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

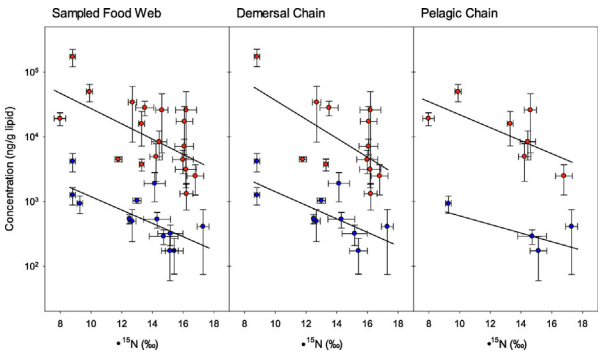
David E. Powell [a], Merete Schøyen [b], Sigurd Øxnevad [b], Reinhard Gerhards [c], Thomas Böhmer [c], Martin Koerner [c], Jeremy Durham [a,*], Darren W. Huff [a]

[a] Dow Corning Corporation, Auburn, MI, USA
[b] Norwegian Institute for Water Research (NIVA), Oslo, Norway
[c] Evonik Nutrition & Care GmbH, Essen, Germany

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.

* Corresponding author at: The Dow Chemical Company, 2030 Dow Center, Midland, MI 48674, USA.
E-mail address: jeremy.durham@dowcorning.com (J. Durham).

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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 bycatch 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.

Table 1
Samples collected to evaluate bioaccumulation of cyclic methylsiloxanes across the aquatic marine food webs of the Inner and Outer Oslofjord, Norway (samples collected November 2008).

Code	Common name	Family	Genus species	The Oslofjord[c]				
				TL[a]	Sample[b]	Inner	Outer	Chain[d]
SED-0/1	Sediment (0–1 cm)				I	7	5	
SED 1/2	Sediment (1–2 cm)				I	8	6	
BRL	Sea urchins	Brissidae	*Brissopsis lyrifera*	1.7	I		3	A
WOR	Worms			1.9	I	1	1	A
BMU	Blue mussel	Mytilidae (mussels)	*Mytilus edulis*	2.0	C	5		B
ZPK	Net plankton		200-μm net plankton	2.2	C	1	1	B
JFH	Jellyfish			2.2	C	1	1	B
MUA	Mussel (species A)			2.7	C	2	3	A
MUB	Mussel (species B)			2.8	C	2	3	A
EPE	European plaice	Pleuronectidae (righteye flounders)	*Pleuronectes platessa*	3.2	I	6	5	A
HER	Atlantic herring	Clupeidae (herrings)	*Clupea harengus*	3.3	I	6		B
CSE	Common sole	Soleidae (soles)	*Solea vulgaris*	3.3	I		3	A
SHR	Northern shrimp	Pandalidae (pandalid shrimps)	*Pandalus borealis*	3.4	C	6	6	A
VEE	Vahl's eelpout	Zoarcidae (eelpouts)	*Lycodes vahii*	3.4	I	6		A
RAR	Starry skate	Rajidae (skates and rays)	*Amblyraja radiata*	3.5	I		3	C
COA	Coalfish	Gadidae (cods)	*Pollachius virens*	3.6	I	6	6	B
EWG	European whiting	Gadidae (cods)	*Merlanguis merlangus*	3.6	I	6		A
HAD	Haddock	Gadidae (cods)	*Melanogrammus aegflefinus*	3.6	I	4	12	A
LRD	Long rough dab	Pleuronectidae (righteye flounders)	*Hippoglossoides platessoides*	3.6	I	6	6	A
NOP	Norway pout	Gadidae (cods)	*Trisopterus esmarkii*	3.7	I	6	10	B
PCD	Poor cod	Gadidae (cods)	*Trisopterus minutes*	3.7	I	6		A
NAP	N. Atlantic pollock	Gadidae (cods)	*Pollachius pollachius*	3.9	I	6		A
ACD	Atlantic cod	Gadidae (cods)	*Gadus morhua*	4.3	I	6	6	A/B
EHE	European hake	Merlucciidae (hakes)	*Merluccius merluccius*	4.3	I	4		B

[a] Trophic level (TL) of each species obtained from FishBase (Froese and Pauly, 2017) or the Encyclopedia of Life (EOL, 2017).
[b] Samples were collected and processed as individual samples (I) or as composite samples (C).
[c] Samples were collected from both the Inner and Outer Oslofjord. Numbers indicate the number of samples that were analyzed.
[d] Individual species in the Oslofjord food webs were assigned to food chains A (demersal), B (pelagic), or C (skates and rays) based on $\delta^{13}C$ signatures. Atlantic cod (ACD) were assigned to food chains A and B.

2.3. Laboratory methods

Two laboratories were involved in analyzing samples from the Oslofjord. Samples for analysis by Evonik were transported frozen on dry ice in thermo boxes by car to Essen, Germany. Samples for analysis by Dow Corning were shipped frozen on dry ice in to Auburn, Michigan, USA. Biological samples were processed as whole-body homogenates of individual and pooled samples. Processed samples were characterized and analyzed for cVMS (specifically D4, D5, and D6) following laboratory-specific protocols (Powell et al., 2010). Data provided by the two contributing laboratories were combined into a single dataset that was used for all calculations (Tables S2 and S3 of the SI).

2.3.1. Sample characterization

Sediment samples were characterized for water content, total volatile matter (a surrogate measure of organic matter), bulk density, and total organic carbon (TOC). Biological samples were characterized for lipid and water content and isotopic signatures for nitrogen (N; $\delta^{15}N$ ‰) and carbon (C; $\delta^{13}C$ ‰). Results for sample characterization of biota are summarized in Table 2. Details for sample characterization are provided by Powell et al. (2010); results for individual samples are provided in Tables S2 and S3 of the SI.

2.3.2. Analysis of cVMS

Concentrations of cVMS were measured in extracts of wet sediment and biota (whole-body homogenates) that were spiked with ^{13}C labeled internal standards (^{13}C-D4, ^{13}C-D5, and ^{13}C-D6). Concentrations in extracts were quantified for cVMS using gas chromatography/quadrupole mass spectrometry. Details for sample analyses are provided by Powell et al. (2010). Results of analyses for cVMS in individual samples are provided in Tables S2 and S3 of the SI.

Analytical detection limits were determined from the uncertainty associated with replicate analyses of reagent blanks or samples that were carried through the entire analytical procedure. Detection limits were calculated as the product of the standard deviation for the replicate analyses and the one-tailed t-statistic at 99% confidence for the number of sample analyses (Taylor, 1987). The method detection limit (MDL) was the minimum level of target analyte in a specified matrix that could be measured and reported with 99% certainty as being greater than zero or statistically different from a blank. The limit of quantification (LOQ; defined as 2.5 × MDL) was the minimum level of target analyte in a specified matrix that could be measured and reported with 99% certainty of having an estimation error no > 30% when based on a single measurement. Detection limits are summarized in Table S4 of the SI.

2.3.3. Quality control

Cyclic VMS are widely used in consumer products and may be present in personal care products, commercial products, and lubricants. Therefore, field and vessel crew refrained from using personal care products that might contribute to sample contamination (e.g. hand lotion, sunscreen, deodorant, perfume, shampoo, etc.) and wore nitrile gloves during all sample-handling procedures. Given the significant potential for sample contamination during collection, processing, storage, and analysis, a rigorous quality control (QC) program was implemented to the extent possible in the field and laboratory. Details and results of the QC program can be found in Powell et al. (2010).

3. Calculations and data analysis

3.1. Concentration units

Concentrations of D4, D5, and D6 in biota and sediment were measured in wet samples and expressed on the basis of wet weight.

Table 2
Means and standard deviations (by species) for concentrations used to calculate TMF by bootstrap regression across the sampled food webs of the Oslofjord, Norway (samples collected November 2008). Sample concentrations used to calculate TMF by ordinary least squares regression are provided in Tables S2 and S3 of the SI.

	δ^{13}C (‰)		δ^{15}N (‰)		D4 (ng/g lipid)		D5 (ng/g lipid)		D6 (ng/g lipid)	
Species[a]	Mean	SD[b]	Mean	SD[b]	Mean	SD[b]	Mean	SD[b]	Mean	SD[b]
The Inner Oslofjord										
• Atlantic cod	−16.8	0.251	16.8	0.547	125	33.7	2474	1217	181	73.1
• N. Atlantic pollock	−17.7	0.274	16.2	0.680	267	208	25,802	23,970	562	326
• Poor cod	−17.0	0.415	16.2	0.425	75.4	18.0	1317	580	145	90.2
• Vahl's eelpout	−17.0	0.504	16.2	0.691	191	37.9	3121	1499	509	293
• European whiting	−17.5	0.134	16.1	0.609	192	16.6	7105	2056	201	50.3
• Long rough dab	−17.0	0.364	16.1	0.542	538	382	17,245	11,938	619	429
• Haddock	−17.3	0.717	16.0	0.679	88.6	20.6	4429	1764	488	157
• European hake	−17.7	0.147	14.6	0.399	271	1051	25,832	20,196	535	302
• Norway pout	−17.9	0.288	14.4	0.502	316	41.5	8354	3973	181	33.9
• Coalfish	−18.6	0.660	14.2	0.404	525	1261	4914	2874	838	114
• European plaice	−17.1	0.740	13.5	0.591	414	1881	28,136	7192	543	193
• Atlantic herring	−19.1	0.606	13.3	0.194	115	53.9	15,884	8724	213	90.8
• Northern shrimp	−16.0	0.124	13.3	0.154	99.8	33.9	3723	781	108	9.26
• Mussel (species A)	−16.7	(0.554)	12.7	(0.421)	552	(186)	34,137	(16594)	1118	(437)
• Mussel (species B)	−16.3	(0.540)	11.8	(0.391)	341	115	4468	(2172)	213	(83.4)
• Jellyfish	−17.9	(0.595)	9.90	(0.329)	[17.9]		[32.6]		[70.8]	
• Net plankton	−17.9	(0.595)	9.90	(0.329)	379	(128)	49,594	(24107)	397	(155)
• Worms	−16.5	(0.548)	8.80	(0.292)	2687	(906)	172,781	(83988)	6281	(2453)
• Blue mussel	−17.7	0.499	7.98	0.373	459	84.1	19,129	4341	512	134
The Outer Oslofjord										
• Atlantic cod	−17.4	0.526	17.3	0.390	19.5	6.02	409	335	45.2	9.99
• Haddock	−17.7	0.465	15.4	0.579	15.1	4.72	172	96.5	132	50.8
• Long rough dab	−17.3	0.411	15.2	0.817	42.6	16.0	319	111	107	72.9
• Coalfish	−18.5	0.634	15.1	0.541	16.1	13.0	172	112	53.3	17.6
• Norway pout	−18.0	0.436	14.7	0.937	21.7	6.84	289	74.1	35.6	11.2
• Starry skate	−15.1	0.153	14.7	0.231	68.8	(24.8)	1020	6341	[67.3]	
• Common sole	−16.5	0.321	14.3	0.872	60.7	31.1	531	145	49.0	(16.5)
• European plaice	−16.4	0.715	14.1	0.689	131	23.9	1884	899	345	202
• Mussel (species A)	−16.6	0.107	13.0	0.267	15.1	(5.42)	1029	95.1	306	22.7
• Northern shrimp	−16.2	0.226	12.7	0.253	6.67	0.41	495	257	29.4	2.12
• Mussel (species B)	−16.9	0.135	12.5	0.100	[55.2]		537	87.2	[151]	
• Jellyfish	−17.8	(0.626)	9.27	(0.326)	[2.11]		[30.8]		[13.1]	
• Net plankton	−18.6	(0.654)	9.27	(0.326)	55.7	(20.1)	928	(394)	54.9	(18.5)
• Sea urchins	−16.5	0.581	8.80	0.310	160	(57.5)	4159	1318	3155	1169
• Worms	−16.5	(0.581)	8.80	(0.310)	136	(48.8)	1254	(533)	405	(136)

[a] Species are listed in order of decreasing δ^{15}N signatures.
[b] Means and standard deviations (SD) were used to define species-specific probability density functions (PDFs) for the probabilistic assessments. Concentrations less than the MDL were not included in calculation of mean concentrations. Mean concentrations in brackets [ ] indicate that concentrations were less than the MDL and were excluded from the regression models. Standard deviations in parentheses ( ) were estimated using sampling variances from other studies as described by Powell et al. (2017). Estimated standard deviations were used for all composite samples and for samples having replication less than three (n ≤ 3).

Concentrations of D4, D5, and D6 that were reported on the basis of dry weight were calculated from the measured concentration (i.e. ng/g ww) and water content of the sample. Lipid content of biota and total organic carbon (TOC) content of sediment were measured on dry samples and expressed on the basis of dry weight but were converted to a wet weight basis using the measured water content of the samples. Concentrations of D4, D5, and D6 reported on the basis of lipid content (i.e. biota; ng/g lipid) and total organic carbon content (i.e. sediment; ng/g TOC) were calculated from concentrations that were expressed on the basis of wet weight. Stable isotope abundances were expressed in per mil notation (δ; ‰) as the deviation from the standards in parts per thousand.

3.2. Food web structure and trophic level position

Structure of the sampled food web was evaluated using δ^{15}N and δ^{13}C as continuous variables for estimating the trophic level position occupied by each organism and for assessing the sources and flow of dietary carbon to consumers in the food web, as described by Powell et al. (2017).

The relative trophic level (TL) of each consumer in the sampled food web was calculated from the δ^{15}N signatures of the consumer ($\delta^{15}N_{consumer}$) and a baseline consumer ($\delta^{15}N_{base}$), the TL occupied by the baseline consumer (TL_{base}), and the average trophic discrimination factor for δ^{15}N across the food web (Δ^{15}N) using the following equation (Jardine et al., 2006), which was modified to incorporate standard error; SE (Powell et al., 2011):

$$\boldsymbol{TL \pm SE} = (\boldsymbol{TL_{base} \pm SE}) + \frac{\left(\boldsymbol{\delta^{15}N_{consumer} \pm SE}\right) - \left(\boldsymbol{\delta^{15}N_{base} \pm SE}\right)}{\left(\boldsymbol{\Delta^{15}N \pm SE}\right)} \quad (1)$$

For this study, blue mussel (*Mytilus edulis*) was designated as the baseline consumer, $TL_{base} = 2.0 \pm 0.05$ for the species, and $\Delta^{15}N = 3.8 \pm 3.0$‰ TL^{-1} reported by Hobson and Welch (1992) and applied by Ruus et al. (2016), were used for the calculation of TL.

3.3. Food web magnification

Food web magnification was evaluated using the TMF, which describes the change in concentration of a chemical in organisms that occupy successively higher trophic levels within a food web (Borgå et al., 2012b). 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).

3.3.1. Calculation of TMF

TMF is typically calculated as the antilog of the slope (β) of the linear model ($y = \alpha + \beta x$) for log-transformed lipid-normalized concentration

in the organism ($C_{organism}$; ng/g lipid) regressed on the trophic level position of the organism ($TL_{organism}$; non-dimensional) across the food web (Borgå et al., 2012b). When written in terms of TL and concentration, the slope (i.e., $\beta_{TL}[CONC]$) and TMF may be depicted by the slope-intercept form of the regression model:

$$\boldsymbol{Log\ C_{organism} \pm SE = \alpha + (\beta_{TL}[CONC] \pm SE) \times (TL_{organism} \pm SE)} \quad (2)$$

$$\boldsymbol{Log\ TMF \pm SE = \beta_{TL}[CONC] \pm SE} \quad (3)$$

Alternately, TMF may also be directly calculated from the slope of the linear model of log-transformed concentration regressed on $\delta^{15}N$ (i.e., $\beta_{\delta 15N}[CONC]$) and $\Delta^{15}N$, using the equation (Powell et al., 2017):

$$\boldsymbol{Log\ TMF \pm SE = (\beta_{\delta 15N}[CONC] \pm SE) \times \left(\Delta^{15}N \pm SE\right)} \quad (4)$$

Because samples collected from Oslofjord in 2008 were not analyzed for a reference material (e.g. PCB) it was not possible to benchmark or authenticate $\Delta^{15}N$ for the sampled food webs (Powell et al., 2011; Powell 2013; Powell et al., 2017). For this study, $\Delta^{15}N = 3.8 \pm 3.0‰\ TL^{-1}$ reported by Hobson and Welch (1992) was used for calculation of TMF, as applied by Ruus et al. (2016). Calculation of TMF as a direct multiple of $\Delta^{15}N$ eliminates the requirement of Eq. (1) to identify a baseline consumer and estimate the TL occupied by that organism (i.e., TL_{base}), which are both characterized by fundamental limitations and considerable uncertainty (Layman et al., 2012). Although Eqs. (3) and (4) generate the same value for TMF, total uncertainty (e.g. 95% confidence interval) will be greater for Eq. (4) because uncertainty associated with $\Delta^{15}N$ is incorporated into the calculations.

3.3.2. Regression models

Standard TMFs were calculated as the antilog of slopes obtained from ordinary least-squares (OLS) regression models. Although Eq. (1)–(4) are shown with standard error terms included (i.e. ± SE), OLS regression does not propagate such error through the trophic hierarchy of the food web unless resampling techniques are used (Powell et al., 2017; Starrfelt et al., 2013). Thus TMFs were also calculated using slopes obtained from nonparametric bootstrap (NPB) regression models that used Monte-Carlo resampling with replacement to propagate error. Bootstrap regression (Efron and Tibshirani, 1994; Good, 2006) incorporates probabilistic methods so that a probability distribution is assigned to the outcome of a statistical inference test (e.g. slope of a regression model) that is based on a distribution of continuous random variables, making it a more robust alternative to OLS regression. Details of the regression models used to obtain slopes from which TMFs were calculated are discussed by Powell et al. (2017).

4. Statistical analysis

Statistical analyses were performed using Minitab® (ver. 17.1.0). A Type I error (α) of 0.05 was used to determine the significance of all statistical tests. Analytical results less than the MDL (Tables S3 and S4 of the SI) were treated as missing values. Non-censored values were used for all calculations and analyses. Outlier values were not omitted from the dataset. Log transformations were applied when needed to achieve more normal distribution. Nonparametric bootstrap regression analyses were performed using the LINEST function in Microsoft Excel® 2013 (ver. 15.0) interfaced with Oracle Crystal Ball® (ver. 11.1.2). Results between OLS regression (i.e., regression across samples) and bootstrap regression (i.e., regression across sample means) are not directly comparable, as discussed by Powell et al. (2017) and references therein.

4.1. Merging of datasets

Hierarchical analysis of variance (ANOVA) for unbalanced designs (Sheskin, 2000) was used to test for differences between the two laboratories (species nested within laboratory) for $\delta^{13}C$, $\delta^{15}N$, lipid content, and cVMS concentrations. If the omnibus F value indicated significant differences, a Tukey HSD multiple comparisons test (equal sample sizes) or a Tukey-Kramer multiple comparisons test (unequal sample sizes) was used to compare individual means. Statistically significant differences observed between the two laboratories were typically associated with analytical results near the MDL (Table S4 of the SI). Thus results from the two laboratories were combined into a single dataset in order to increase statistical power. As a result, TMFs were more variable than would have been observed if differences between the two laboratories had not existed.

4.2. Separation of sampled food web

Cluster analysis of mean $\delta^{13}C$ and $\delta^{15}N$ in lipid-extracted samples indicated that species across the sampled food webs could be grouped according to their most probable food chain association (Fig. S2 of the SI). Lipids may be ^{13}C–depleted relative to proteins thus confounding interpretation of fish trophodynamics, especially when based on samples with C:N ratios >3.5 (Sweeting et al., 2006). Although not quantified for samples that were collected in 2008 (Powell et al., 2010), C:N ratios for samples collected from the Inner Oslofjord in 2015 (Ruus et al., 2016) were typically >3.5 (range 3.30 to 4.94), suggesting that lipid interference should have been taken into consideration. Nonetheless, single-factor ANOVA with a Dunnett a posteriori multiple comparisons test (Sheskin, 2000) was performed to separate each species into one of four arbitrarily defined food chains based on $\delta^{13}C$, which represents the source and flow of dietary carbon to consumers (Post, 2002). Species with $\delta^{13}C$ signatures less than those for Atlantic cod (*Gadus morhua*; $\delta^{13}C_{cod}$) were assigned to food chain B, species with $\delta^{13}C$ signatures greater than those for northern shrimp (*Pandalus borealis*; $\delta^{13}C_{shrimp}$) were assigned to food chain C, species with $\delta^{13}C$ signatures less than those for Atlantic herring (*Clupea harengus*; $\delta^{13}C_{herring}$) were assigned to food chain D, and the remaining species assigned to food chain A (cod were assigned to both food chains A and B):

- Food chain A: $\delta^{13}C_{cod} \le \delta^{13}C_{species} \le \delta^{13}C_{shrimp}$ (14 of 22 species)
- Food chain B: $\delta^{13}C_{herring} \le \delta^{13}C_{species} < \delta^{13}C_{cod}$ (7 of 22 species)
- Food chain C: $\delta^{13}C_{shrimp} < \delta^{13}C_{species}$ (1 of 22 species)
- Food chain D: $\delta^{13}C_{species} < \delta^{13}C_{herring}$ (0 of 22 species)

Based on the ecology of the grouped species, food chains A and B were identified as the demersal and pelagic components, respectively, of the sampled food webs. Food chain C included only starry skate (Amblyraja radiata) that were collected from the Outer Oslofjord. For the purpose of the TMF evaluations, starry skate were not included as a component of the sampled food web for the Outer Oslofjord.

4.3. Calculation of TMF

Trophic magnification factors were calculated (Eq. (4)) from the slopes of OLS models (TMF_{OLS}) and nonparametric bootstrap models (TMF_{NPB}) that regressed log-transformed lipid-normalized concentration on $\delta^{15}N$. Bootstrap regression was performed using bivariate Monte-Carlo resampling ($n = 10{,}000$ trials, with replacement) of probability density functions (PDF) that were defined for each species as normal sampling distributions for $\delta^{15}N$ (‰) and as lognormal sampling distributions for concentrations. Species-specific PDFs were defined by the mean and standard deviation of the sampling distributions for each species in the sampled food web. Covariance between sampled distributions was not assumed. Studentized deleted residuals were used to

indicate data points that were possible outliers in the regression models (Sheskin, 2000). A Studentized deleted residual >2.0 in absolute value was interpreted as an indication that a species may have been subjected to different conditions of exposure relative to the other species. Details of the statistical methods, including the bootstrap analyses are provided by (Powell et al., 2017).

4.4. Comparison to other studies

Field TMFs for cVMS reported by other studies were recalculated by Powell et al. (2017) using NPB regression (Eq. (4)) across summary statistics (mean and standard deviation, by species) for $\delta^{15}N$ and lipid normalized concentrations reported by each study. Lipid normalized concentrations were used for comparisons since some studies analyzed whole-body homogenates whereas others analyzed specific tissues (e.g. liver, axial muscle, eggs, etc.). Lipid content and wet weight concentrations in a tissue may be significantly different from that of the whole organism (Niimi and Oliver, 1983) such that lipid normalization of tissue concentrations can lead to unreliable conclusions (Hebert and Keenleyside, 1995). Moreover, it is erroneous to assume that hydrophobic chemicals partition only to lipids. Nonetheless, it is standard practice to calculate and interpret TMF based on lipid-normalized concentrations that were, preferably, determined using whole-body homogenates.

For comparison purposes, TMF_{NPB} values, including those for the Oslofjord, were calculated using a standard $\Delta^{15}N$ value of 3.4‰ TL^{-1} (Post, 2002), as applied by Borgå et al. (2012b). Thus uncertainty associated with $\Delta^{15}N$ was not incorporated into the 95% confidence intervals for TMF_{NPB}. Analysis of Co-Variance (ANCOVA) of summary data (mean and standard error, by species) was used to test for differences between results for the Inner and Outer Oslofjord (this study) and results reported by other studies for slopes and log-transformed concentrations. If the omnibus F test was significant a Tukey-Kramer multiple comparisons test (unequal sample sizes) was used to identify means that were different.

5. Results and discussion

5.1. Sampled food webs

Marine ecosystems such as the Oslofjord typically have very complex food webs that are defined by multiple, interconnected food chains that are confounded by a great diversity in prey organisms and feeding relationships. The sampled food web in the Oslofjord consisted of 22 species and included zooplankton, benthic macroinvertebrates, shellfish, and finfish (Table 1). Structure of the sampled food web may be evaluated directly from isotopic niche scatterplots of the measured data (Fig. 1), as described by Powell et al. (2017). Generally, zooplankton, benthic macroinvertebrates (worms and urchins), and blue mussel (*Mytilus edulis*) occupied the lowest trophic positions (TL ≈ 2 to 3); shrimp (*Pandalus borealis*), mussels, and finfish, such as the Pleuronectids (flounders), Clupeids (herrings), and most Gadids (cods), occupied the middle trophic positions (TL ≈ 3 to 4); and cod (*Gadus morhua*) occupied the highest trophic position (TL >4) of the sampled food web (Fig. 1).

Length of the sampled food webs based on trophic levels obtained from FishBase (Froese and Pauly, 2017) were estimated to be 2.4 trophic steps for the Inner Oslofjord and 2.6 trophic steps for the Outer Oslofjord (Table 1). Trophic length was also estimated by dividing the range of $\delta^{15}N$ across the sampled food web (Table 2) by the $\delta^{15}N$ trophic discrimination factor for food web ($\Delta^{15}N$). Unfortunately, it was not possible to benchmark or authenticate $\Delta^{15}N$ for the sampled food webs because samples collected from Oslofjord in 2008 were not analyzed for a reference material (e.g. PCB). As discussed by Powell et al. (2017) and the references cited therein, identification of $\Delta^{15}N$ for a food web remains one of the most unresolved areas of isotope ecology and experimental work continues to be needed. When based on $\Delta^{15}N = 3.4‰\ TL^{-1}$ (Post, 2002), as applied by Borgå et al. (2012b), length of the sampled food web was (16.8 − 7.98) / 3.4 = 2.6 trophic steps for the Inner Oslofjord and (17.3 − 8.80) / 3.4 = 2.5 trophic steps for the Outer Oslofjord. When based on $\Delta^{15}N = 3.8‰\ TL^{-1}$ (Hobson and Welch, 1992), as applied by Ruus et al. (2016), length of the sampled food web was 2.3 trophic steps for the Inner Oslofjord and 2.2 trophic steps for the Outer Oslofjord. The $\Delta^{15}N = 3.8‰\ TL^{-1}$ reported by Hobson and Welch (1992) was obtained by meta-analysis of isotope discrimination factors across an Arctic marine food web and, presumably, represented the most appropriate value for the marine food web in the Oslofjord. This was supported by our data indicating that $\Delta^{15}N = 3.82‰\ TL^{-1}$; which was the slope of the model for $\delta^{15}N$ regressed on relative trophic level across the zooplankton → shrimp → cod food chain (Powell et al., 2010).

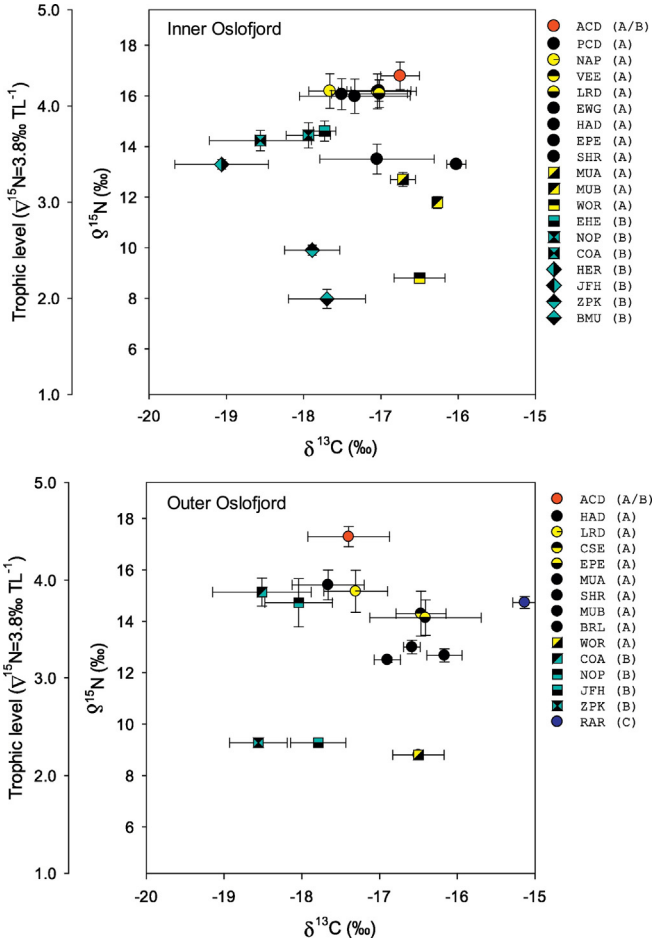

Fig. 1. Isotopic niche scatterplot (mean ± standard deviation; Table 2) of the aquatic marine food webs in the Inner and Outer Oslofjord (sampled November 2008). Food chains occupied by each species (A/B, A, B, C) are identified in the legend of each plot. Individual data are provided in Tables S2 and S3 of the SI.

Contaminants in a food web may originate from multiple sources and trophic transfer of a contaminant across a complex food web (i.e. bioaccumulation) may be obscured by the overlap and convergence of multiple food chains that comprise the food web. Stable isotope signatures (Table 2) suggested that the food webs in the Oslofjord were trophically compressed and confounded by overlapping food chains and omnivorous feeding (Fig. 1). The isotopic signatures for herring and shrimp indicated that these species occupied similar trophic positions (i.e. similar $\delta^{15}N$) in the sampled food webs but were feeding on different food chains (i.e. different $\delta^{13}C$) with different sources of carbon at the base. In order to better define the food web in the Oslofjord, individual species of the sampled food webs were thus assigned to one of two ecologically defined components or food chains using $\delta^{13}C$ as a

continuous variable for assessing source and flow of dietary carbon to consumers (Powell et al., 2010): 1) a pelagic food chain that included zooplankton, herring, and pelagic-neritic finfish and 2) a demersal food chain that included benthic invertebrates, shrimp, and demersal finfish. Isotopic signatures (Fig. 1) indicated that cod occupied the highest trophic level in the sampled food webs and were feeding on both shrimp and herring, which are the preferred forage for cod in the Oslofjord. Observation of gut contents of select individuals indicated that cod were feeding exclusively on shrimp at the time of collection, supporting the isotopic data indicating these species were separated by a single trophic level step. However, this may also have been an artifact of cod feeding on shrimp while retained in the trawl.

It was not possible to identify distinct demersal or pelagic food chains because of overlapping and converging $\delta^{13}C$ signatures that increased with carbon flow up the food web (Fig. 1), which was indicative of omnivorous feeding across the food web. Nonetheless, carbon flow across the Oslofjord food webs must have originated from at least two sources. Carbon flow in the demersal food chain (benthic organisms at the base) was assumed to be benthic in origin, whereas carbon flow in the pelagic food chain (zooplankton at the base) was assumed to be pelagic in origin. Therefore, the trophic dynamics in the Oslofjord were best described as a compressed benthipelagic food web.

5.2. Exposure

Because of the physical-chemical properties (Table S1 of the SI) of very low water solubility and very high partitioning from water to air (K_{AW}) and to organic carbon (K_{OC}), cVMS materials released to aquatic environments are adsorbed to particles that deposit to sediments. Thus the primary source of these super hydrophobic chemicals to a food web is not from water, but from discharged biomass that is a direct source of diet to resident biota near the base of the food web. Hence, sediments may be used as an indicator of relative exposure of organisms to cVMS discharged to the Oslofjord.

Concentrations of cVMS in surface sediments were considerably greater in the Inner Oslofjord, relative to concentrations in the Outer Oslofjord (Powell et al., 2010). The differences observed for concentrations of cVMS between surface sediments in the Inner and Outer Oslofjord were likely indicative of the source and the propensity for cVMS to deposit to sediments in the vicinity where released. Unfortunately, the experimental design for this study was not developed to detect the presence of spatial concentration gradients that are expected to exist for cVMS across surface sediments in the Oslofjord (Schøyen et al., 2016). Because of the semi-enclosed nature of the Oslofjord, and the sill near Drøbak that separates the Inner and Outer Oslofjord, cVMS and other chemical substances in wastewater discharged below the pycnocline become trapped in the Inner Oslofjord. As a result, exposure concentrations in the Inner Oslofjord are significantly elevated compared to concentrations found in the Outer Oslofjord and surrounding areas. Comparison of organic carbon normalized concentrations of cVMS in the sediments, which represents the primary source of cVMS to resident biota, showed that exposure levels in the more polluted Inner Oslofjord were about 2× higher for D4, 32× higher for D5, and 7× higher for D6, relative to the less polluted Outer Oslofjord.

5.3. Concentrations in biota

As was expected, concentrations of cVMS in biota from the Outer Oslofjord were less than concentrations in biota from the Inner Oslofjord. Generally, concentrations in biota from the Outer Oslofjord were less than the laboratory-specific MDLs for 3% to 8% of the samples analyzed by Dow Corning and for 9% to 76% of the samples analyzed by Evonik (Table S4 of the SI). In contrast, concentrations in biota from the Inner Oslofjord were less than the MDLs in 2% of the samples analyzed by Dow Corning and <18% of the samples analyzed by Evonik.

Mean wet-weight concentrations of cVMS in biota (ng/g ww) were variable among species and were statistically correlated with lipid content (Pearson's $r \geq 0.53$; $p \leq 0.02$; $n = 19$ species) in the Inner Oslofjord but not the Outer Oslofjord (Pearson's $r \leq 0.43$; $p \geq 0.14$; $n = 15$ species). This difference suggested that bioaccumulation of cVMS in the Inner and Outer Oslofjord was not due to simple water-to-lipid partitioning (i.e., bioconcentration) alone, but was influenced by other processes such as exposure, bioavailability, and possibly metabolism.

Lipid-normalized concentrations of cVMS in biota (ng/g lipid) were highly variable across species and were considerably greater in biota from the Inner Oslofjord, relative to concentrations in species from the Outer Oslofjord (Tables S2 and S3 of the SI). Similar to that observed for sediments, the differences in concentrations of cVMS reflected the higher exposure concentrations encountered in the more polluted Inner Oslofjord. Depending on species, mean lipid normalized concentrations of cVMS in biota (Table 2) from the Inner Oslofjord, relative to the less polluted Outer Oslofjord, were about 15× higher (range 3× to 37×) for D4, 40× higher (range 6× to 140×) for D5, and 7× higher (range 2× to 16×) for D6. Generally, concentrations in biota from the Inner and Outer Oslofjord differed by a factor >25× for species that had strong associations with the bottom sediment, such as benthic invertebrates and some demersal finfish.

Mean lipid-normalized concentrations of cVMS (by species) were greatest in biota from Inner Oslofjord compared to all other locations where food web studies have been conducted, as summarized by Powell et al. (2017). Mean lipid-normalized concentrations of cVMS in biota from Outer Oslofjord were greater than concentrations reported for Lake Randsfjorden (Borgå et al., 2013), were comparable to concentrations reported for Dalian Bay (Jia et al., 2015) and Lake Pepin (Powell et al., 2009), and were less than concentrations reported for Lake Erie (McGoldrick et al., 2014), Tokyo Bay (Powell et al., 2017), and Lake Mjøsa (Borgå et al., 2012a; Borgå et al., 2013).

5.4. Bioaccumulation

Lipid-normalized concentrations of cVMS in biota were typically greatest in the lowest trophic level species (i.e., the benthic macroinvertebrates and zooplankton) and decreased with increasing $\delta^{15}N$ (Fig. 2), which is an indicator of relative tropic level position in the sampled food webs (Fig. 1). Bioaccumulation of non-ionic substances, such as cVMS, is a function of bioconcentration and biomagnification (Burkhard et al., 2013). As discussed by Powell et al. (2017), bioconcentration is a point measure of the non-trophic uptake and accumulation of a chemical by an organism from abiotic media (primarily water but also sediment and air). Biomagnification is the slope or change in concentration of a chemical in organisms across a food web as a result of trophic uptake and accumulation relative to the change in TL of the organisms that define the food web. Bioaccumulation of cVMS by low-TL species in the Oslofjord was, presumably, primarily controlled by bioconcentration processes and lipid partitioning behavior (Drouillard et al., 2004; Gobas et al., 2015; McGoldrick et al., 2014), which are determined by interactions between lipid content (deBruyn and Gobas, 2007), type of lipid (van der Heijden and Jonker, 2011), and chemical-specific lipid partition coefficients (Seston et al., 2014). In high-TL species, biomagnification processes determined by dietary uptake and biotransformation presumably controlled bioaccumulation of cVMS. Modeling indicated that >80% of the mass of a hydrophobic chemical ($\log K_{OW} > 6$) accumulated by TL >3 organisms of the Oslofjord food web may be attributed to dietary uptake (Fig. S3 of the SI). Because of subsequent biotransformation (Arnot et al., 2008a; Arnot et al., 2008b), a chemical space may thus exist in the Oslofjord where BCF is high (>2000) and TMF is <1.0, as shown in the chemical space diagram (Fig. 3), which was generated using the MBAW model described by Kim et al. (2016).

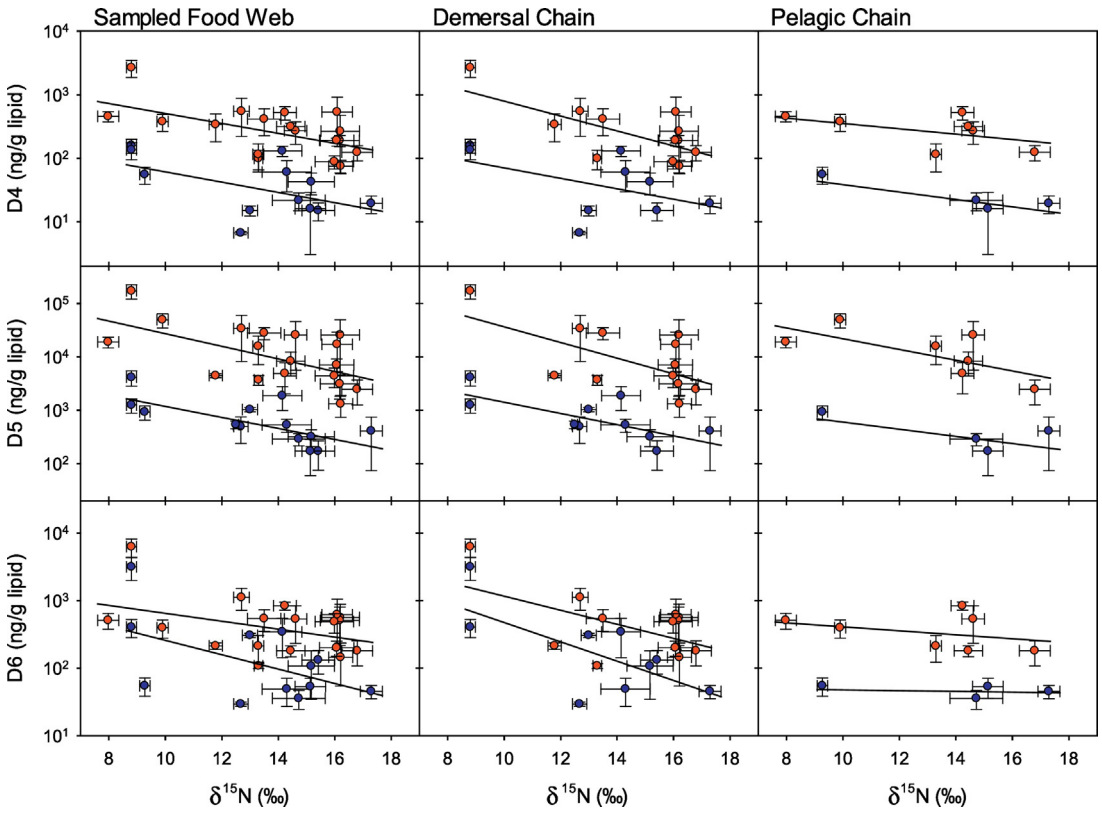

Fig. 2. Bootstrap regression models used to calculate TMF for cVMS concentrations (mean ± standard deviation; Table 2) across the aquatic marine food webs of the Inner Oslofjord (red circles) and the Outer Oslofjord (blue circles) that were sampled November 2008. Results of both bootstrap (BS) and ordinary least squares (OLS) regression models are summarized in Table 3. Individual data are provided in Table S2 and S3 of the SI.

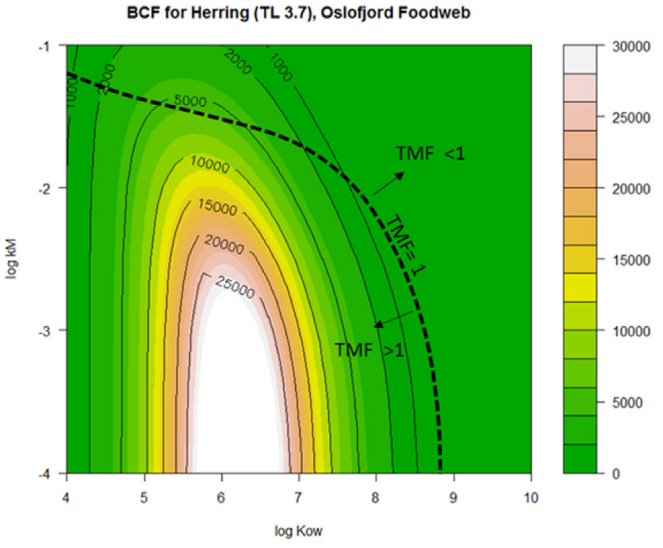

Fig. 3. Chemical space diagram showing the relationship between BCF and TMF as a function of biotransformation (k_M) and K_{OW}. The diagram was generated using the MBAW model (Kim et al., 2016). The BCF contour plot was based on Atlantic herring (TL = 3.7; lipid fraction = 8.8%) in the Oslofjord marine food web in the absence of concentration gradients (sediment concentration = 1 ng / g − dw; sediment:water fugacity ratio = 1). The TMF = 1.0 isoline was based on the entire Oslofjord marine food web. The area above and to the right of the TMF = 1.0 isoline represents chemicals estimated to have TMF < 1. The area below and to the left of the TMF = 1.0 isoline represents chemicals estimated to have TMF > 1.

5.5. Trophic magnification

5.5.1. Sampled food webs

Lipid-normalized concentrations of cVMS were inversely related to δ^{15}N (and by extension TL) across the sampled food webs in the Inner and Outer Oslofjord (Fig. 2). TMFs describe the average change in chemical concentration that occurs across a food web in response to carbon flow from one TL to the next and are the preferred method for evaluating bioaccumulation within well-defined food webs (Borgå et al., 2012b; Law et al., 2006; Muir et al., 2004). As previously discussed, lengths of the sampled food webs were estimated to be 2.3 trophic steps for the Inner Oslofjord and 2.2 trophic steps for the Outer Oslofjord when based on $\Delta^{15}N = 3.8‰\ TL^{-1}$ (Hobson and Welch, 1992), as applied by Ruus et al. (2016).

Regardless of the regression method or model that was used, TMFs for cVMS across the sampled food webs in the Oslofjord were <1.0 with 0% probability of being >1.0 (Table 3). TMF_{OLS} determined across samples ranged from 0.3 to 0.7 and were all statistically significant (i.e., slope ≠ 0; $p \le 0.03$) with coefficients of determination (r^2) ranging from 0.059 to 0.358. TMF_{NPB} determined across species means ranged from 0.4 to 0.6 with r^2 values ranging from 0.165 to 0.393 and 0% probability that TMFs were >1.0 (i.e., slope ≥ 0). Results between the different regression methods (i.e., regression across samples compared to regression across sample means) are not directly comparable for *p*-values and probability for TMF > 1.0 (Powell et al., 2017).

Trophic magnification factors obtained using OLS regression were not markedly different from TMFs obtained using NPB regression, indicating that unbalanced sample collection had minimal impact on the regression models (Fig. 4). Goodness of fit of the regression models indicated that TL, as measured by δ^{15}N, accounted for 6% to 36% of the uncertainty associated with OLS regression slopes compared to 16% to 39% of the uncertainty associated with NPB regression slopes. Thus

Table 3
Regression analysis results and trophic magnifications factors (TMF) for cyclic volatile methylsiloxanes (cVMS) in the aquatic marine food webs of the Oslofjord, Norway (samples collected November 2008).[a]

Test Material (end-point)[b]	Ordinary Least Squares Regression (individual samples)						Bootstrap Regression (means by species)					
	Inner Oslofjord Food Web			Outer Oslofjord Food Web			Inner Oslofjord Food Web			Outer Oslofjord Food Web		
	Sampled	Demersal	Pelagic	Sampled	Demersal	Pelagic	Sampled	Demersal	Pelagic	Sampled	Demersal	Pelagic
D4												
• n	80	53	31	41	29	14	18	12	7	13	9	4
• slope	−0.059	−0.081	−0.040	−0.075	−0.074	−0.051	−0.084	−0.127	−0.045	−0.079	−0.087	−0.065
• sd	0.145	0.189	0.111	0.196	0.209	0.114	0.014	0.021	0.015	0.081	0.020	0.026
• r-sqr	0.143	0.161	0.120	0.132	0.120	0.188	0.331	0.489	0.249	0.230	0.250	0.578
• *p*-Value	0.001	0.003	0.056	0.019	0.065	0.121	0.013	0.011	0.272	0.100	0.173	0.229
• TMF	0.6	0.5	0.7	0.5	0.5	0.6	0.6	0.4	0.7	0.6	0.6	0.7
• 95% C.I.	0.4–0.8	0.3–0.8	0.5–1.0	0.3–0.9	0.3–1.0	0.4–1.1	0.1–0.9	0.1–0.8	0.3–0.9	0.1–0.9	0.1–0.9	0.1–0.9
• Prob >1							0%	0%	0%	0%	0%	1%
D5												
• n	85	57	34	65	45	22	18	12	7	14	10	4
• slope	−0.098	−0.132	−0.093	−0.130	−0.136	−0.031	−0.123	−0.154	−0.106	−0.101	−0.109	−0.069
• sd	0.192	0.274	0.133	0.177	0.158	0.176	0.019	0.028	0.024	0.022	0.027	0.038
• r-sqr	0.209	0.194	0.345	0.358	0.436	0.033	0.351	0.383	0.463	0.393	0.461	0.492
• *p*-Value	<0.001	0.001	<0.001	<0.001	<0.001	0.419	0.010	0.032	0.072	0.017	0.030	0.293
• TMF	0.4	0.3	0.4	0.3	0.3	0.8	0.4	0.3	0.5	0.5	0.5	0.6
• 95% C.I.	0.3–0.6	0.2–0.6	0.3–0.7	0.2–0.5	0.2–0.5	0.4–1.5	0.1–0.8	0.1–0.8	0.1–0.8	0.1–0.8	0.1–0.8	0.1–1.0
• Prob >1							0%	0%	0%	0%	0%	4%
D6												
• n	77	50	32	53	37	20	18	12	7	12	9	4
• slope	−0.037	−0.066	−0.036	−0.136	−0.148	−0.006	−0.064	−0.112	−0.033	−0.113	−0.150	−0.010
• sd	0.151	0.209	0.111	0.211	0.188	0.088	0.016	0.024	0.020	0.018	0.021	0.022
• r-sqr	0.059	0.094	0.099	0.301	0.397	0.005	0.165	0.313	0.144	0.291	0.469	0.306
• *p*-Value	0.033	0.030	0.080	<0.001	<0.001	0.772	0.100	0.060	0.448	0.072	0.041	0.536
• TMF	0.7	0.6	0.7	0.3	0.3	0.9	0.6	0.5	0.8	0.5	0.4	0.9
• 95% C.I.	0.5–1.0	0.3–0.9	0.5–1.0	0.2–0.5	0.2–0.5	0.7–1.4	0.2–0.9	0.1–0.8	0.3–1.0	0.1–0.8	0.1–0.8	0.5–1.4
• Prob >1							0%	0%	5%	0%	0%	33%

[a] All TMF values were derived from the slope of the regression model of log-transformed dependent variable (lipid normalized concentration) on the isotopic signature ($\delta^{15}N$) of the organism. Regression models were based individual samples (ordinary least squares regression) or sample means by species (bootstrap regression). Regression slopes were converted to TMF using Eq. (4). A trophic discrimination factor ($\Delta^{15}N$) of 3.80 ‰ TL^{-1} (Hobson and Welch, 1992) was used for the TMF conversion, as suggested by Ruus et al. (2016).

[b] Results between OLS regression and bootstrap regression are not directly comparable, as discussed by Powell et al. (2017) and references therein. Bootstrap results represent the median values across 10,000 Monte-Carlo resampling events. Similarly, OLS confidence intervals were calculated from the standard error of the regression whereas bootstrap confidence intervals were obtained from the probability density function of the Monte-Carlo regression.

$\delta^{15}N$ appeared to be a relatively weak descriptor of bioaccumulation for cVMS in the Oslofjord and accounted for the relatively wide 95% confidence intervals observed for both TMF_{OLS} and TMF_{NPB}. The general lack of fit between $\delta^{15}N$ and lipid normalized concentrations further suggested that accumulation and trophic transfer of cVMS materials in the Oslofjord was a complex process that was likely confounded by overlapping and convergent food chains in the food web. Nonetheless there was no evidence to indicate that cVMS magnified across the sampled food webs in the Oslofjord.

Sensitivity analysis to concentration group factors (i.e., factors grouped across all species by $\Delta^{15}N$, cVMS concentration, and $\delta^{15}N$) indicated that uncertainty associated with $\Delta^{15}N$ accounted for >90% of the

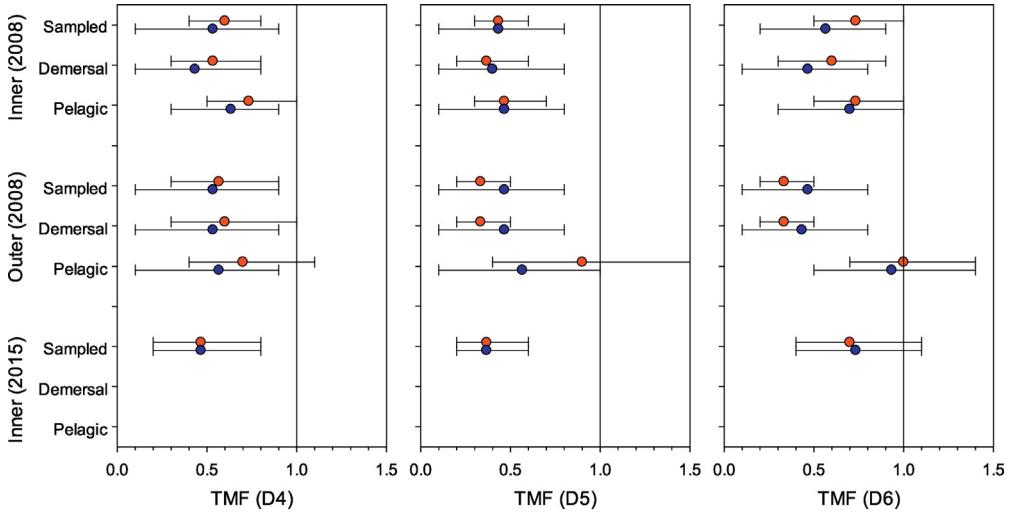

Fig. 4. Comparison of means and 95% confidence intervals for field TMF of cVMS (D4, D5, D6) across the aquatic food webs in the Inner and Outer Oslofjord based on samples that were collected in 2008 (Powell et al., 2010) and 2015 (Ruus et al., 2016). Red circles are the TMF values obtained by OLS regression (Eq. (3)) across samples. Blue circles are the TMF values obtained by Bootstrap regression across summary statistics (sample means and standard deviations).

total uncertainty associated with TMF_{NPB} values for the sampled food webs (Tables S5 and S6 of the SI; Fig. S4 of the SI). In contrast, sensitivity analysis indicated that concentration and $\delta^{15}N$ accounted for 80% to 91% and 9% to 20%, respectively, of the total uncertainty associated with slope of the regression models for the sampled food webs. Because TMF is a direct multiple of $\Delta^{15}N$ (see Eq. (4)) benchmarking, as it is discussed by Powell et al. (2017), may be used to eliminate $\Delta^{15}N$ from the calculation and possibly reduce total uncertainty. Unfortunately, benchmarking could not be applied to the Oslofjord because samples were not analyzed for a benchmark chemical. Thus detailed sensitivity analyses were conducted on slope rather than TMF.

Sensitivity analysis using species group factors (i.e., factors grouped within a species by concentration and $\delta^{15}N$) for the sampled food webs indicated that individual species accounted for 0.1% to 38% of the total uncertainty associated with slope of the regression models (Tables S5 and S6 of the SI). The greatest amounts of uncertainty were associated with low-trophic level species (e.g. benthic invertebrates and zooplankton) near the base of a food web and high-trophic level species (e.g. piscivorous finfish) near the top of the food web (Fig. 5). This pattern of relative uncertainty being greatest near the ends of the food web and lowest near the middle of the food web occurs because the margin of error of a regression model is greatest towards the edges of the regression line and minimal near the middle of the regression line. For cVMS in the Oslofjord, relative uncertainty associated with low-trophic level species near the base of a food web decreased the value of the regression slope (i.e. decreased TMF) whereas relative uncertainty associated with high-trophic level species near the top of the food web increased the value of the regression slope (i.e. increased TMF). Total uncertainty associated with the regression slope, and by extension TMF, may be reduced by placing greater emphasis on collection of species near the base and near the top of the food web. However, this will have minimal effect on the pattern of relative uncertainty.

5.5.2. Pelagic and demersal components

Contaminants in a food web may originate from multiple sources such that trophic transfer across the food web is obscured by the overlap and convergence of multiple food chains that comprise the food web. Omnivorous feeding across food chains that have different or multiple exposures to a contaminant may have a strong influence on calculation of TMF, thus making it especially difficult to interpret results (Kim et al., 2016; McLeod et al., 2015). As previously discussed, stable isotope signatures for species in the sampled food web suggested that trophic structure and dynamics in the Oslofjord were confounded by omnivorous feeding across overlapping and convergent food chains. Thus

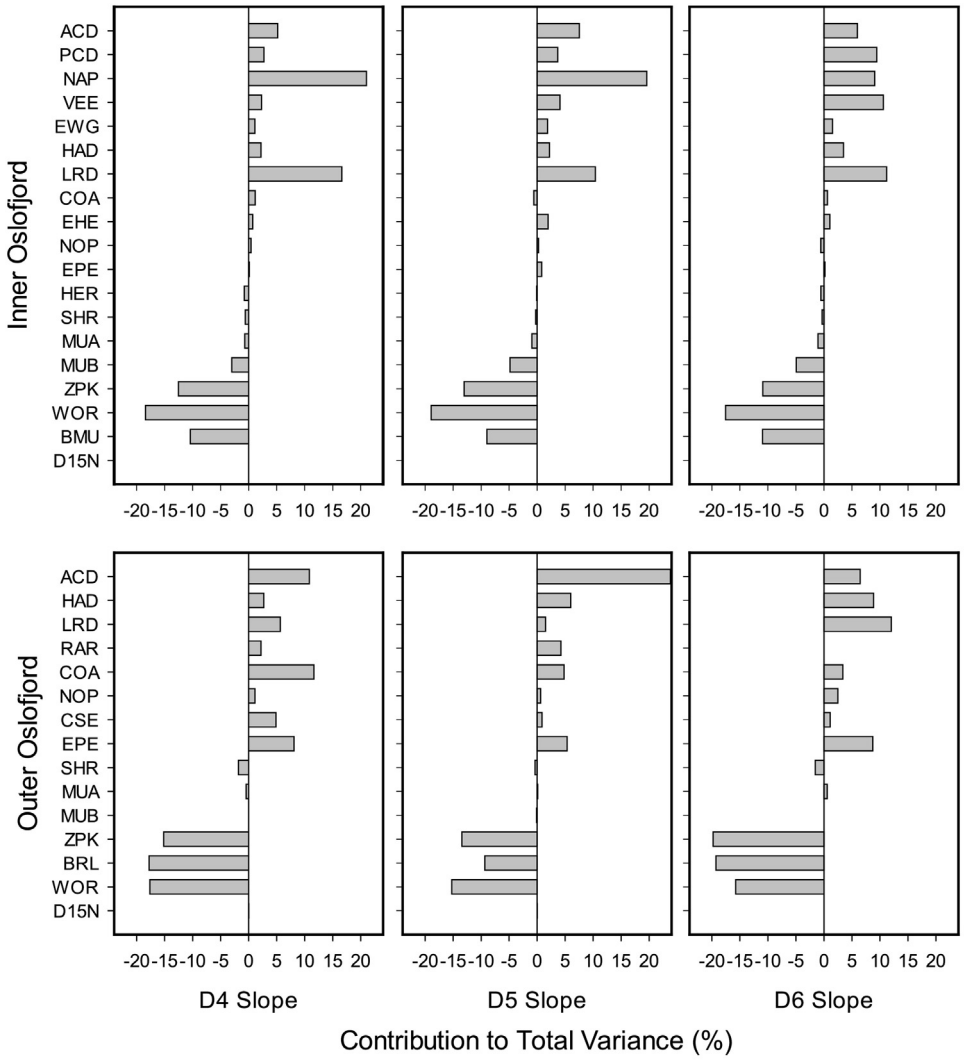

Fig. 5. Sensitivity evaluation of the TMF regression slopes to each species in the aquatic marine food webs of the Inner and Outer Oslofjord (sampled November 2008). Sensitivity is the percentage contribution of each species on the left side of the figure to the overall variance associated with the TMF regression slope. The percent contribution to the overall variance was calculated by squaring the rank correlation coefficients between each factor and the TMF, and normalizing them to 100%. The sign for the percent contribution indicates either that there was an increase (i.e., the rank correlation coefficient was positive) or a decrease (i.e., the rank correlation coefficient was negative) in the TMF regression slope.

trophic magnification was also evaluated for the demersal and pelagic components of the sampled food webs in the Oslofjord. The demersal component consisted of 12 species (food chain length 2.1 steps) in the Inner Oslofjord and 10 species (food chain length of 2.2 steps) in the Outer Oslofjord. The pelagic component consisted of 8 species (food chain length 2.3 steps) in the Inner Oslofjord and 5 species (food chain length of 2.1 steps) in the Outer Oslofjord.

Similar to that observed for the sampled food webs, TMFs for cVMS were all less than a value of 1.0 across the pelagic component (range 0.4 to 0.9) and demersal component (range 0.3 to 0.6) of the sampled food webs (Table 3) and were very consistent between the Inner and Outer Oslofjord. The probability that TMF values for cVMS were greater than a value of 1.0 was 0%, with the exception of the pelagic component in the Outer Oslofjord where the probability of TMF > 1.0 was 1%, 4%, and 33% for D4, D5, and D6, respectively. The inability to detect significant regression slopes for cVMS across the pelagic component of the Outer Oslofjord ($p = 0.23$ to 0.54) was attributed to the small sample size available for the regression models ($n = 14$ to 22 samples across 4 species). Typically, OLS regression models require large sample sizes of $n > 60$ to have sufficient power to detect significant slopes for contaminants with apparent TMFs in the range of 0.5 to 2.0 (Conder et al., 2012).

The relative difference between regression slopes for cVMS in samples across the demersal and pelagic components of the sampled food webs ranged from 35% to 68% for the Inner Oslofjord and from 37% to 109% for the Outer Oslofjord. Similarly, the relative difference between regression slopes for cVMS in species across the demersal and pelagic components of the sampled food webs ranged from 37% to 109% for the Inner Oslofjord and from 29% to 175% for the Outer Oslofjord. In all cases, regression slopes for cVMS were greatest in the pelagic component, suggesting that TMFs in the pelagic component were greater than TMFs in the demersal component. However, the observed differences between slopes were not statistically significant (ANCOVA, $p > 0.20$).

The high level of agreement for TMFs between the pelagic and demersal components of the sampled food webs appeared to indicate that trophic transfer of cVMS was not related to type of food chain. Furthermore, the high level of agreement for TMFs between the Inner and Outer Oslofjord appeared to indicate that trophic transfer of cVMS was not related to exposure. Thus we conclude that bioaccumulation and trophic magnification of cVMS was the same in the Inner and Outer Oslofjord, regardless of exposure or food web component.

5.6. Comparison to other studies

Trophic magnification factors are preferable to other measures for evaluating bioaccumulation within an ecosystem that has a well-defined food web (Borgå et al., 2012b; Law et al., 2006; Muir et al., 2004) or between multiple ecosystems (Gobas et al., 2009; Houde et al., 2008). Results presented here (Table 3) differ from those previously reported for the Oslofjord (Powell et al., 2010). These differences occurred because 1) the results presented here did not include concentrations less than the MDL (Table S4 of the SI) in the regression models and 2) $\Delta^{15}N = 3.8‰\ TL^{-1}$ was used to derive TMF. In contrast, the previously reported results included non-censored concentrations less than the MDL (negative values treated as missing values) and $\Delta^{15}N = 3.4‰\ TL^{-1}$ was used to derive TMF. Comparison of results indicated that slopes of regression models that included concentrations less than the MDL (i.e., the results previously reported by Powell et al. 2010) were greater than slopes of regression models that did not include concentrations less than the MDL. However, the difference between slopes was significant ($p < 0.05$) for D4 only.

Trophic magnification factors for cVMS in samples collected from the Inner Oslofjord in 2008 (Table 3) were in agreement with TMFs reported by Ruus et al. (2016) for samples collected from the Inner Oslofjord in 2015 (summarized in Table S7 of the SI). Although slopes of the regression models were not significantly different between the two studies ($p > 0.70$), the power to detect a significant slope was lower for the 2015 data because fewer samples were collected. The sampled food web evaluated by Ruus et al. (2016) was defined by 6 species ($n = 18$ samples) and had a trophic length of 2.7 steps ($\Delta^{15}N = 3.8‰\ TL^{-1}$). For contaminants with apparent TMFs in the range of 0.5 to 2.0, OLS regression models typically require large sample sizes (i.e. $n = 60$ to 100) in order to have sufficient power to detect significant slopes (Conder et al., 2012). Nonetheless, both studies show no evidence for biomagnification of D4, D5, or D6 across the sampled poikilothermic food web in the Inner Oslofjord.

Trophic magnification factors may be broadly applied across ecosystems that differ considerably in location and characteristics, such as between freshwater and marine environments (Houde et al., 2008; Tomy et al., 2007; Wan et al., 2007). As was summarized and discussed by Powell et al. (2017), other studies (Table S8 of the SI) have reported TMFs for cVMS in the pelagic marine food web of Tokyo Bay (Powell et al., 2017), in a mixed marine food web (i.e. confounded pelagic and demersal food webs) of Dalian Bay (Jia et al., 2015), in a demersal freshwater food web of Lake Pepin (Powell et al., 2009), in pelagic freshwater food webs of Lake Mjøsa (Borgå et al., 2012a; Borgå et al., 2013) and Lake Randsfjord (Borgå et al., 2013), and a mixed freshwater food web in Lake Erie (McGoldrick et al., 2014). The impacts of experimental design on the different study areas were evaluated by comparing reported TMFs (calculated using OLS regression) to TMFs that were recalculated using NPB regression (Powell et al., 2017). Generally, TMF_{NPB} was less than the reported TMF_{OLS} because of unbalanced sample designs where some species were collected and analyzed in large numbers (e.g., large fish that occupy higher trophic levels) relative to other species that were more difficult to collect or analyzed as a few composite samples (e.g. benthic invertebrates that occupy lower trophic levels). Nonetheless, the impact of experimental design appeared to be minimal for the Oslofjord, with the exception of D5 in the pelagic component of the Outer Oslofjord (Fig. 4).

Highly significant differences (ANCOVA; $p < 0.01$) and inconsistencies (i.e., TMF < 1.0 < TMF) were observed between the Oslofjord and some of the other study areas where trophic magnification of cVMS has been evaluated (Table S8 of the SI). Generally, TMF_{NPB} for cVMS were <1.0 for the Oslofjord and all other study areas (range 0.3 to 0.9), except for the mixed marine food web in Dalian Bay (range 1.2 to 2.2) and the pelagic freshwater food webs in Lake Mjøsa (range 1.3 to 3.2) and Lake Randsfjorden (range 1.6 to 2.3). Exceptions to this general observation were $TMF_{NPB} = 0.8$ for D6 in Lake Mjøsa (sampled 2010), $TMF_{NPB} = 0.8$ for D4 in Lake Mjøsa (sampled 2012), and $TMF_{NPB} = 0.6$ for D4 in Lake Randsfjorden. As discussed by Powell et al. (2017), field data (Table S8 of the SI) suggested that differences and inconsistencies observed for TMFs across the study areas, including the Oslofjord, did not appear to be related to environment (marine vs freshwater), relative levels of study area contamination, type of food web (pelagic vs demersal), or structure of the food web (species composition and length). Rather, the TMF contradictions between study areas appeared to be related to food web dynamics and variable conditions of exposure, such as may occur from omnivorous feeding across food chains and organism movement across spatial concentration gradients within a study area (Kim et al., 2016; McLeod et al., 2015). For example, the migration pattern of cod differs from that of herring, with cod being stationary whereas herring migrate between the fjords and ocean. Neither migration pattern nor concentration gradients of siloxanes where examined in this study. Nonetheless, the impact of food web dynamics and variable conditions of exposure appeared to be minimal within the Oslofjord. Analysis of Studentized deleted residuals used to identify problematic data points and possible outliers (Powell et al., 2017) indicated that few organisms within the Oslofjord may have been subjected to variable conditions of exposure (Figs. S5 and S6 of the SI).

6. Conclusions

The objective of this work was to apply newly developed methods to re-evaluate bioaccumulation and trophic transfer of cVMS (D4, D5, and D6) across the marine food webs in the Inner and Outer Oslofjord, Norway as was first reported by Powell et al. (2010). Results reported here are in agreement with the previoulsy reported work and provide further support that trophic dilution of cVMS, not trophic magnification, occurred across the sampled food webs in the Oslofjord. Moreover, these results for the Oslofjord were consistent with most other food web studies, suggesting that bioaccumulation and trophic transfer of cVMS was not related to:

- environment,
- type of food web,
- food web structure, or
- relative level of overall exposure across food webs.

Rather, contradictory results in comparison to field data from other studies appeared to be related to variable exposures across food webs as a result of omnivorous feeding and organism movement across spatial concentration gradients. Modeling (Kim et al., 2016) illustrates that hydrophobic substances such as cVMS, which biotransform and thus are subject to a lower degree of biomagnification, are most sensitive to bias from sample collection location, unbalanced sampling designs, and the confounding impact of itinerant organisms (e.g. Atlantic herring, northern shrimp) that roam across spatial concentration gradients.

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Appendix A. Supplementary data

Text, equations, tables, and figures that provide details of: experimental methods (sample collection, sample analysis, quality control); calculations (methods for calculation of TL and TMF); statistics and data analysis, including bootstrap methods; and results. This material is available free of charge via the Internet at: https://doi.org/10.1016/j.scitotenv.2017.11.237.

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