

One-off survey of 2,4,6-tri-*tert*-butylphenol and short chained chlorinated paraffins in the Göta Älv estuary, Sweden

For Swedish Environmental Protection Agency

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1. Introduction

As an assignment from the Swedish Environmental Protection Agency, the Swedish Research Institute (IVL) has performed measurements of 2,4,6-tri-*tert* butylphenol and Short Chain Chlorinated Paraffins (SCCPs) in sediments. The study has been carried out based on Annex 2: *Strategy for a base line one off survey for SCCPs* (Agenda Item 7, ASMO 06/7/2-E-(L)) and from the OSPAR meeting, *Meeting of the environmental assessment and monitoring committee* (ASMO, Hamburg: 24-28 April 2006).

These measurements is a Swedish contribution to an “OSPAR base line one off survey” with sampling and analysis of SCCPs and 2,4,6-tri-*tert*-butylphenol in sediments collected in Göta Älv estuary on the Swedish west coast. This sampling was planned according to the advice to the design of the one-off surveys of chemicals identified for priority actions by ICES 2005 according to points 1-3:

1. The purpose of the one-off surveys is to gain a rapid overview of the occurrence of certain priority chemicals in the marine environment. This could be achieved already by small scale surveys through a limited number of samples, using one sampling type only (for example sediments) and concentrating sampling in estuaries;
2. A minimum of five samples per Contracting Party was required for a focused survey comprising one sample for reference, two samples from polluted areas and two samples from less polluted areas;
3. Sampling could be carried out for the purpose of several one-off surveys for different substances if provided in quantities of 50-500 g of the top centimetres of the sediments. If frozen and kept in a sample bank, the samples could be used at any time when the budget became available for their analysis and for the completion of the survey;

This project was carried out in cooperation between IVL and the consultant Marine Monitoring Ltd.

Apart from the 2,4,6-tri-*tert* butylphenol, analysis of 2,4-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenol were also included in this study.

1.1. Butylphenols

Tertiary butylphenols are phenolic compounds, containing at least one tertiary butyl group. 2,4,6-Tri-*tert*-butylphenol is on the OSPAR List of Chemicals for Priority Action.

1.1.1. Classification

In Figure 1 the molecular structures and the CAS number of the three butylphenols included in this study are presented. 2,4,6-tri-*tert*-butylphenol may be toxic, persistent and bioaccumulative, although data are limited and may need further validation (OSPAR 2003).

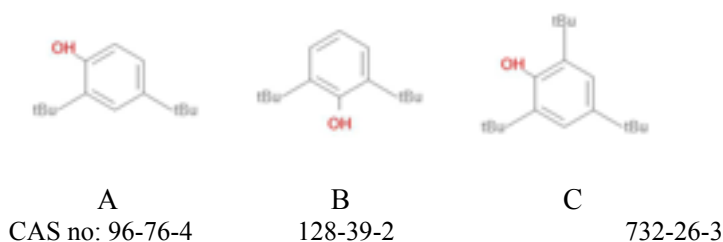


Figure 1. The molecular structures and CAS number of the butylphenols included in this study A) 2,4-di-tert-butylphenol, B) 2,6-di-tert-butylphenol and C) 2,4,6-tri-tert-butylphenol.

1.1.2. Production and use

2,4,6-Tri-*tert*-butylphenol is not thought to be produced in sufficient quantity to classify it as a High Production Volume Chemical (HPVC) and the production within EU has been reported to be in order of 10 tonnes per annum (OSPAR, 2003). According to the European Chemical Substances Information System (ESIS), there are only two companies in EU that are registered as Low Production Volume (LPV) producers/importers of 2,4,6-tri-*tert*-butylphenol (ESIS 2008).

Tertiary butylphenols are not produced in Sweden, but are imported as pure chemicals and in chemical products. 2,4,6-Tri-*tert*-butylphenol and other tertiary butylphenols are used as chemical intermediates in production of antioxidants in rubber and plastic, as lubricating agents in the transport sector, and as additives for gasoline and fuel oil distillate. 2,4,6-Tri-*tert*-butylphenol is also formed as a by-product in the production of 4-*tert*-butylphenol and it may also be included in resins used by the offshore sector (KemI 2004, OSPAR 2003).

The use of 2,4,6-tri-*tert*-butylphenol in Sweden have been relatively constant between 1999-2005, but the number of products that include this substance has declined from 21 to 8 during the same period of time. Denmark is the country in Scandinavia that has reduced the use of 2,4,6-tri-*tert*-butylphenol the most during the last years (from 36.4 tonnes in 2003 to 0.9 in 2005) (KemI SPIN 2008).

1.1.3. Emission sources and pathways to the marine environment

Information about the emissions and sources of 2,4,6-tri-*tert*-butylphenol are limited. Many of the *tert* butylphenols are expected to be released to municipal wastewater and further to the sewage treatment plants (STPs), making the STPs to potential secondary source of emissions. Releases to air of *tert* butylphenols are also possible for some applications, e.g private and industrial use of paints, glues and solvents (Remberger 2004).

2,4,6-Tri-*tert*-butylphenol used as an intermediate is likely to reach the marine environment via the discharge of wastewater from land-based production processes where the substance is produced or formulated into products. Other possible sources of emission are diffuse releases due to its presence as an impurity or degradation product in final formulations or articles. However, at present there is insufficient information available to assess the relative importance of these potential sources (OSPAR 2003).

1.2. SCCP

Chlorinated paraffins (CPs) are chlorinated derivatives of n-alkanes, having carbon chain lengths ranging from 10 to 38, with a chlorine content ranging from about 30 to 70% (by weight). SCCPs, CAS No 85535-84-8, have carbon chain lengths ranging from 10 to 13 (C₁₀-C₁₃) and a chlorine content more than 48% by weight.

1.2.1. Classification

In PARCOM Decision 95/1 on the Phasing Out of Short Chained Chlorinated Paraffins, Contracting Parties agreed (with reservations from Portugal and the United Kingdom) on the phasing out of SCCPs. SCCPs are included on the OSPAR List of Chemicals for Priority Action (OSPAR 2001).

The SCCPs are environmentally hazardous substances that are very persistent in the environment and are not biodegradable. They also adsorb strongly to sludge and sediments and are likely to bioaccumulate in organisms (OSPAR 2001). SCCPs may also be transported long distances through the air.

1.2.2. Production and use

The use of SCCPs in EU has been reduced from 13 000 tonnes in 1994 to 4 000 tonnes in 1998 (nearly 70%), mainly due to voluntarily agreements by the industry (OSPAR 2001). According to ESIS, there are eight High Production Volume (HPV) producers/importers of SCCPs registered in the EU (ESIS 2008).

The use of SCCPs in Sweden has decreased with more than 95% since 1995. The total use of SCCPs during 2005 was 12 tonnes (KemI 2007). SCCP and other chlorinated paraffins are not produced in Sweden, but imported as pure chemicals and in chemical products. SCCPs are mainly used in extreme pressure lubricants in the metal industry. They are also used in fillers or sealers, glues and coating material in the building industry, as flame-retardant in textiles and rubbers and fat liquoring agents in the leather industry.

1.2.3. Emission sources and pathways to the marine environment

The use of metal working fluids is the most important source of releases of SCCPs into the environment. The main emission sources for SCCPs to water, sediment and sewage sludge are production sites for SCCPs, production sites of metal working fluids and leather finishing agents, as well as metal working and leather finishing plants. Metal working plants are also sources for releases to landfills while leather finishing plants constitute an emission source to the air. Rubber working plants are emitting SCCPs to water, air and soil (OSPAR 2001).

As considered in PARCOM Decision 95/1, products that contain SCCPs are also potential sources of emissions. This can be the case during the whole life cycle, production and use, and when the articles become waste and are sent to landfill (OSPAR 2001).

The SCCPs enter the marine environment via inputs from rivers and atmospheric deposition. High levels of SCCPs in biological samples from the Arctic areas may indicate that these chemicals are effectively transported over long distances (OSPAR 2001).

2. Sampling sites

The sediment samples were collected at three sites in the Göta Älv estuary close to Göteborg at the Swedish west coast in September 2007, see Figure 2. Two samples were collected at the sites Eriksberg and Rivö, respectively, and one sample at the reference site Klinten.



Figure 2. The sampling site Eriksberg is located at the outlet of Göta Älv, and the sampling sites Rivö and Klinten at the inner part of the estuary.

The sampling site Klinten is considered as a background station, relatively far from the common water ways. The sampling site Eriksberg is expected to be the most affected area due to its location in the harbour of Göteborg. Rivö is considered as a transitional site between the two other sites. Table 1 summarizes the coordinates, depth and bottom conditions at the sampling sites.

Table 1. The sampling date, coordinates, depth and the bottom conditions at the sampling sites

	Sampling date	X coordinates (RT 90)	Y coordinates (RT 90)	Depth (m)	Bottom sediments
Eriksberg	2007-09-26	6403799	1268142	10	Clay
Rivö	2007-09-26	6399788	1260573	6	Clay with low contents of sand
Klinten	2007-09-26	6394257	1258422	9	Clay mixed with silt, scent of hydrogen sulphide

3. Methods

The surface sediment samples (0-2 cm) were collected with ponar grab and stored in pre-cleaned and burned glass bottles and were frozen prior to analysis.

The analyses of tert butylphenols were performed by IVL. The determination of SCCPs was done by NILU, Kjeller, Norway.

The analyses of butylphenols were performed as follows: The water in the sediment was separated by centrifugation. Three consecutive acetone extracts of the sediment were pooled. The acetone was diluted with the separated pore water and ultra pure water and was extracted with a mixture of hexane and methyl *tert*-butyl ether (MTBE). The organic extract was shaken with carbonate buffer pH 10, reduced in volume by evaporation and chromatographed on a silica gel column. The extract was analyzed by GC-MS using electron ionisation in selected ion monitoring mode.

SCCP were analysed using GC-high resolution-MS in electron capture negative ion (ECNI) mode. Methane was used as the moderating gas at a pressure of about 2×10^{-5} mbar. The [M-Cl]⁻ ion of each formula group were monitored, and the pattern of the formula groups was used for quantification.

The dry weight of the sediments was determined by drying 3-5 g of the sediments in 105°C for 24 hours.

4. Results and discussion

The concentrations of butylphenols (2,4,6-tri-*tert*-butyl-phenol, 2,4-di-*tert*-butyl-phenol and 2,6-di-*tert*-butyl-phenol) and SCCPs found in sediments from the estuary of Göta Älv are given in Table 2.

Table 2. The concentration of butylphenols and SCCP in surface (0-2 cm depth) sediments at the Swedish Göta Älv estuary.

Sampling site	Sample ID	DW %	Unit	2,4,6-Tri-t-bu-phenol	2,4-Di-t-bu-phenol	2,6-Di-t-bu-phenol	SCCP (C ₁₀ -C ₁₃)
Eriksberg	1930:1a	32	ng/g DW	0.21	0.75	<0.2	8.1
Eriksberg	1930:1b	32	ng/g DW	<0.1	<0.2	<0.2	13
Rivö	1930:3a	38	ng/g DW	0.17	<0.2	0.72	<0.3
Rivö	1930:3b	38	ng/g DW	<0.1	<0.2	<0.2	<0.3
Klinten	1931:2a	26	ng/g DW	<0.1	<0.2	<0.2	<0.3

The butylphenols were detected sporadically in the sediment samples and in relatively low concentrations. The highest concentrations of butylphenols were measured at Eriksberg (0.21 ng/g DW 2,4,6-tri-*tert*-butyl-phenol and 0.75 ng/g DW 2,4-di-*tert*-butyl-phenol), and at Rivö (0.17 ng/g DW 2,4,6-tri-*tert*-butyl-phenol and 0.72 ng/g DW 2,6-di-*tert*-butyl-phenol) but only in one of the two samples from each site. The substances were not detected at the background site Klinten.

In a screening study performed 2003, butylphenols were analysed in coastal sediments from the Stockholm municipality (central Stockholm). The concentration of 2,4,6-tri-*tert*-butyl-phenol varied between <0.02 and 0.45 ng/g DW. 2,4-Di-*tert*-butylphenol was detected in only one sample and 2,6-di-*tert*-butylphenol was not found in any of the samples (Remberger et al.,

2004). These values are in the same order of magnitude compared to the concentration of tert butylphenols in the estuary of Göta Älv determined in this study.

The highest concentrations of SCCPs were found in the samples from Eriksberg (8.1-13 ng/g DW). SCCPs were not found in any of the samples from Rivö or Klinten.

No detectable concentrations of chlorinated paraffins in sediment from Swedish lakes could be found in a screening study performed 2003-2004 (detection limit 8 ng/g DW) (Järnberg et al., 2005).

SCCPs were determined in sediment samples in the vicinity of Stockholm, with highest concentration in central Stockholm and lower in lakes and coastal areas (Sternbeck et al., 2003). The concentration in coastal sediments varied between <0.3 and 63 ng/g DW except for two values that were exceptionally high (350 and 1000 ng/g DW). Compared to this study, the concentration of SCCPs measured in Göta Älv estuary were relatively low.

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