ANALYSIS OF SHORT-CHAIN (C_{10}-C_{13}) AND MEDIUM-CHAIN CHLORINATED PARAFFINS (C_{14}-C_{17}) IN NORWEGIAN SEDIMENT AND WATER SAMPLES BY GC/ECNI-MS

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Introduction

Chloroparaffins are produced by chlorination of n-alkanes (C_{10}-C_{30}). Due to their physical properties they are e.g. used as high-pressure additives in lubricants in the metal-processing industry, as softeners in PVC or as flame retardants [1,3]. Technical chloroparaffins consist of a mixture of straight-chain chloroparaffins of different chain length and degree of chlorination. The degree of chlorination can vary between 30-70 % depending on field of application [1,2]. Because of their physical and chemical features, chloroparaffins are hardly biologically degradable under environmental conditions [3]. Some data on chloroparaffins levels in the environment have been published [4,6,9], which admit to conclude that short-chain chloroparaffins (SCCP; C_{10}-C_{13}) and medium-chain chloroparaffins (MCCP; C_{14}-C_{17}) are ubiquitously detectable. In examinations, the toxicity especially of SCCP and MCCP in aquatic organism as well as the carcinogenic features of these compounds in animal tests could be proved. Medium-chain chlorinated paraffins show a similar eco-toxicological profile as short-chain chlorinated paraffins [3,8]. Therefore, attempts are made on a national and international basis to ban the production and use of short and medium-chain chloroparaffins.

Because of the complex composition of technical chloroparaffin products, the exact quantification of SCCP and MCCP standards is very difficult. Thus, no validated analytical method for the determination of chloroparaffins in environmental samples exists at the moment, which makes published data difficult to compare.
A relatively simple and selective method of analysis for the determination of short-chain chloroparaffins in environmental samples has been developed by Eurofins / GfA three years ago [6]. This method has been enhanced to include the determination of medium-chain chloroparaffins in solid and aqueous environmental matrices. In all these cases the quantification was done by GC/ECNI-MS. With this extended and improved method, several sediment and water samples from different Norwegian locations have been examined for their SCCP and MCCP content.

Materials and Methods

First of all the sediment samples were freeze-dried and approximately 10 g of each dry sample was soxhlet-extracted with toluene for 12 hours (which corresponds to about 160 extraction cycles). Water samples (approximately 1 litre) were filtrated for separation of suspended solid matter if present. The filtrate was liquid/liquid-extracted by means of toluene. After drying, the filter with the solid matter was soxhlet-extracted (12 hours) by using the toluene from liquid/liquid-extraction of the aqueous phase. Consequently, the raw extract comprised the dissolved and the particle-bound chloroparaffins (C_{10}-C_{17}) of the water samples.
After adding cis-chlordane as internal standard an aliquot of the raw extract was cleaned from organic matrix by means of concentrated sulfuric acid. Remaining sulphur compounds could be effectually removed by column chromatography via benzenesulphonic acid/silica gel/H_2SO_4 (44 %) and silica gel/silver nitrate (10 %). In a further clean-up step, the chloroparaffins could be separated from interfering organochlorine compounds such as PCBs by means of column chromatography using basic alumina (2 % H_2O) (1. fraction: 10 ml n-hexane/toluene (9:1); 2. fraction: 6 ml hexane; 3. fraction: 10 ml dichloromethane). No PCBs could be detected in the third fraction, while the recoveries of the different chloroparaffin mixtures and the internal standard were in the range of 90 % ± 10 %.

The identification and quantification of the chloroparaffins (C_{10}-C_{17}) was done by GC/ECNI-LRMS-SIM according to the method of Tomy et al [5]. The gas chromatographic separation of the chloroparaffins were carried out on a fused silica capillary column (DB-5 (J&W Scientific); 25 m; 0.32 mm i.d.; 0.25 µm film). The temperature of the injector (pulsed-splitless) was 250 °C, the ion-source temperature 150 °C and the quadropole temperature 100 °C. The most abundant isotope of the $[M\text{-}Cl]^-$-ion was used for quantification of the individual chloroparaffins. The second abundant isotope of this cluster was taken for identification (isotope ratio) to recognize possible interferences from other compounds or chloroparaffins themselves.
The identified chloroparaffin groups were quantified by means of the internal standard. The response factors of the individual chloroparaffins (defined by chain length and degree of chlorination) relative to the internal standard were determined using calibration mixtures containing chloroparaffins with different chlorine content. Seven different chloroparaffin standard mixtures were applied (SCCP: 51,5 %, 55,5 %, 60 % and 63 % chlorine content; MCCP: 42 %, 52 % and 57 % chlorine content) and the mixture which shows the most similar pattern to the analysed sample was used for the quantification.

Results and Discussion
The concentrations of the chloroparaffins (C_{10}-C_{17}) in 20 sediment (S1–S20) and 2 water samples (W1–W2) were determined by means of the forementioned method of analysis (compare Fig. 1 and Fig. 2). Chloroparaffins could be detected in most of the samples from different Norwegian locations. As shown in Figure 1 the SCCP concentrations in the sediment samples varied between 40 and 3650 ng/g (dry weight) and 40-70 ng/l in the water samples respectively. The MCCP concentrations in the sediment samples were in a similar range (50-3240 ng/g dry weight), the MCCP value in one water sample was significantly higher (1490 ng/l) (Figure 2).
Compared to published data of the SCCP concentrations in sediment and water, the concentrations determined here range in the same order of magnitude. In Norwegian sediment samples values of SCCP and MCCP between 10 – 7400 ng/g dw were reported [9]. Hüttig et al. [4] reported concentrations of total CP in sediment collected from the North and Baltic sea in the range of 5-499 ng/g dw.

Figure 1: Concentration of short-chain chlorinated paraffins in sediment (S1-S20) and water samples (W1-W2); subdivided into chain lenght (C_{10}-C_{13})

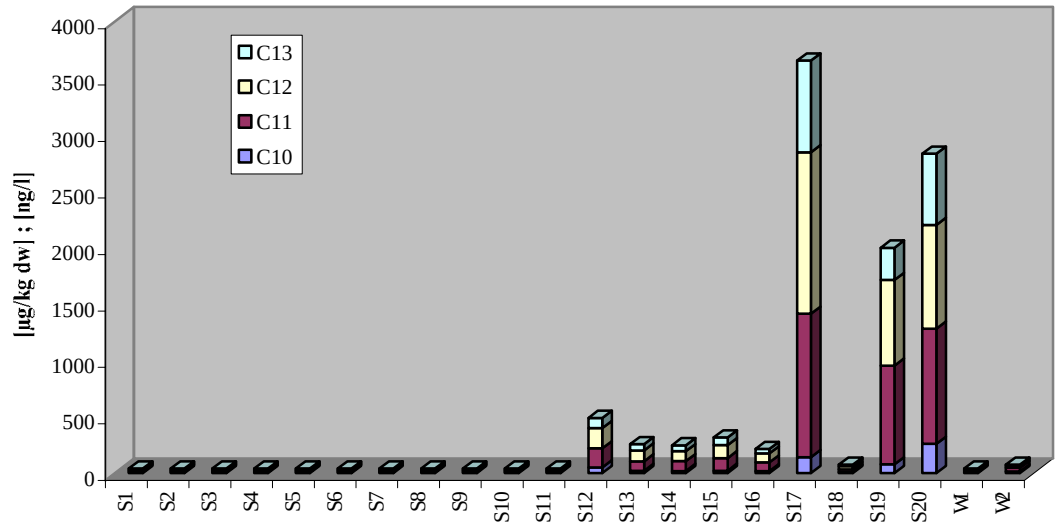
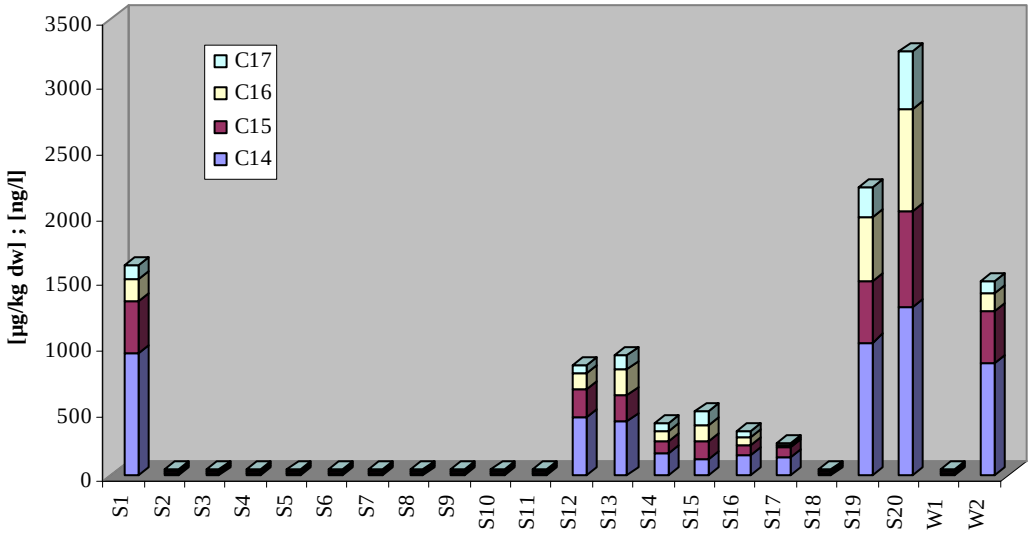


Figure 2: Concentration of medium-chain chlorinated paraffins in sediment (S1-S20) and water samples (W1-W2); subdivided into chain lenght (C_{14}-C_{17})

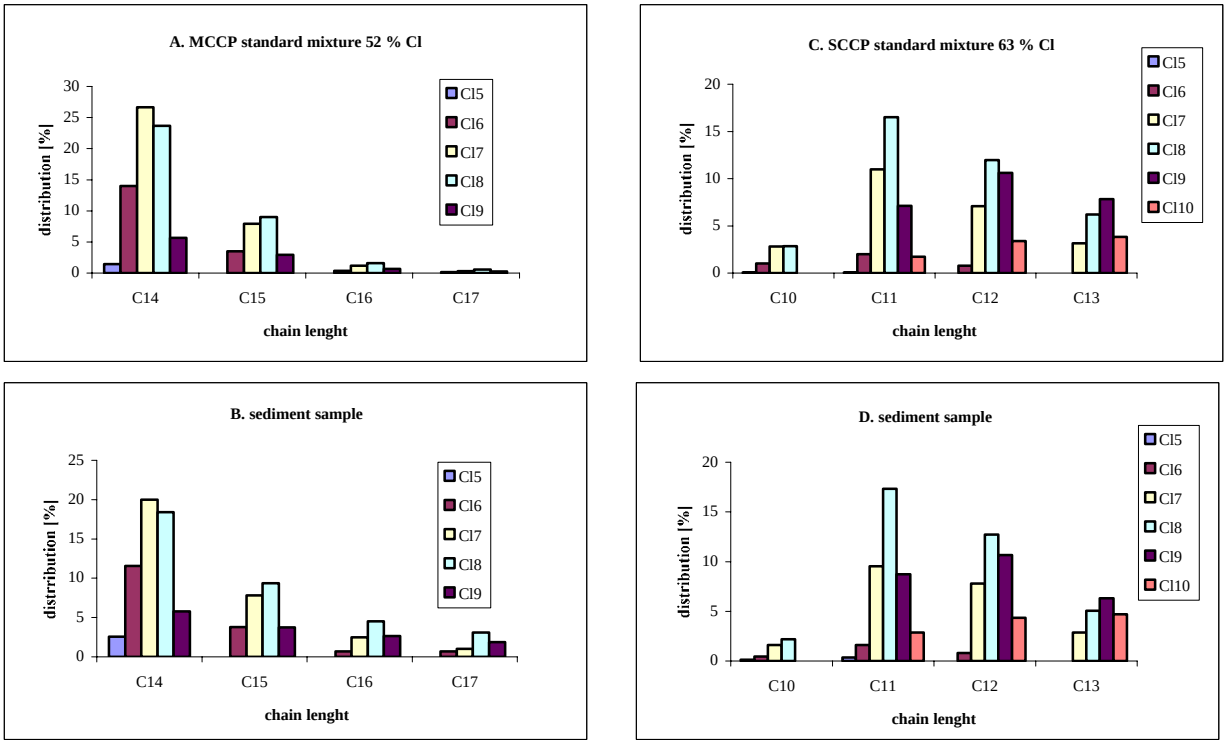


In most of the samples the concentrations of the MCCP were slightly above the SCCP values except one sediment (S1)and water sample (W2) the MCCP concentrations were significantly higher. Only in one sediment sample (S17) the SCCP dominate by a factor of 10. In all analysed environmental samples the undecanes and dodecanes (SCCP) were most abundant, the pattern of the SCCP is slightly different between the samples (chlorine content 59-63%). Contrary to the SCCP, the MCCP pattern were nearly identical and tetradecane congeners prevailed in the samples.

Chloroparaffin standard mixtures used for the quantification of SCCP and MCCP should have a similar pattern (degree of chlorination) to that of the sample to avoid errors in the quantification (Figure 3). Minor differences in the chlorine content (3 %) showed that considerable deviations of 30-90 % can occur. Tomy et al. [5] already reported that discrepancies of 100 % and more are possible, if the chlorine content does not fit to the analysed sample.

In case of this method of analysis, the recovery rate of the internal standard in the examined sample extract came up to 70-95 %, the limit of detection (LOD) for the individual chloroparaffin-groups (selected after chain-lenght and chlorine content) was 1-4 µg/kg. The reproducibility of SCCP and MCCP with this method was proven by double and multiple determination and addition of native chloroparaffins. In case of the examination for the MCCP, the coefficient of variation ranged between 1,4 % and 16,8 % and the recovery rates in the spiked samples varied between 81 % and 123 %. The validation data for the SCCP were in the same level and were reported elsewhere [6].

Figure 3: Relative concentrations [%] of the C10-C17 chloroparaffin-groups with 5-10 chlorine atoms (Cl5-10) in two different standard mixtures (A. and C.) and two sediment samples (B. and D.)



Conclusion

This study shows that we developed a selective and sensitive method that combined SCCP and MCCP analysis in environmental samples. It is essentiel to use a standard mixture with the same chloroparaffin pattern as that of the analysed sample, but only a few numbers of different chloroparaffin standard mixtures (variation in chain lenght and degree of chlorination) and individual standards are commercial available. Hence, to increase the accuracy of the quantification of chloroparaffins, more individual standards and mixtures are needed.

References

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