



Cyclic volatile methylsiloxanes in fish from the Baltic Sea



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ABSTRACT

Laboratory studies suggest that the cyclic volatile methylsiloxanes (cVMS) octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) will persist in the aquatic environment and bioaccumulate in fish. Here these cVMS were measured in herring collected in the Swedish waters of the Baltic Sea and the North Sea and in grey seals from the Baltic Proper. D4, D5, and D6 were present in herring muscle at concentrations around 10, 200, and 40 ng g⁻¹ lipid weight, respectively. The ratio of these concentrations was similar to the relative magnitude of estimated emissions to water, suggesting that the efficiency of overall transfer through the environment and food web was similar (within a factor 2–3) for the three chemicals. The concentrations of D5 and D6 were similar in herring caught in the highly populated Baltic Proper and in the less populated Bothnian Sea and Bothnian Bay. The D4 concentrations were lower at the most remote northern station, suggesting that D4 is less persistent than D5 and D6. Herring from the North Sea had lower levels of all three chemicals. The concentrations of D4, D5 and D6 in grey seal blubber were lower than the lipid normalized concentrations in herring, indicating that they do not biomagnify in grey seals.

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1. Introduction

Three cyclic volatile methylsiloxanes (cVMS), namely octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6), have been identified as priority chemicals for environmental risk assessment (Howard and Muir, 2010). They are high production volume chemicals used in the production of silicone polymers and as solvents or fragrance carriers in personal care products, household products, and cleaning agents (Hori and Kannan, 2008; Brooke et al., 2009a,b,c). Use of these products results in emissions to wastewater, and despite effective removal in sewage treatment plants a small fraction of the cVMS is present in the plant effluent (Dewil et al., 2006). Risk assessments prepared by the United Kingdom indicate that the major environmental exposure pathway of concern for these chemicals begins with discharge of sewage treatment plant effluent to recipient waters. There it is expected that the very hydrophobic properties of the cVMS (log K_{ow} of 6.49, 8.03, and 9.06, respectively (Brooke et al., 2009a,b,c)) will result in them partitioning to sediment, where they will persist, accumulate, and bioaccumulate in aquatic food webs. These chemicals are under

consideration for regulation as very persistent, very bioaccumulative (vPvB) substances in the European Union (Brooke et al., 2009a,b,c).

Field measurements demonstrating exposure of aquatic organisms to cVMS are scanty. All three cVMS have been detected in fish collected from the vicinity of wastewater discharges (Schlabach et al., 2007; Warner et al., 2010). Off Svalbard, D5 and D6 were also quantified in 1 of 5 and 2 of 5 fish, respectively, collected at a site remote from wastewater discharges (Warner et al., 2010). cVMS were also occasionally detected in biota samples analyzed in a screening study conducted in the Nordic countries. There the concentrations ranged from <5–100 ng g⁻¹ wet weight (ww), whereby detectable levels appeared to be associated with diffuse/urban sources (Kaj et al., 2005). To date there is little information available on cVMS levels in biota distant from suspected sources. This information is needed to assess the potential for long range transport of cVMS in the aquatic environment and to establish the spatial implications of cVMS emissions.

In this study we analyze cVMS concentrations in biota from the Baltic Sea. The Baltic is a marginal sea with a large population (~85 million) within its watershed and a long water residence time (~25 years), which makes it susceptible to anthropogenic contamination. We analyzed cVMS in herring that were collected from around the Baltic Sea and in grey seals sampled in the Baltic Proper.

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2. Methods

2.1. Samples

Herring (*Clupea harengus*) has been used in the Swedish Marine Monitoring Program since the early 1970s and 1980s to assess PCB and DDT contamination. The specimens in the present study were collected in 2007 and stored in the sample specimen bank at -25°C . The sampling sites are shown in Fig. 1. The sampling date, sampling coordinates and sample characteristics such as gender, age and size are presented in Table S1. 10 g skin-free dorsal muscle tissue was excised in a sample preparation room under a counter-flow of particle filtered air. Duplicate samples (~ 10 g ww) were prepared for the analysis of cVMS and lipid determination. The samples were immediately wrapped in aluminum foil, vacuum-sealed in polyethylene bags, and frozen (-17°C) until analysis.

Grey seal (*Halichoerus grypus*, blubber only) is a top consumer in the Baltic food web. Herring are the principle prey of the grey seal, accounting for 82% of their diet (Routti et al., 2005). Samples were obtained from three seals that had drowned in nets north of Västervik (station #6 see Fig. 1) in the autumn of 2008. The seals were autopsied and blubber samples were stored in the sample specimen bank. Subsamples of 1–2 g blubber were prepared from parts of the tissue that had not been exposed to the air or the package material. Three herring from the nearby monitoring station Byxelkrok (#7, Fig. 1) that were sampled in the same year were also analyzed. Further characteristics of the samples are presented in Table S1.

All sampling was done according to the ordinary procedure applied in the Swedish Marine Monitoring Program. This does not include the use of field blanks. To address this, additional herring samples were collected (station #4, see Fig. 1) using the same sampling procedure, but with field blanks present both in the water as well as in the boat. The field blanks were pouches of polyester fabric ($\sim 2 \times 2$ cm) filled with ~ 60 mg precleaned ENV+ sorbent (a hydroxylated polystyrene–divinylbenzene copolymer purchased from Biotage AB, Uppsala, Sweden). Two pouches were connected to the fishing net during sampling and two pouches were handled in parallel with the fish in the boat. The pouches were subsequently wrapped in aluminum foil and kept frozen in polyethylene bags until analysis.



Fig. 1. Map of the sampling sites.

2.2. Analysis of cVMS

Extraction of the biological samples was performed with a purge and trap method, recently described in (Kierkegaard et al., 2010). In brief, the frozen intact muscle tissue together with the surrogate standards (^{13}C -labeled D4, D5, and D6 dissolved in ethyl acetate, 50 μL in a vial insert sealed with an ice plug) were added to a glass flask filled with pre-boiled water (MilliQ). The mixture was subsequently heated and stirred while the cVMS released to the gas phase was carried with a stream of nitrogen to a sample trap containing 20 mg ENV+ where the analytes were sorbed. The heat and vigorous stirring caused the fish tissue to fully disintegrate into a smooth slurry. The extraction was allowed to continue for 24 h for the Baltic herring and for 48 h for the seal and herring samples from 2008. The ENV+ sorbent was subsequently eluted with 0.9 mL n-hexane directly into a GC vial for immediate GC/MS analysis.

The field blank pouches were dried with a stream of nitrogen (precleaned by passage through ENV+) and extracted with 1 mL of n-hexane containing the surrogate standards. An aliquot was taken for GC/MS analysis.

The extracts were quantified on a Trace GC Ultra (Thermo Electron Corp.) equipped with a MD800 MS detector (Fisons Instruments SpA) using electron ionization (EI). The 5 μL of the extract was injected in a large volume splitless injector at a temperature of 220°C . The GC temperature program and ions monitored are supplied in (Kierkegaard et al., 2010).

A procedural blank and a control sample were analyzed with every extraction round of 8 samples. The procedural blank included all steps in the analytical procedure beginning with the addition of the internal standard. The control sample was a herring homogenate stored frozen in portions of 10 g. The extraction and all handling of the ENV+ traps were performed in a clean air cabinet. Details of other measures taken to reduce contamination during sample preparation and instrumental analysis are described elsewhere (Kierkegaard and McLachlan, 2010; Kierkegaard et al., 2010).

The limit of quantification (LOQ) was calculated from the mean of the procedural blanks run with the samples ($n = 7$ for herring from 2007 and $n = 8$ for the samples from 2008) plus 10 times their standard deviation. The results were not blank corrected.

2.3. Determination of lipid content

The lipid content was determined gravimetrically. The sample was mixed with sodium sulfate and extracted with n-hexane/dichloromethane (1:1 v:v) using ASE according to the German ASU method 00.00-38 (BVL, 1998). The solvent was evaporated to dryness and the residue weighed. The analysis was performed by the Oekometric GmbH.

2.4. Statistical methods

Homoscedasticity, i.e. whether the variances among the groups differed or not, was tested with Bartlett's test. For D4 and D5, significant heteroscedasticity prevailed (i.e. the variances were significantly different), also with log normalized concentrations. Therefore the non-parametric Mann–Whitney U-test was used to check the cVMS median concentrations in herring for significant differences between the Baltic stations (#1–3, 5, 7–9, Fig. 1) and two stations in the northern Kattegat (#11) and Skagerrak (#12) that are strongly influenced by North Sea water.

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