

SCREENING OF CHLORINATED PARAFFINS IN NORWAY

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Introduction

Chlorinated paraffins (CPs) are straight chain alkanes with varying degrees of chlorination. They have been produced since the 1930's to an extent of approximately 300 kilotons estimated for the western world¹ per year. CPs are mainly produced by direct chlorination of a petroleum fraction with molecular chlorine in the presence of UV-light¹. CPs have been used as high temperature and pressure lubricants as well as secondary plasticizers and flame retardants in plastics and paints^{1,2}. Recently CPs have been banned in all terms in Norway.

CPs are divided into three main categories, short chain (SCCP, C₁₀-C₁₃), medium chain (MCCP, C₁₄-C₁₇) and long chain (LCCP, C₁₈-C₃₀), and further by their degree of chlorination, low (<50%) and high (>50%)². Because of their relatively high assimilation and accumulation potential, the short chain and more highly chlorinated SCCPs have been the most widely studied. Although SCCP generally have shown low toxicity to mammals, SCCPs have a carcinogenic potential in rats and mice². In addition, dose-response studies have shown that oral intake of SCCP by mice, results in an increase in liver weight, which is considerable compared to reference materials⁶. They have also shown to be toxic towards certain species in the aquatic environment², although at concentration levels several orders of magnitude higher than for TCDD³. The complexity of CP mixtures makes it difficult to provide an analytical method for their precise and specific quantitative determination. Technical CP mixture consists of several thousand components, and due to the large number of isomers, complete chromatographic separation seems impossible at this point. This analytical challenge has resulted in different approaches to analysis of CP¹⁻⁵.

The aim of this project is to get an overview of the levels of SCCP in selected parts of the Norwegian environment. In this first part of the project, the focus has been on the risk of leaking from sewage deposits, air transport potentials and levels in marine biota.

Methods and Materials

Sample collection

Samples of sediment from landfills were collected from six different localities from the southern parts of Norway. Samples of cod liver and blue mussels were collected from three different parts of the Oslofjord to indicate a spatial distribution of PCA accumulation in these species. Furthermore, three samples of moss were analysed to indicate a potential of atmospheric spread of the PCA. The sampling sites are shown in figure 1.

Extraction and clean up

All the samples were added ¹³C-PCB 118 as an internal standard prior to the sample preparation. The sediment samples were filtered, and then Soxhlet extracted two times. First with Acetone and second with Acetone/Hexane. The moss and biological samples were homogenised with Sodium sulphate prior to cold extraction with Hexane/Acetone and Ethyl acetate/Cyclohexane respectively.

All the samples were further cleaned on a GPC system, sulphuric acid treated and then concentrated prior to the GC/MS analyses.

Analysis of PCA by GC/HRMS-EI

An HP5890 GC coupled to a VG AutoSpec, high resolution mass spectrometer was used for all of the analyses. The MS was operated in ECNI mode with Argon at a pressure of 2·10⁻⁵ mbar as reagent gas, monitoring the [M-Cl]⁻ ions for the different formula groups of the CPs. The quantification of the CPs were performed according to the method derived by Tomy⁹.

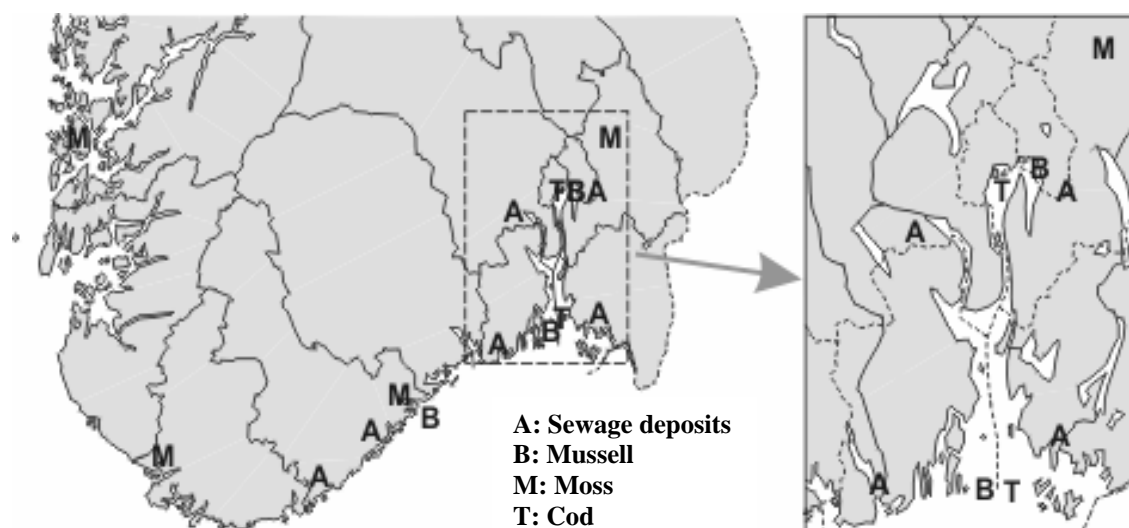


Figure 1. Sampling sites shown in a map of the south part of Norway.

Results and Discussion

The sampling sites (in the south of Norway) are shown in figure 1. Considerable amounts of SCCP were found in all samples. The results, shown in Table 1, are reported as the sum of C₁₀–C₁₃ SCCPs with 5-10 Chlorine substitutions. When interpreting these results, it should be taken into account that SCCP is a very complex mixture. An ideal internal standard is hard to find, and the analyses are very sensitive to the performance of the mass spectrometer. Two sediment

samples were also chosen for MCCP analysis, based on the measurement of six different formula groups⁸, and are reported as the sum of C₁₄-C₁₇ CP.

Table 1. The concentrations of Σ SCCP and Σ MCCP in sediments, moss, cod liver and mussel. The lipid content of cod liver and mussel samples are also shown.

	SCCP (ng/g ww)	MCCP (ng/g ww)	Lipid content (%)
Sediments			
Støleheia Kristiansand	860	n.a.	
Heftingsdalen Arendal	6500	2700	
Grinda Larvik	660	n.a.	
Lindum Drammen	19400	11400	
Grønmo Oslo	1190	n.a.	
Øra Fredrikstad	330	n.a.	
Moss			
Valvik	35	n.a.	
Molde	100	n.a.	
Narbuvoll	3	n.a.	
Codd liver			
Oslofjord (inner)	750	n.a.	35.5
Oslofjord (inner)	370	n.a.	32.8
Oslofjord (outer)	25	n.a.	31.4
Oslofjord (outer)	23	n.a.	31.1
Mussel			
Oslofjord (inner)	130	n.a.	1.6
Oslofjord (outer)	80	n.a.	3.1
Risøy	14	n.a.	1.7

The highest concentrations of CPs were found in sediment samples from Lindum and Heftingsdalen. There are reasons to believe that these high concentrations are due deposition of waste from mechanical or shipping industry. These high concentrations are therefore not surprising. The concentrations of SCCP in sediments samples reported here are in the same order of magnitude as concentrations found in sediments from industrial areas in the UK¹⁰. The sediment samples show a technical pattern of SCCPs suggesting that the sources are near the sampling locations.

The results from the moss samples indicate a potential of transport of SCCP by air. The potential of SCCP being transported by air is also supported by the results from a previous report⁷, where considerable concentrations of SCCP were found in ambient air samples from Bear Island. The concentrations were too high to be considered as a result of long range alone, but it can not be excluded.

The concentrations of SCCPs in the marine biological samples show an indication of more contamination of SCCPs in the inner than outer Oslofjord. Although the sample amounts are small, this is in agreement with previous studies of PCB and brominated flame retardants in cod liver from Oslofjord.

Chlorinated paraffins are, as mentioned earlier, banned in Norway. It is therefore important to continue with the environmental mapping of these pollutants to get more information of environmental levels and understanding of the long range transport.

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