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Bioaccumulation and trophic transfer of cyclic volatile methylsiloxanes (cVMS) in the aquatic marine food webs of the Oslofjord, Norway

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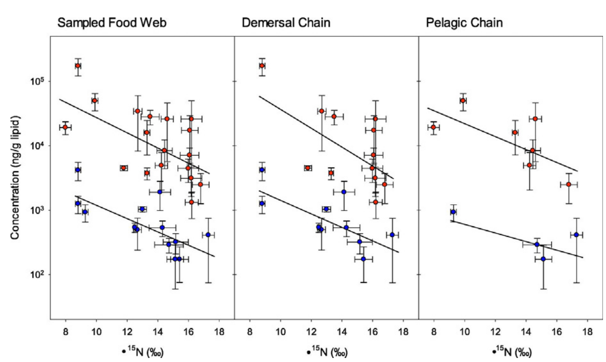
HIGHLIGHTS

- Cyclic volatile methysiloxanes (cVMS) monitored in biota and sediment from the Oslofjord, Norway.
- Assessed bioaccumulation of cVMS across the decoupled demersal and pelagic food webs.
- TMFs calculated by standard and alternative methods, to control bias and incorporate uncertainty.
- TMFs in the Inner Oslofjord same as in the less polluted Outer Oslofjord, hence not related to exposure.
- No indication of biomagnification of cVMS across food webs.

GRAPHICAL ABSTRACT



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ABSTRACT

The trophic transfer of cyclic methylsiloxanes (cVMS) in aquatic ecosystems is an important criterion for assessing bioaccumulation and ecological risk. Bioaccumulation and trophic transfer of cVMS, specifically octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), were evaluated for the marine food webs of the Inner and Outer Oslofjord, Norway. The sampled food webs included zooplankton, benthic macroinvertebrates, shellfish, and finfish species. Zooplankton, benthic macroinvertebrates, and shellfish occupied the lowest trophic levels (TL ≈2 to 3); northern shrimp (*Pandalus borealis*) and Atlantic herring (*Clupea harengus*) occupied the middle trophic levels (TL ≈3 to 4), and Atlantic cod (*Gadus morhua*) occupied the highest tropic level (TL > 4.0). Trophic dynamics in the Oslofjord were best described as a compressed food web defined by demersal and pelagic components that were confounded by a diversity in prey organisms and feeding relationships. Lipid-normalized concentrations of D4, D5, and D6 were greatest in the lowest trophic levels and significantly decreased up the food web, with the lowest concentrations being observed in the highest trophic level species. Trophic magnification factors (TMF) for D4, D5, and D6 were <1.0 (range 0.3 to 0.9) and were consistent between the Inner and Outer Oslofjord, indicating that exposure did not impact TMF across the marine food web. There was no evidence to suggest biomagnification of cVMS in the Oslofjord. Rather, results indicated that trophic dilution of cVMS, not trophic magnification, occurred across the sampled food webs.

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1. Introduction

1.1. Background

Cyclic volatile methylsiloxanes (cVMS) are a class of silicone compounds having an unusual combination of physical-chemical properties. These materials are widely used in industrial and consumer applications worldwide, including use as key intermediates for the manufacture of siloxane polymers (Allen et al., 1997; Hobson et al., 1997), in dry cleaning solvents and industrial cleaning fluids (Horii and Kannan, 2008; Wang et al., 2013), and in a variety of personal care products such as shampoos and hair-conditioners, skin creams, cosmetics, and deodorants (Montemayor et al., 2013). Due to their use pattern, wastewater is the principal disposal pathway for cVMS found in consumer and industrial applications. As a result, wastewater effluents are the primary source of cVMS to aquatic environments, (Hirner et al., 2003; Kaj et al., 2005a; Kaj et al., 2005b) where volitalization to the atmosphere and deposition to sediment are expected to occur (Hughes et al., 2012; Kim et al., 2013; Mackay et al., 2014; Whelan, 2013; Whelan and Breivik, 2013).

Generally, cVMS (Table S1 of the Supporting Information; SI) have low to moderate molecular weights (297 to 445 amu), are relatively volatile (vapor pressure 4.7 to 132 Pa at 25 °C), and have low water solubility (5 to 56 μg/L), resulting in large air/water partition coefficients (log K_{AW} 2.74 to 3.13) and octanol/water partition coefficients (log K_{OW} 6.98 to 8.87). In contrast to other neutral organic chemicals, the organic carbon/water partition coefficients (K_{OC}) of cVMS are more than two orders of magnitude less than would be predicted from the K_{OW}. Combined, these partitioning properties allow cVMS materials to occupy a unique chemical space. Cyclic volatile methylsiloxanes are discharged through water treatment facilities into receiving waters during both manufacturing of polymers and product use and have been measured in surface waters, sediment and biota from the Inner Oslofjord (Powell et al., 2010; Ruus et al., 2016; Schlabach et al., 2007).

1.2. Objectives

The objective of this work was to apply newly developed methods (Powell et al., 2017) to re-evaluate bioaccumulation and trophic transfer of three cVMS across the marine food webs in the Oslofjord, Norway as was first reported by Powell et al. (2010). The Oslofjord receives discharges of treated wastewater from the nearby city of Oslo, resulting in pollution problems within the aquatic system. Relatively little data is currently available on the behavior of cVMS materials in the environment and the ultimate fate of cVMS within ecosystems is poorly understood. Due to the tendency of lipophilic compounds to bioaccumulate, trophic transfer and magnification are important criteria for assessing ecological risk of chemicals in aquatic ecosystems. Therefore, the presence of cVMS materials in the Oslofjord necessitates an evaluation of the trophic transfer of these chemicals in the marine food web.

Trophic transfer was evaluated using trophic magnification factors calculated from the slopes of regression models that were developed to control bias and uncertainty associated with trophic level structure, food web dynamics, and experimental design. Trophic magnification factors (TMFs) were derived using two methods: 1) the standard approach based on ordinary least-squares regression models (Borgå et al., 2012b) and 2) alternative approaches based on bootstrap regression models (Powell et al., 2017). No attempt was made to control bias from variable exposure resulting from movement of organisms across spatial concentration gradients present in the study area (Kim et al., 2016; McLeod et al., 2015). The three cVMS evaluated were octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6) and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6).

2. Experimental

2.1. Study area

The study area was located in the Oslofjord, Norway (Fig. S1 of the SI). The Greater Oslo statistical metropolitan region, including the city of Oslo, which is located on the shore of the Oslofjord, is the most densely populated region of Norway, with a population of 1.6 million people in 2016. The Oslofjord is characterized by several sills that divide the deeper habitats into several interconnected basins throughout the length of the fjord. The main sill, located near Drøbak at a water depth of 19.5 m, separates the Inner Oslofjord (surface area of about 191 km^2) from the more southern fjordic system, which is referred to as the Outer Oslofjord. A ridge extending southwards from the city of Oslo at a water depth of about 50 m divides the Inner Oslofjord into two major basins, the Bunnefjord (max depth ca 164 m) to the east and the Vestfjord (max depth ca 160 m) to the west, which is linked to the Outer Oslofjord at Drøbak. Water circulation within the Inner Oslofjord is estuarine with a pycnocline situated at about 20 m water depth, which acts as a physical barrier that restricts water circulation and limits exchange of the surface and deep waters. Major deep-water renewals occur on a cycle of about 1–2 years in the Vestfjord and about 3–4 years in the Bunnefjord. Because of the semi-enclosed nature of the Oslofjord, chemical substances in municipal wastewater that is discharged below the pycnocline become trapped in the Inner Oslofjord, resulting in elevated levels compared with those found in the Outer Oslofjord and surrounding areas. Additional details on the Oslofjord are discussed by Powell et al. (2010) and provided in the SI.

2.2. Sample collection

Surface sediments, bulk zooplankton, macroinvertebrates, and fish were collected from the Inner and Outer Oslofjord in November 2008 (Table 1; Fig. S1 of the SI). With the exception of blue mussel all samples were collected from aboard the Norwegian research vessel *F/F Trygve Braarud* (University of Oslo). Surface sediments were collected using a double Gemini corer (10-cm inner diameter) or a 0.1-m^3 van Veen grab that was used when the corer did not yield an acceptable sample. The surface sediment layer was sectioned into the 0–1 and 1–2 cm strata that were retained and stored in glass containers. Duplicate samples were retained from each sediment station. Zooplankton were collected using a 200 μm WP-2 plankton net (vertical hauls), separated into jellyfish and net plankton, and retained in glass storage containers. Blue mussel (*Mytilus edulis*) were collected from the Inner Oslofjord in October 2008 by Norwegian Institute for Water Research (NIVA) at five stations. Mussels were collected from hard substrate subtidal zones by wading and skin diving. At least 20 blue mussels (30–49 mm shell length) were collected from each station and retained in plastic storage bags. Other macroinvertebrates were collected by benthic sledge (i.e., Waren sledge, which is an extended Ockelmann sledge) or as by-catch from bottom trawls (20 × 20 mm mesh size and trawl speed about 1.8 knots), separated by species, and retained in plastic storage bags (shrimp, mussels, urchin) or glass storage containers (benthic worms). Fish were collected by bottom trawl, separated by species, and retained in plastic storage bags. In the field after collection, while aboard the *F/F Trygve Braarud*, retained samples were processed and labeled for distribution between Dow Corning Corporation (DCC) and Evonik Nutrition & Care GmbH (Evonik) and stored in the dark at about −18 °C in a conventional freezer. Sediments and fish were stored as individual samples, whereas macroinvertebrates and zooplankton samples were pooled and stored as composite samples by species. Additional details for sample collection are provided by Powell et al. (2010) and summarized in the SI.