Environmental Pollution 190 (2014) 109–114

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Allometric relationships to liver tissue concentrations of cyclic volatile methyl siloxanes in Atlantic cod

Nicholas A. Warner [a,*], Therese H. Nøst [a,b], Hector Andrade [c], Guttorm Christensen [c]

[a] NILU-Norwegian Institute for Air Research, FRAM Centre, Hjalmar Johansens Gate 14, NO-9296 Tromsø, Norway
[b] Department of Community Medicine, University of Tromsø, NO-9037, Tromsø, Norway
[c] Akvaplan-niva, FRAM Centre, Hjalmar Johansens Gate 14, NO-9296 Tromsø, Norway

ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form
19 March 2014
Accepted 21 March 2014
Available online 16 April 2014

Keywords:
Cyclic volatile methyl siloxanes
Accumulation
Fish
Length
Weight

ABSTRACT

Spatial distribution and relationship of allometric measurements (length, weight and age) to liver concentrations of cyclic volatile methyl siloxanes (cVMS) including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclosiloxane (D6) in Atlantic cod (*Gadus morhua*) collected near the community of Tromsø in Northern Norway were assessed. These congeners were benchmarked against known persistent polychlorinated biphenyls (PCBs 153 and 180) to assess accumulation behavior of cVMS. D5 was the dominate cVMS detected in all fish livers with lipid normalized concentrations up to 10 times or greater than those observed for PCB 153 and 180. D4 and D6 concentration were negatively correlated with fish length and weight, indicating a greater elimination capacity compared to uptake processes with increasing fish size for these chemicals. These results indicate relationships between allometric measurements and cVMS concentrations may account for concentration variations observed within fish and should be assessed in future studies evaluating cVMS bioaccumulation potential.

1. Introduction

Cyclic volatile methyl siloxanes (cVMS) are chemicals that are widely used within the industrial and public domains. Dominant usage of the congeners octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclosiloxane (D6) can be found within the personal care product and cosmetic industry (Horii and Kannan, 2008). However, these congeners are also key intermediates/constituents in polymer synthesis, cleaning products, and surface treatment agents with production/use volumes reaching the kiloton range or higher within Europe, United States and Canada (Wang et al., 2013). Properties such as high thermal stability and inertness of these chemicals are attributed to their wide application in various products, but are also of concern for regulatory bodies regarding their environmental persistence (Brooke et al., 2009a,b,c; Environment Canada and Health Canada, 2008a,b). The majority of cVMS emissions to the environment occur via the atmosphere due to their high vapor pressures (Flaningam, 1986) and low water solubility (log K_{ow} 6.5–9.06) (Xu and Kropscott, 2012). cVMS have been shown to undergo long range transport (Krogseth et al., 2013; McLachlan et al., 2010) but have very low deposition potential (Wania, 2003), which has been confirmed by field observations in biota from remote Arctic fjords (Warner et al., 2010) and Swedish lakes (Kierkegaard et al., 2010). Wastewater emissions represent the other significant transport route of cVMS to the environment. Once emitted into aquatic environments, cVMS volatilization from water is hindered through partitioning to dissolved or suspended particulate matter (Whelan et al., 2010). Deposition of suspended particulate matter to the sediment compartment allows cVMS exposure to aquatic ecosystems where biomagnification may occur in aquatic biota via dietary uptake.

Controversy exists over the bioaccumulation potential of cVMS between regulatory, industry, and scientific communities. Non-published reports by industry indicate that cVMS undergo trophic dilution in aquatic food webs (Powell et al., 2010, 2009) and is supported by recent model predictions of the pelagic food web in the Oslofjord (Whelan and Breivik, 2013). However, these findings are in conflict with other studies that have reported bioaccumulation potential (Kierkegaard et al., 2013, 2011; Warner et al., 2010) and food web accumulation of cVMS (Borgå et al., 2012), resulting in much confusion and debate. Although it is

* Corresponding author.
E-mail address: nicholas.warner@nilu.no (N.A. Warner).

http://dx.doi.org/10.1016/j.envpol.2014.03.031
0269-7491/

unclear why discrepancies are observed between the various studies, site specific differences and/or allometric parameters (length, weight, age) of individual fish may play a significant role in variation observed in accumulated cVMS concentrations and need to be investigated.

The objectives of the present study were to 1) investigate the spatial distribution of D4, D5 and D6 in Atlantic cod near the community of Tromsø in Northern Norway; 2) compare these cVMS congener concentrations to known persistent organic pollutants (e.g., PCBs); and 3) assess allometric relationships (fish length, weight and age) to cVMS accumulation in Atlantic cod.

2. Methods and materials

2.1. Sample collection

Samples of Atlantic cod (*Gadus morhua*) and sediment were collected in November 2010 and April 2011 near the community of Tromsø, Norway. Sampling was conducted at two locations during both sampling campaigns (Fig. 1.). Tromsøysund is the harbor located next to the town of Tromsø (69° 38.539′ N/18° 58.250′ E) and Nipøya is a small island located approximately 30 km northeast of Tromsø (69° 49.432′ N/19° 22.276′ E). Due to its location away from Tromsø and anthropogenic sources of cVMS (i.e., wastewater effluent), Nipøya was considered the remote location in this study. All field sampling personnel refrained from using any personal care products to avoid accidental contamination of collected samples. Atlantic cod were captured opportunistically by a rod and reel with total fish length and weight recorded (Table S1, supporting information). Whole fish were wrapped in aluminum foil and frozen at −20 °C within a few hours after collection. Collection of sediment was done using a Van Veen Grab sampler (0.1 m^2). The top 2 cm of sediment was collected using a solvent-rinsed stainless steel spoon and placed in glass jars and frozen at −20 °C a few hours after collection.

To assess potential field contamination, sediment and fish liver collected from remote Arctic regions were used to serve as field blank material. These field blank materials were chosen as they contain low levels of cVMS and mimic the sample matrix under investigation (Warner et al., 2013). All field blank material was analyzed both before and after field exposure to assess contamination that occurred within the field. Sediment and fish liver field blank materials were distributed on aluminum foil on the deck of the sampling boat while sampling was occurring. Once sampling was completed, field blank materials were re-collected and stored in a glass jars at −20 °C shortly after sampling. Concentrations were field blank corrected in cases where field blank concentrations were found above detection limits. All information regarding analysis of field blank material is reported in Table S2A of the supporting information.

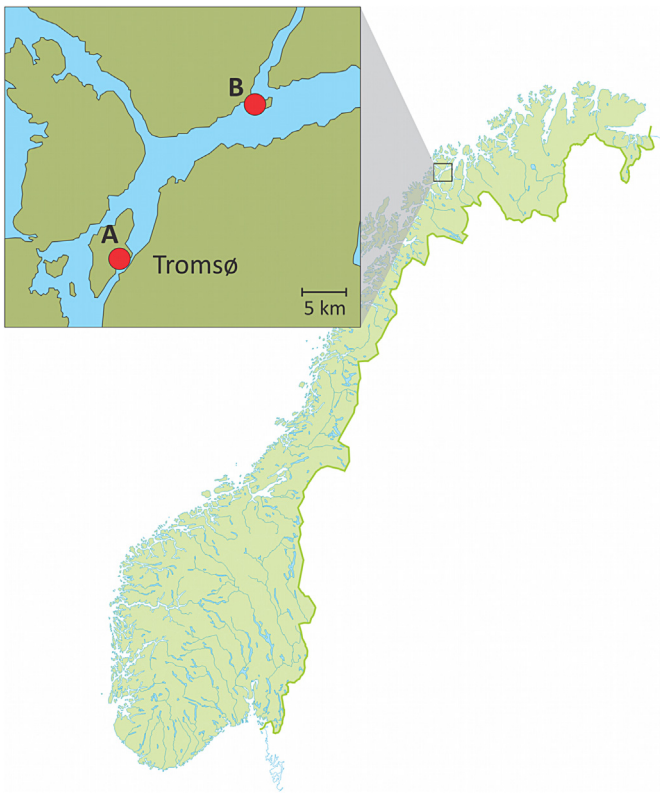

Fig. 1. Map of Norway and sampling locations of Tromsøysund (A) and Nipøya (B) near the community of Tromsø.

2.2. Determination of fish age and conditional status

Otoliths were extracted from individual cod for age determination. The left otolith was embedded in epoxy and sectioned through the core using a low-speed saw. The resulting slices (0.5 mm thick) were then read and photographed using a microscope equipped with transmitted light and a camera. Age is determined by count annuli where a single annulus was defined as one translucent band plus and adjacent opaque band (i.e., one year in age). Conditional status of individual cod was assessed using the relationship between individual fish weight and length to calculate Fulton's conditional factor (K)

$$K = w_i \Big/ (l_i)^3 \quad (1)$$

where w_i represents somatic weight and l_i represents total length of the individual fish. Fish conditional status is directly proportional with K (i.e., higher K values represent better conditional status of fish). Conditional status of fish is reported in Table S1 of the supporting information.

2.3. cVMS extraction and analysis

Extraction procedures for siloxanes in cod liver and sediment have been previously published within the literature (Warner et al., 2013). In brief, all sample handling (liver dissection, homogenization and extraction) was carried out within a clean room facility (U.S. Federal Standard 209e) at NILU -Norwegian Institute for Air Research, Kjeller, Norway. Liver and sediment material was homogenized using a stainless steel Ultra Turrax homogenizer. Approximately 0.5 g of sample material was weighed into 2.0 mL Eppendorf Protein LoBind centrifuge tubes and spiked with [^{13}C]-enriched octamethylcyclotetrasiloxane (D4) (99% purity), decamethylcyclopentasiloxane (D5) (99% purity) and dodecamethylcyclohexasiloxane (D6) (92% purity) and vortexed briefly with the sample material. Sample material was extracted with hexane for 30 min using a vortex mixer followed by centrifugation. A 400 μL aliquot was transferred to a 2 mL GC vial followed by the addition of Tris(trimethylsilyloxy)silane (M3Q) (98% purity, Aldrich, Germany) as a recovery standard prior to analysis.

Samples were analyzed on a Hewlett Packard (HP) 6890 gas chromatograph equipped with HP 5973 mass spectrometer in electron impact mode. Injection was done in splitless mode using a split/splitless injector equipped with a Merlin microseal septum (Restek Corporation, Bellefonte, PA, USA). Two masses corresponding to the [M−CH_3] fragment were monitored for quantification and confirmation purposes. Column details and chromatographic conditions have been previously published (Warner et al., 2013). Non-labeled standards of D4 (≥99% purity, Fluka, Switzerland), D5 (≥97% purity Fluka, Switzerland), and D6 (≥95% purity, Gelest Inc. PA, USA) were used for quantification. Extraction recovery of mass-labeled standards for sample analysis was ^{13}C-D4: 74 ± 11%, ^{13}C-D5: 80 ± 11%, and ^{13}C-D6: 81 ± 12%.

Sample matrix can significantly contribute to the analytical variation introduced in trace analysis. This is particularly true for cVMS, where not accounting for this variation has been show to significantly increase the chance of reporting false positives at concentrations close to detection limits (Warner et al., 2013). Therefore, method detection limits (MDL) were calculated as a function of variance measured in repeated analysis of matrices fortified at low concentrations (approximately 2–7 times instrument detection limits) (Glaser et al., 1981)

$$\mathrm{MDL} = t_{0.99,\, n-1} \times s_{o,\, \mathrm{matrix}} \quad (2)$$

Where t represents the one-tailed t-value at 99% confidence, n represents the number of matrix replicates, $s_{o,\,\mathrm{matrix}}$ represents the standard deviation obtained in replicate analysis of the representative matrix. Matrices used for MDL determination consisted of Atlantic cod liver collected from the Svalbard Archipelago and sediment from Sanford Lake (MI, USA) provided by Dow Corning Corporation (Midland, MI, USA). Both matrices were previously analyzed for cVMS to determine appropriate fortification levels. Variation of fortified matrices and calculated MDLs are provided in Tables S3 and S4 of the supporting information.

2.4. PCB extraction and analysis

Approximately 2–3 g of fish liver homogenate was homogenized with burnt sodium sulfate (600 °C) in a 1:20 ratio (sample: sodium sulfate) and stored in the freezer overnight. Dried homogenate was transferred and packed into glass columns. Isotope-labeled internal standards (^{13}C-labeled PCBs) were added to the packed homogenate and extracted three times with 50 ml of 3:1 cyclohexane:acetone solvent mixture. Lipid removal from extracts was done using gel permeation chromatography (GPC). Additional clean-up was carried out using florisil (burnt at 450 °C). Samples were evaporated to approximately 200 μl, transferred to a GC vial with the addition of 20 μl of 200 pg/μl of octachloronapthalene (OCN) as