples is a straightforward procedure, however quantification is a complicated task due to possible interferences in the chromatogram, in addition to the various issues with standards. Most data to date have been produced with lengthy and complicated analytical methods, often requiring specialist equipment. Several Canadian studies used gas chromatography with high resolution mass spectrometry (GC–HRMS) for analysis of environmental samples (Tomy and Stern, 1999; Tomy et al., 1999; Houde et al., 2008).
Studies at the University of Basel focused on SCCP analysis by gas chromatography with low resolution mass spectrometry, but applied very detailed analysis of the chromatograms, including evaluation of isotope ratios and high-resolution GC peak shapes (Reth and Oehme, 2004). They also investigated the suitability of a range of highly specialised equipment for SCCP analysis, including gas chromatography with negative ion chemical ionisation mass spectrometry using a methane/dichloromethane gas mixture as reagent gas, electron ionisation tandem mass spectrometry and GC–HRMS (Zencak et al., 2005). Other instrumentation used for SCCP analysis are GC–HRMS with metastable atom bombardment and two-dimensional gas chromatography linked to a time of flight (ToF) mass spectrometer (Eljarrat and Barcelo, 2006).

Whilst due to its complexity SCCP analysis surely benefits from such methods, laboratories obliged to complete routine monitoring, for example for the WFD, require more straightforward methods, which allow the processing of higher sample numbers and do not require highly specialised equipment and operators. Sample extraction and clean-up are very similar for most published methods. Solid samples are commonly extracted by soxhlet (Tomy et al., 1999) or pressurised liquid extraction (Tomy and Stern, 1999) and cleaned up by silica and/or Florisil (Tomy et al., 1999; Reth et al., 2005) column chromatography or gel permeation chromatography (Houde et al., 2008). Currently there are two main analytical methods optimised and validated. The main analytical approach is by gas chromatography with electron capture negative ionisation-mass spectrometry (GC–ECNIMS), as for example proposed by the European ISO CD T2010 working group (Geiss et al., 2010). An alternative method proposed by the Institute for Reference Materials and Measurements of the European Commission (IRMM) is carbon skeleton analysis. Both approaches have their limitations (see results and discussion) and are likely to give different results for the same sample (Pellizzato et al., 2009). There is currently no certified reference material available for SCCPs in marine samples. As determined SCCP concentrations depend on the method applied, establishing the true SCCP concentration of a sample of unknown SCCP composition is a difficult task, and monitoring bodies might have to resort to agreeing on a standard method giving comparable concentrations. The IRMM for example proposes a standard method to be used in the EU, which should, in connection with certified standards and reference materials, establish an operationally defined measurement (Pellizzato et al., 2009).

Marine Scotland Science investigated SCCP concentrations in the Firth of Clyde by two analytical methods, GC–ECNIMS and carbon skeleton analysis by gas chromatography with flame ionisation detection (GC–FID). The Firth of Clyde is the most industrialised and urbanised area of Scotland, and effluent and accidental discharges from engineering works, military bases, textile and paper industries and a coal power station have resulted in contamination of the area. Thus it was expected that, if SCCPs were present in Scottish waters, the highest concentrations would be found in the Clyde. The advantages, disadvantages and limitations of both methods are discussed, and preliminary concentrations from the Firth of Clyde are presented.

2. Materials and methods

2.1. Sampling

Samples in this study were collected in the Firth of Clyde, west Scotland, in November 2007. Sediment samples were collected by Day Grab at four locations in the Firth of Clyde: Pladda, Garroch Head, Holy Loch and Skelmorlie (Fig. 1). Three samples were collected from Garroch Head, Holy Loch and Skelmorlie. However, due to sampling problems, only two samples were obtained from Pladda. Samples were immediately transferred to solvent washed aluminium cans and frozen at −20 °C. Before analysis, samples were freeze dried and grounded.

2.2. Sample extraction and clean-up

2.2.1. Preparation of standard solutions

Solvents used were HPLC grade iso-hexane and acetone from Rathburn Chemicals Ltd., Scotland, UK. Three chlorinated SCCP technical mixtures (51.5%, 55.5% and 63% chlorination, 100 ng L⁻¹, Ehrenstofer, Germany) were used to prepare SCCP calibration standards. Five dilutions were prepared for each of the technical mixtures, at concentrations of 75, 50, 20, 10 and 2 ng L⁻¹, respectively. 13C-Hexachlorobenzene (13C HCB, 100 ng L⁻¹, Cambridge Isotopes Ltd., UK) was included as internal standard in the calibration standards for GC–ECNIMS analysis at a concentration of 0.2 ng L⁻¹. 2,2,4,4,6,8,8-Heptamethylnonane (HMN; 98% purity, Sigma Aldrich, UK) was included as internal standard in the calibration standards for carbon skeleton analysis by GC–FID at a concentration of 10 ng L⁻¹. Alkanes-Mix10 (C₁₀–C₁₅, 500 ng L⁻¹, Ehrenstofer, Germany) was used to make up five alkane calibration standards for carbon skeleton analysis at concentrations of 25.0, 12.5, 5.0, 2.5 and 0.5 ng L⁻¹ in iso-hexane.

For determination of the limit of detection (LoD) and recoveries of the GC–ECNIMS method a spiking solution containing 2.5 ng L⁻¹ of the 55%Cl SCCP technical mixture (Ehrenstofer, Germany) was prepared.

2.2.2. Spiking of samples for LoD and recoveries in GC–ECNIMS analysis

As there is currently no suitable certified reference material available, spiked sample had to be used for LODs and recoveries. For the LOD 10 g wet mussel (n = 7) or 20 g dry sediment (n = 7)
were spiked with 250 ng 55%Cl SCCP technical mixture. For recoveries of low concentration 1 g wet mussel \((n = 7)\) or 20 g dry sediment \((n = 7)\) was spiked with 250 ng 55%Cl SCCP technical mixture, for recoveries of higher concentration 10 g mussel \((n = 7)\) or 20 g sediment \((n = 7)\) was spiked with 2.5 μg 55%Cl SCCP technical mixture.

2.2.3. Pressured liquid extraction (PLE)

Prior to use, all glassware and pressurised liquid extraction (PLE) cells were rinsed with acetone and iso-hexane. Anhydrous sodium sulphate was washed ultrasonically with dichloromethane (DCM) followed by iso-hexane and dried at 150 °C. Glass fibre filters were muffled at 200 °C for 12 h. PLE cells (100 ml) were tightly packed with the following \(\text{from bottom to top of the cell}:\) 2 filter papers, sodium sulphate (10 g), 5% deactivated alumina (15 g), 1 filter paper, freeze dried sediment (20 g) mixed with equal amounts \(\text{(by weight)}\) sodium sulphate, sodium sulphate to 0.5 cm from the top, followed by another filter paper. Samples were extracted in iso-hexane at 100 °C and 1500 psi \(\text{(5 min heating, 2 \times 5 min static cycles, 50% cell flush, 120 s purge with N}_2(\text{g}))\).

2.2.4. Extract clean-up and concentration

Any remaining co-extractive and other organic contaminants \(\text{(e.g. polychlorinated biphenyls (PCBs))}\) were separated from the SCCPs in a Florisil clean-up step adapted from Reth et al. (2005). Glass chromatography columns \(\text{(22 cm \times 1 cm ID)}\) were packed with 1.5% deactivated Florisil \(\text{(4 g, Sigma Aldrich, UK)}\), which had been muffled at 600 °C. The columns were conditioned with iso-hexane \((5 \text{ mL})\) before the extracts were added. The extracts were eluted with 15 mL iso-hexane followed by 25 mL acetone. The iso-hexane fraction contained PCBs and toxaphenes and was discarded. The acetone fraction was concentrated by rotary evaporation and solvent exchanged to iso-hexane. \(^{13}\text{C} \text{ HCB (30 μL of a 0.1 ng μL}^{-1} \text{ solution)}\) and \(^{13}\text{C HCB (30 μL of a 0.5 ng μL}^{-1} \text{ solution)}\) were added as internal standards to the sample before concentration to approximately 50 μL.

2.3. GC–ECNIMS analysis

SCCP concentrations were determined by GC–ECNIMS using an HP6890 Series gas chromatograph interfaced with an HP5973N MSD, fitted with a cool on-column injector. A medium polarity column \(\text{(RTX1614, 15.0 m \times 0.25 μm \times 0.10 μm film thickness; Thames-Resteck, UK)}\) was used for the analyses \(\text{(RTX1614, 15.0 m \times 25 μm \times 0.10 μm film thickness; Thames-Resteck, UK)}\). The carrier gas was helium, set at a constant pressure of 15 psi. Methane was used to cause dechlorination and hydrogenation of CPs to alkanes in the injector. For this, a single tapered liner was packed with the following layers \(\text{(from bottom to top, as described by Koh et al. (2002)}\)): 0.5 cm glass wool, 0.1 cm CaCO₃ \(\text{(Sigma-Aldrich, UK)}\), 1 cm palladium catalyst, 0.2 cm glass wool. The palladium catalyst was prepared from palladium(II)chloride \(\text{(99% purity, Sigma-Aldrich, UK)}\) as described by Koh et al. (2002). Analysis with the modified liner quantified the carbon skeletons produced by the CPs plus any alkanes present in the extract. For the quantification of alkanes only, the liner was emptied, cleaned and packed with 0.5 cm glass wool. A non-polar column was used for the analyses \(\text{(Ultra 1, 25.0 m \times 200 μm \times 0.33 μm film thickness; Agilent Technologies, UK)}\). The carrier gas was hydrogen at a flow rate of 3.5 ml min\(^{-1}\). The injector and detector temperatures were held at 300 °C. The oven temperature was held at 50 °C for 3 min. Thereafter the temperature was raised to 10 °C min\(^{-1}\) up to a final temperature of 280 °C and held at this temperature for 25 min.

Each sample was analysed with and without the palladium liner. Sample results were calculated as in

\[
\text{Total SCCP (ng g}^{-1} \text{ dry weight)} = \sum_{C_{10-13}} \left( (C\text{ alk}\cdot C\text{P}_{\text{RF}} - C\text{ alk}_{\text{b}}) - (C\text{ alk}\cdot C\text{P}_{\text{b}} - C\text{ alk}_{\text{b}}) \right) \times CF \times SW
\]

\(\text{(1)}\)

Where \(C\text{ alk}\cdot C\text{P}_{\text{RF}}\) is the alkane&CP concentration in ng alkanes in the sample \(\text{(sample run with palladium catalyst), C alk}_{\text{b}}\) the alkane concentration in ng alkanes in the sample \(\text{(sample run without Pd catalyst), C alk}\cdot C\text{P}_{\text{b}}\) the alkanes&CP concentration in ng alkanes in the blank, \(C\text{ alk}_{\text{b}}\) is the alkane concentration in ng alkanes in the blank, \(C F\) the conversion factor from ng alkane to ng CP \(\text{(depends on level of chlorination), and SW is the sample dry weight [g].}\)

The GC–FI D was calibrated in the units ng alkanes μL\(^{-1}\) with dilutions of the Alkanes-Mix 10, with heptamethylnonane as internal standard. For comparison with the GC–ECNIMS method, results were converted to ng 55.5%Cl SCCPs μL\(^{-1}\) by multiplying by 2.17. This number was derived by establishing the average number of chlorine atoms in CPs of a given %Cl \(\text{(Eqs. 2a and 2b), followed by calculation of the average molecular weight of the CP and the corresponding alkane (The %Cl in a SCCP is the percentage of chlorine in the product molecular weight (Campbell and McConnell, 1980))}\)

\[
35.5 \times CI = \frac{\% Cl}{100} \times ((H - Cl) + 12 \times C + 35.5 \times Cl)
\]

\(\text{(2a)}\)

Which, solved for number of chlorine atoms in the SCCP, gives:

\[
CI = \frac{H + 12 \times C}{35.5 - 34.5}
\]

\(\text{(2b)}\)

Where CI is the number of chlorine atoms in the SCCP, \(H\) the number of hydrogen atoms in the corresponding alkane, \(C\) the number of carbon atoms, and %Cl is the percentage chlorination of the SCCP, e.g. 55.5%. 55.5% chlorinated C10 paraffin for example would therefore have an average of 4.82 chlorine atoms. Assuming an average molecule of \(C_{10}H_{17.5}Cl_{4.82}\), the CP would therefore have a weight of 308.29 g mol\(^{-1}\) compared to 142 g mol\(^{-1}\) of the corresponding alkane \(\text{(C}_{10}H_{22}),\) being 2.17 times heavier.

3. Results and discussion

3.1. GC–ECNIMS analysis

As GC–ECNIMS is the most widely used method for CP analysis, it was the method selected for investigation, and was validated in-house for shellfish and marine sediment. The following parameters were determined:
3.2. Linear response range

Triplicate analysis of the five standards for each of the three technical mixes (51.5%Cl, 55.5%Cl and 63%Cl) showed that the instrument response in the concentration range of 2–75 µg mL⁻¹ was linear. Correlation coefficients were 0.992, 0.995 and 0.997 for the 51.5%, 55.5% and 63% technical mixes respectively. However, the response increased significantly with increased chlorination, which is a recognised problem of SCCP analysis by ECNIMS (Huettig and Oehme, 2006). 55.5% and 63% chlorination gave 2 and 5 times (respectively) the instrument response of 51.5% chlorination. As the chlorination level of the sample is typically unknown, the 55.5% chlorinated standard was used for further method validation and sample quantification.

3.2.1. Instrument precision

The 55.5% technical mix was run at concentrations of 10 and 67.5 ng µL⁻¹ on separate days (n = 7), giving a variation of 13% for both concentrations.

3.2.2. Limit of detection

(LoD): The LoD was determined as 9.2 µg kg⁻¹ wet weight for biota and 2.9 µg kg⁻¹ dry weight for sediment.

3.2.3. Recovery

Recoveries ranged from 69–121% for sediment and 66–107% for biota.

The method validation shows that the extraction and clean-up step of the method are suitable for SCCP analysis, as >65% of SCCPs are extracted and carried through the clean-up step. Recoveries are comparable to other GC–ECNIMS methods. For example, Geiss et al. (2010) reported method recoveries of 68–119% from spiked water samples. Nicholls et al. (2001) reported recoveries for sediment spiked with SCCPs of 50–119% (n = 7) and for fish of 59% and 97% (n = 2). The main source of uncertainty encountered during method validation is that the instrument response increases strongly with the level of chlorination, which will be unknown in real samples. For example, quantification of a sediment sample spiked with 55.5% technical mix gave recoveries of 42%, 118% and 259% when quantified against calibration standards made from 63%, 55.5% and 51.5% technical mix respectively. In the literature it is generally recommended that single SCCP congeners are quantified to establish the chlorination level of the sample, so that calibration standards of similar chlorination level to the sample can be chosen (Tomy et al., 1997; Coelhan, 1999). However, this requires multiple integrations of each sample, ideally followed by preparation of calibration standards of suitable chlorination level for quantification, which is not practical for routine analysis. Geiss et al. (2010) tackled the dependence of response on chlorination level by calibrating the instrument with a multiple linear regression, using standards of three different chlorination levels and quantifying just two m/z signals (327 and 423), which were identified as the most suitable signals to allow quantification that is not affected by chlorination level. They report recoveries of 72%, 88% and 112% from water samples from the river Ruhr spiked with dilutions (0.2 and 0.4 µg L⁻¹) of the 51.5%, 55.5% and 63% chlorinated custom mixes from Ehrenstorfer. However, when the 51.5%, 55.5% and 63% chlorinated custom mixes from Ehrenstorfer (50 µg L⁻¹) were quantified with this method by the authors, recoveries were 58%, 103% and 244% respectively, which is very similar to the results obtained by the method described here.

As the chlorination level of CPs in the Clyde sediments is unknown, the samples were quantified against the 55.5% SCCP technical mix, accepting that this could cause over- or underestimation of the SCCP concentration (depending on the chlorination level of SCCPs in the sample) and therefore render this method only semi-quantitative. However, for integration of chromatograms of the Clyde sediment samples, the main problem was possible interferences by other organic compounds. For example, for the Holy Loch sample (Fig. 2), the retention time span of the unresolved complex mixture (UCM) only partly coincides with the 55.5% SCCP standard. It must therefore be assumed that the clean-up did not remove all possible interferences. Similar observations of a UCM in marine sediment samples far exceeding the retention time span of the UCM in the standard were made by Huettig and Oehme (2006) when using Florisil clean-up, triple quadrupole GC–ECNIMS and the analytical method described by Reth et al. (2005).

Tests on the Florisil clean-up showed that polychlorinated biphenyls (PCBs) are eluted in the iso-hexane fraction and are therefore not present in the final extract (Webster et al., 2009). Polybrominated diphenyl ethers were partly eluted with the SCCPs, but they do not form interfering mass fragments. It is also reported in the literature that PCBs as well as toxaphenes, dichlorodiphenyltrichloroethane (DDT) and its metabolites, chlorinated benzenes and chlorinated aromatics are eluted in the hexane fraction (Tomy et al., 1997; Reth et al., 2005) Medium and long chain chlorinated paraffins however cannot be separated from SCCPs by the Florisil clean-up. Table 2 shows that most of the ions monitored could originate from MCCPs as well as SCCPs. Bearing this in mind, chromatograms were integrated as indicated by the grey box in Fig. 2a, possibly overestimating SCCP concentrations in the samples by the inclusion of some MCCPs.

No straightforward solution has been presented in the literature for exclusion of MCCPs by GC–ECNIMS analysis. Reth and Oehme (2004) propose that interference by MCCPs could, to some extent, be identified by investigating isotope ratios of individual congeners. They also point out that C16 and C17 MCCPs, which can form interfering mass fragments. It is also reported that chlorinated aromatics are eluted in the hexane fraction (Tomy et al., 1997; Reth et al., 2005) Medium and long chain chlorinated paraffins however cannot be separated from SCCPs by the Florisil clean-up. Table 2 shows that most of the ions monitored could originate from MCCPs as well as SCCPs. Bearing this in mind, chromatograms were integrated as indicated by the grey box in Fig. 2a, possibly overestimating SCCP concentrations in the samples by the inclusion of some MCCPs.

Fig. 2. Total ion chromatogram (TIC) of (a) the Holy Loch Site 2 (the area integrated was that in the grey box), (b) the 55.5% chlorinated SCCP technical mix with internal standard (13C-Hexachlorobenzene (13C HCB)) and (c) a 53% chlorinated MCCP (C14–C17) technical mix from Ehrenstorfer (full scan).
However, most could also be fragments of MCCP congeners with lower chlorination levels. It is not reported if this possibility was investigated or that the MCCPs were proven to be removed in the clean-up.

### 3.3. Carbon skeleton analysis

Carbon skeleton analysis was investigated as an alternative method of analysis of the same extracts, as it does not have any of the major uncertainties described for GC–ECNIMS. The instrument response does not depend on chlorination level, and MCCPs are easily distinguished from SCCPs by retention time of the produced n-alkanes. The SCCPs are converted in the palladium liner to n-alkanes of chain length C10, C11, C12 and C13, giving 4 easily distinguished alkane peaks, rather than the UCM observed following analysis by GC–ECNIMS.

Whilst the instrument response itself is not dependent on chlorination level of SCCPs in the sample, conversion of results to SCCP concentrations in weight does depend on the average chlorination level of the SCCP mixture in the sample. If this is unknown, it will add uncertainty to the calculation of the SCCP concentration. For example, assuming average chlorination of 63% would require multiplication of the carbon skeleton weight by 2.6, compared to multiplication by 2.17 for 55.5% chlorination. Therefore if a sample which actually has a chlorination level of 63% is assumed to have a chlorination level of 55%, this would lead to SCCP concentration in the sample being underestimated by about 16% if analysed by carbon skeleton analysis, compared to an overestimation by about 150% if the GC–ECNIMS were calibrated with a 55.5% chlorinated SCCP solution.

The five dilutions of the 55.5% Cl SCCP standard (with HMN added as internal standard) in the range of 2–75 ng µL⁻¹ were analysed as samples using the palladium catalyst. The linearity of conversion of SCCPs to alkanes in this range was good with $r^2$ values of >0.999. Recoveries for the conversion of the SCCP to n-alkanes using the palladium catalyst were calculated from the sum of calculated SCCPs of each chain length (C10 to C13) compared to the theoretical concentration of the SCCP technical mix and ranged from 73% to 133% for the five dilutions (one analysis per dilution). Carbon chain lengths C11 and C12 were dominant (33% and 38% of the sum of SCCPs), followed by C13 (21% of the sum of SCCPs), with C10 least abundant (8% of the sum of SCCPs). These results are comparable with those of Pellizzato et al. (2009).

The sample extracts which had been analysed by GC–MS were also analysed with the carbon skeleton method. As for analysis by GC–ECNIMS, an average SCCP chlorination level of 55.5% was assumed in the samples, therefore results were converted from ng alkane kg⁻¹ sample dry weight weight to ng 55.5%Cl SCCPs kg⁻¹ sample dry weight by multiplying by 2.17 (see Materials and Methods). Example chromatograms of Holy Loch Site 2 with and without the palladium catalyst, as well as a chromatogram of the Alkane-Mix 10, are shown in Fig. 3. Some C10 to C13-alkanes were present in the sample (Fig. 3c), but over 85% of the C10 to C13 carbon skeletons visible on the chromatogram of the SCCP derived alkanes & those alkanes already present in the sediment (Fig. 3b) originate from SCCPs. Similarly, for longer chain carbon skeletons,

![Fig. 3.](image-url)
which were not quantified, the amounts of carbon skeletons formed from chlorinated paraffins outweighed the \( n \)-alkanes present in the extract. However, Fig. 3c shows that there are some alkanes present in the sample which would be included in the calculation of the SCCP concentration, if the sample was not also analysed without the palladium liner. For the results presented in Table 1, alkane concentrations quantified without the palladium liner were subtracted from the total amount of carbon skeletons quantified with the palladium liner and the difference was converted to ng g\(^{-1}\) 55.5% Cl SCCPs.

3.4. Comparison of GC–ECNIMS vs carbon skeleton for Firth of Clyde samples

The 11 sediment samples from the Firth of Clyde were analysed by both methods. SCCP concentration ranges were determined as 0.4–69 μg kg\(^{-1}\) dry weight by GC–ECNIMS and 17–379 μg kg\(^{-1}\) by carbon skeleton analysis (Table 1).

Whilst the results from the two methods are in good agreement for some sites, for most sites the carbon skeleton analysis returns higher concentrations than the GC–ECNIMS method. This is unexpected, as it was anticipated that some MCCPs would be included in the calculated SCCP concentrations by the GC–ECNIMS method, whilst the carbon skeleton method separates MCCPs and SCCPs very clearly. Carbon skeleton analysis showed in fact that all samples contained medium and long chain CPs, as shown in Fig. 3 on the example of a Holy Loch Site 2 chromatogram and in Fig. 4 in summary for all chain lengths at all sites.

Medium and long chain chlorinated paraffins were not quantified, but the chromatograms show they are clearly present in significant concentrations and are very likely the main source of the interference observed in the SCCP UCMs observed during the GC–ECNIMS analysis.

The lower values by GC–ECNIMS compared to carbon skeleton analysis at some sites may indicate that average SCCP chlorination levels are significantly less than the assumed 55.5%, causing an underestimation by GC–ECNIMS and a slight overestimation by carbon skeleton analysis. This would be in agreement with reports by Huetting and Oehme (2006), that congeners with 4 and 5 chlorine atoms were not detected at all by GC–ECNIMS with the analytical method of Reth et al. (2004) in sediments from the North and Baltic Sea, whilst chloride attachment chemical ionisation mass spectrometry of the same extracts showed congeners with 4 and 5 chlorine atoms to be present at equal or even higher concentrations than higher chlorinated congeners.

3.5. Discussion of SCCP concentrations in the Firth of Clyde

Bearing in mind the quantification uncertainties discussed, the determined SCCP concentrations in the Firth of Clyde were compared with data from the literature. Table 1 shows that with both methods, concentrations were clearly lower at Pladda than at the other 3 sites (with the exception of Skelmorlie Site 3 by carbon skeleton analysis), which was expected. Pladda is a relatively clean site south of the Island of Arran, reasonably remote from known point sources of pollution, whilst Garroch Head, Skelmorlie and Holy Loch are all near possible point sources of contamination. Garroch Head was the sewage sludge dump site for the Glasgow area from 1904 to 1998, with more than 1500,000 tonnes of sewage sludge dumped there annually. Holy Loch is furthest up the Clyde estuary and therefore may be subject to industrial and urban

### Table 1

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<th>Sample location</th>
<th>GC–MS (μg kg(^{-1}))</th>
<th>GC–FID (μg kg(^{-1}))</th>
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### Table 2

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<td>327, 329</td>
<td>( C_{11}H_{18}Cl_{6} )</td>
<td>( C_{17}H_{32}Cl_{4} )</td>
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<tr>
<td>361, 363</td>
<td>( C_{11}H_{17}Cl_{7} )</td>
<td>( C_{17}H_{31}Cl_{5} )</td>
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<td>341, 343</td>
<td>( C_{12}H_{20}Cl_{6} )</td>
<td>( C_{17}H_{30}Cl_{6} )</td>
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<td>375, 377</td>
<td>( C_{12}H_{19}Cl_{7} )</td>
<td>( C_{17}H_{29}Cl_{5} )</td>
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<td>409</td>
<td>( C_{13}H_{24}Cl_{7} )</td>
<td>( C_{17}H_{28}Cl_{5} )</td>
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<td>411</td>
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<td>( C_{17}H_{27}Cl_{6} )</td>
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<td>389, 391</td>
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<td>( C_{17}H_{26}Cl_{6} )</td>
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<tr>
<td>425</td>
<td>( C_{13}H_{24}Cl_{7} )</td>
<td>( C_{17}H_{25}Cl_{6} )</td>
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Fig. 4. Peak areas of CPs (difference between peak areas of CPs plus alkanes and alkanes only) for each carbon chain length at each site.
inputs from the inner Clyde estuary. Holy Loch is also close to the main dredge spoil disposal point within the Clyde estuary, and it served as a naval base from 1961 to 1992. Skelmorlie is situated between the dredge spoil disposal point and a nuclear power station. Polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) concentrations in Clyde sediment have previously been reported by Webster et al. (2007). As CPs have partly replaced PCBs for use in metal working fluids, as additives in paints, coatings and sealants and also as flame retardants, sewage sludge and dredge spoils are possible sources of CPs. Table 3 shows that the SCCP concentrations reported here are of the same magnitude as total PCB (sum of 23 congeners) concentrations reported for these sites by Webster et al. (2007). There are few data available to date against which to compare these results. Castells et al. (2008) report higher SCCP concentrations of 210–1170 µg kg⁻¹ dry weight in coastal marine sediments from Barcelona. Determined by GC–ECNIMS scanning for [HCl₂]⁻ and [Cl⁻]⁻ ions and even higher SCCP concentrations from sediments at the mouth of Besos River, close to a submarine wastewater discharge, in the range of 1250–2090 µg kg⁻¹ dry weight. They also determined total PCBs (sum of 12 congeners), which were with concentrations of 2.33–44.0 µg kg⁻¹ dry weight for coastal marine sediments and 22.64–37.74 µg kg⁻¹ dry weight within the range of total PCBs reported here. Iozza et al. (2008) report total SCCP concentrations of 21 µg kg⁻¹ dry weight in the surface slice of a Swiss lake sediment core (by GC–ECNIMS method of Reth et al. (2004)), compared to a total PCB (6 congeners) concentration of just 1.3 µg kg⁻¹ dry weight. Even if it is taken into account that the PCB concentrations in the Clyde are the sum of 23 congeners compared to 12 and 6 respectively (Castells et al., 2008; Iozza et al., 2008), SCCP to PCB concentration ratios in the Clyde are relatively low compared to these studies. Iozza et al. (2008) also analysed deeper slices of the same core, which showed that CP concentrations overtook PCB concentrations in the 1970s and 80s, and CP flux into the sediment was still increasing in 2002. In UK marine sediments, total C₁₀–C₂₀ CP concentrations were determined in the 1970s by thin layer chromatography (Campbell and McConnell, 1980). In this survey the only Scottish sediment quantified was from the Minches, where concentrations were below the rather high detection limit of 50 µg kg⁻¹ wet weight. The Minches are remote from known point sources of organic contamination, and SCCP concentrations therefore comparable to the results reported here for Pladda. The highest concentrations of CPs (C₁₀–C₂₀) were 500 µg kg⁻¹ wet weight in Barmouth harbour, which exceed any concentrations reported here from the Firth of Clyde (Campbell and McConnell, 1980). More recently (2006) SCCPs and MCCPs in sediment from the North and Baltic Seas were quantified by GC–ECNIMS (analytical method by Reth et al. (2004)) with SCCP concentrations ranging from 8 to 63 µg kg⁻¹ dry weight and MCCP (C₁₄⁺C₁₅) concentrations ranging from 22 to 149 µg kg⁻¹ dry weight (Huettig and Oehme, 2006). Also quantified by GC–ECNIMS (analytical method by Tomy et al. (1997)) were 20 marine sediments from different Norwegian locations. The sediments were found to have much higher SCCP concentrations of 40–3650 µg kg⁻¹ dry weight and MCCP concentrations of 50–3240 µg kg⁻¹ dry weight (Petersen et al., 2006). Overall the SCCP concentrations reported here by both methods are therefore well within the (rather wide) range of SCCP concentrations reported from other marine sediments in Europe.

4. Conclusion

Overall it was confirmed that the GC–ECNIMS method is only semi-quantitative, due to the uncertainty linked to the dependence of the instrument response on CP chlorination level and the lack of distinction between many SCCP and MCCP congeners. However, whilst carbon skeleton analysis was expected to give comparatively lower SCCP concentrations due to its capability to clearly separate MCCPs from SCCPs, it in fact gave higher SCCP concentrations for a number of sites, suggesting that SCCPs at these sites may have relatively low chlorination levels.

SCCPs were detected in all 11 sediment samples analysed, even at Pladda, the most offshore site. This establishes that SCCPs are present in the Scottish marine environment and further investigations are necessary. Furthermore, the carbon skeleton analysis showed that there are considerable amounts of longer chain CPs present in these sediments which may be of concern if these do prove more toxic than has been assumed to date.

Despite the analytical issues discussed, the SCCP concentrations determined from sediments in the Clyde were with a range of 0.4–379 µg kg⁻¹ dry weight well within the range of SCCP concentrations reported from marine sediments to date.

Acknowledgements

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References


Haldgren, S., Danneu, P.D., 1988. Effects of polychlorinated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and chlorinated paraffins (CPs) on thyroid hormone levels and enzyme activities in rats. Organohalogen Compd. 35, 391–394.


<table>
<thead>
<tr>
<th>Site</th>
<th>Total SCCPs (µg kg⁻¹ dry weight)</th>
<th>Total PCBs (µg kg⁻¹ dry weight)</th>
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<tbody>
<tr>
<td>Pladda</td>
<td>0.4–20</td>
<td>0.1–7.1</td>
</tr>
<tr>
<td>Garroch Head</td>
<td>8.6–379</td>
<td>5.2–96</td>
</tr>
<tr>
<td>Holy Loch</td>
<td>60–128</td>
<td>20–86</td>
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<tr>
<td>Skelmorlie</td>
<td>5.6–164</td>
<td>3.1–57</td>
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</tbody>
</table>


