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Food Web Accumulation of Cyclic Siloxanes in Lake Mjøsa, Norway

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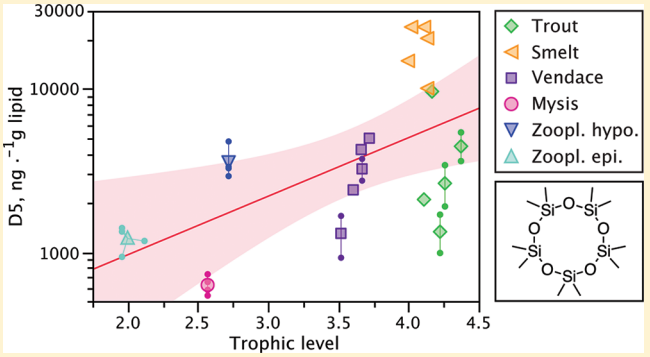
Supporting Information

ABSTRACT: The biomagnification of the cyclic volatile methyl siloxanes octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexatetrasiloxane (D6) was analyzed in the Lake Mjøsa food web in Norway from zooplankton and *Mysis* to planktivorous and piscivorous fish. The trophic magnification factor (TMF) for D5 was determined and compared with TMFs of several legacy contaminants: polychlorinated biphenyl (PCB) congeners 153 and 180, polybrominated diphenyl ether (PBDE) congeners 47 and 99, and *p,p′*-DDE. D5 showed TMF significantly greater than 1, implying food web biomagnification (TMF = 2.28, CI: 1.22−4.29). This contrasts with two studies that reported TMF < 1, which may reflect variability in TMF between food webs. The Lake Mjøsa D5 TMF was sensitive to the species included at the higher trophic level; whole food web TMF differed from TMF excluding smelt (*Osmerus eperlanus*) or brown trout (*Salmo trutta*) (TMF_{-SMELT} = 1.62, CI: 0.96−2.72; TMF_{-TROUT} = 3.58, CI: 1.82−7.03). For legacy contaminants (e.g., PCB-153 and PCB-180), the TMFs were less sensitive to the food web composition, and a better model fit was obtained compared to D5. The differences in biomagnification behavior between D5 and the legacy contaminants suggest that the biomagnification of D5 is being governed by species-specific properties such as biotransformation rate or tissue distribution that differ from those of legacy contaminants.



INTRODUCTION

International agreements have resulted in restricted production and use of several environmental contaminants, such as those identified in the Stockholm Convention on POPs.[1] Recently, model-based tools have been used to screen for potential emerging contaminants in the environment.[2−4] Cyclic volative methylsiloxanes (cVMS) were among a group of chemicals identified as potential emerging contaminants of concern in the environment due their predicted persistence and/or bioaccumulative characteristics.[3]

Siloxanes such as cVMS are used in several industrial applications, as additives in fuel, in consumer products such as car polish, cleaners, and waxes, and in personal care and biomedical products.[5] Due to previous limitations and challenges in the analytical quantifications of cVMS in environmental matrices, empirical data on levels in the environment are still scarce. However, due to recent development and improvement of the analytical quantification methods,[6,7] environmental measurements are increasing. Recently, the cVMS decamethylcyclopentasiloxane (D5 CAS no. 541−02−6) was measured in air samples[8] and was shown to be a potential global contaminant.[9] cVMS have been detected in various media of the Nordic environment,[5] and D5 has shown pronounced bioaccumulation in both invertebrates and fish.[10,11] Results of the potential to biomagnify (concentration increase in an organism relative to its diet, due to uptake from diet)[12] are contradictory as some studies report biomagnification when investigating only single predator−prey relationships, whereas food web bioaccumulation studies indicate overall decreasing cVMS concentrations with increasing trophic level in the food web.[13,14] There is a scarcity of studies of bioaccumulation behavior and trophic transfer of cVMS in well-defined food webs.

Compared to other bioaccumulation metrics, trophic magnification factors (TMFs) have been suggested as a more reliable tool for evaluation of chemicals' behavior in food webs.[15,16] TMFs represent the average factor of change in concentration between two trophic levels in the food web, and are determined by the slope of the solvent (e.g., lipid) normalized contaminant concentration regressed onto the trophic level of the food web organisms.[17,18] When assessing behavior of emerging contaminants, it is important to study well-known food webs, and to compare with well-known contaminants. Likewise, it is necessary to assess the trophic position of the organisms, for example, by analysis of stable isotopes of nitrogen ($\delta^{15}N$).[19] The $\delta^{15}N$ value increases in the food web because the lighter isotope (^{14}N) is eliminated from the organisms to a greater extent than the heavier isotope (^{15}N).

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Table 1. Stable Isotope Signatures of Carbon ($\delta^{13}C$) and Nitrogen ($\delta^{15}N$), Estimated Trophic Level (TL), Lipid Content and Concentrations of cVMS and Selected Legacy Contaminants (ng/g Lipid Weight), in the Lake Mjøsa Food Web Collected Autumn 2010[a]

	zooplankton											
species	epilimnion	hypolimnion	mysis		vendace			smelt			trout	
matrix	whole pooled	whole pooled	whole pooled		muscle			muscle			muscle	
n	4[e]	4[e]	4[e]		5			5			5	
				mean		SE	mean		SE	mean		SE
$\delta^{13}C$	−30.3	−34.3	−30.5	−30.0	±	0.2	−27.1	±	0.1	−27.8	±	0.7
$\delta^{15}N$	8.4	10.9	10.4	14.0	±	0.1	15.5	±	0.1	16.0	±	0.2
TL	2.0	2.7	2.6	3.6	±	0.0	4.1	±	0.0	4.2	±	0.0
length, cm				20.7	±	0.3	22.6	±	0.6	58.3	±	5.4
weight, g				69.8	±	1.6	76.2	±	9.5	2228.0	±	748.5
lipid, %	0.3	1.1	2.0	3.9	±	0.3	0.9	±	0.3	1.9	±	0.7
D4[b]	<83[d]	<190[d]	<38[d]		<71			<150		190	±	80
D5	<1210[d]	3600	630	3200	±	650	18700	±	2700	4000	±	1480
D6[c]	<870	<230[d]	<51[d]	100	±	18	640	±	160	130	±	20
PCB-153	13	18	16	49	±	2	210	±	45	420	±	190
PCB-180	5	5	4	19	±	1	89	±	21	180	±	83
p,p′-DDE	55	82	79	189	±	10	610	±	130	1310	±	550
BDE-47	22	38	35	98	±	7	530	±	140	1290	±	620
BDE-99	70	100	80	30	±	2	14	±	4	190	±	110

[a]When more than 50% of the samples were quantified below limit of quantification (LOQ), this is noted by <. All measured values were included in the summary statistics, thus the estimated means are to be viewed as maximum estimates. [b]All invertebrate samples had D4 concentrations below the limit of quantification (LOQ), see SI Table S5 for details. [c]Only one of the invertebrate samples (epilimnic zooplankton) had D6 concentrations above LOQ. All fish samples, with the exception of one trout, had D6 concentrations above the LOQ, see SI Table S5 for details. [d]Species with 100% of the samples below the LOQ. [e]As the four samples were from the same pooled trawls, only the arithmetic mean value is presented and used in the weighted regression. See SI Table S5 for individual results per sample.

The objective of the present study was to assess food web biomagnification of the cVMS octamethylcyclotetrasiloxane (D4 CAS no. 556−67−2), D5 and dodecamethylcyclohexasiloxane (D6 CAS no. 540−97−6) by quantifying TMFs in the Lake Mjøsa (Norway) pelagic food web leading to brown trout (*Salma trutta*) as the top predator. We compare the food web bioaccumulation behavior with that of legacy compounds, both chlorinated (dichlorodiphenyldichloroethylene−DDE, polychlorinated biphenyl-PCB) and brominated (polybrominated diphenyl ether-PBDE) contaminants that were studied in the food web in a parallel study.[20]

MATERIALS AND METHODS

Food Web and Sample Collection. Representatives of the pelagic food web were sampled in Lake Mjøsa, Norway during the autumn of 2010 (11th September −28th October) (Table 1, Supporting Information (SI) Tables S1 and S2). Lake Mjøsa (60°53′N 10°41E) is Norway's largest lake (117 km long, 14 km wide, ∼65 km^3 of water, 153 m average depth, 453 m maximum depth (SI Figure S1)). There is intensive agricultural activity and some industry in the surrounding area and the lake has a long history of pollution by contaminants such as mercury, dioxins, PCB and PBDE.[20−22] The Lake Mjøsa food web leading to brown trout (*Salma trutta*) is well-studied and has been monitored for several years.[22−24]

Zooplankton from the epilimnion (predominantly water fleas *Daphnia galeata*), and hypolimnion (predominantly copepods *Limnocalanus macrurus*) were collected midlake near Skreia, south of Helgøya (SI Figure S1) by horizontal trawling at separate depths above and below the thermocline which was about 30 m during time of sampling (zooplankton net 250 μm Nylon single strand, custom-made at the Norwegian Institute for Water Research (NIVA), with brass cup and brass mesh). *Mysis relicta* was picked with tweezers from the hypolimnion trawls. As the zooplankton sampling coincided with a bloom, phytoplankton was separated from the epilimnion zooplankton by additionally filtering the samples through a sieve of zooplankton netting while flushing gently with water from the lake. Immediately after collection, the samples were divided into subsamples for analysis of cVMS, legacy contaminants (halogenated POPs) and stable isotopes of nitrogen and carbon, and stored frozen until chemical analysis. Mysis and zooplankton were kept in 50 mL preheated glass jars.

The fish vendace (*Coregonus albula*, 19.5−21.3 cm, 64.5−73.0 g), smelt (*Osmerus eperlanus*, 20.5−23.7 cm, 45.3−97.5 g) and brown trout (43.5−75 cm, 0.88−5.14 kg) were collected with gill nets with assistance of local fishermen. Each sample of trout consisted of filets from one individual fish, whereas each sample of smelt and vendace consisted of pooled filets from 2−3 individuals (SI Table S2). The fish were stored frozen whole until sample preparation (dissection of skinless muscle fillet) at NIVA, and dissected muscle was stored in transparent preheated glass jars. Vendace and trout were collected west of Helgøya, and smelt was collected both west of Helgøya (one sample) and east of Helgøya near Ottestad (four samples) (SI Table S2, Figure S1). The three fish species are all pelagic and cover vast areas in searching for food. The influence of sampling location on contaminant exposure was therefore assumed to be negligible.

To reduce the risk of contamination during sampling, all sample preparation was conducted outdoors, that is, the material was outdoors from the time of sampling until it was freezer-ready for storage until shipment to Department of Applied Environmental Science (ITM, Stockholm University, Sweden). NIVA personnel and local fishermen avoided

personal care products 24 h prior to field work. All large surfaces (e.g., tubs for gill nets, gill nets after retrieval before the fish were collected, the table for sample preparation and fish dissection) were covered in aluminum foil. The aluminum foil for large surfaces was precleaned with laboratory grade acetone and methanol, whereas aluminum foil placed under the lids of the sample jars was preheated. The fish were stored frozen in aluminum foil until the filets were dissected outdoors on a surface covered in clean aluminum foil. All equipment was cleaned in acetone and methanol between samples. The samples were only in contact with clean utensils of stainless steel (tweezers, knife, scalpel). The sample containers were kept frozen in sealed PE bags until analysis of cVMS in December 2010 and February 2011.

Field blanks were collected during sampling. Precleaned field blanks (passive samplers: polyester pouches containing ∼60 mg ENV+) were exposed to air and handled in the same manner as the samples. The field blanks followed the samples in all phases of collection and preparation, with the exception that they were not attached to the gill nets under water. The field blanks were never in contact with the biota, but were positioned in between the gill nets when the gill nets were retrieved. Field blanks were attached to the zooplankton net to control for potential contamination from sampling equipment. Field blanks were added to separate glass jars in the same way as Mysis was picked from the hypolimnion samples. Other field blanks were treated as the epilimnion zooplankton. After exposure the field blanks were wrapped in aluminum foil and kept frozen in sealed PE bags until analysis.

Chemical Analysis of cVMS. The samples were analyzed for cVMS with a purge and trap method[6] using an extraction time of 36 h. Extraction and sample preparation were performed in a clean air cabinet under a laminar flow of filtered air. The fish fillets were partly thawed and cut into 0.5−1 cm^3 pieces directly in the jar. An aliquot was added to the extraction vessel. The sample mass was determined by weighing the jar before and after subsampling. The mysis and zooplankton were analyzed as delivered without subsampling. The mass was determined by weighing the jar. The surrogate standards (^{13}C-labeled D4, D5, D6, in 50 μL of an ethyl acetate solution) were added frozen (a glass vial insert with the IS below a frozen plug of Milli-Q water). A glass syringe filled with ∼20 mg of ENV+ sorbent (hydroxylated polystyrene-divinylbenzene copolymer, Biotage AB, Uppsala, Sweden) was used as the sample trap. The elution volume was 0.9 mL.

For analysis the field blank pouches were dried with precleaned nitrogen and subsequently extracted with 1−1.5 mL hexane containing the surrogate standards. An aliquot was analyzed on the GC/MS. Four unexposed ENV+ pouches were analyzed for comparison (one that had been returned from NIVA unused and three from the same batch that had been stored at ITM). The mean cVMS content of the unexposed pouches was subtracted from the cVMS content of the field blanks when evaluating the results, as cVMS had been observed to slowly leak out of thoroughly precleaned ENV+ during storage.

Quality Analysis and Quality Control of Siloxane Analysis. In addition to procedural blanks and field blanks, an internal matrix control (herring homogenate) was analyzed with each round of eight samples. Furthermore, three of the brown trout and two of the vendace samples were analyzed in duplicate, whereby the duplicate samples were obtained by taking pieces of fish from the same jar. The limit of quantification (LOQ) was set to the mean plus 10 times the standard deviation of the procedural blanks. Samples that contained less than 5 times the corresponding field blank were also classified as below LOQ. The cVMS results were not blank corrected.

Chemical Analysis of Halogenated POPs and Trophic Level Descriptors. Legacy halogenated contaminants were analyzed to enable comparison of the food web bioaccumulation behavior of well-studied POPs to that of cVMS. Chlorinated POPs (DDT and PCB) and PBDE were extracted and analyzed at the Norwegian Institute for Air Research (NILU-Kjeller) using established methodologies.[21,24] The chlorinated POP and PBDE data are presented in detail elsewhere.[20] In the present study, only PCB-153, PCB-180, p,p′-DDE, PBDE-47, and PBDE-99 are included for comparison with the cVMS (benchmarking). The lipid content of the samples was determined gravimetrically. Aliquots of the samples were homogenized in Na_2SO_4 to remove water and eluted with dichloromethane. The solvent was evaporated into dryness, and the remaining residue was weighed.

Stable isotopes of nitrogen (δ^{15}N) and carbon (δ^{13}C) were analyzed at the Institute for Energy Technology (IFE-Kjeller) according to standard protocols.[20] δ^{13}C was included to identify whether the carbon source to the food web was predominantly pelagic or benthic.[25] Neither lipids nor carbonate were removed or extracted from samples prior to analysis of the isotopic signature.

Data Treatment. The relative trophic level (TL) of each sample (consumer) was calculated from δ^{15}N using an enrichment factor ΔN of 3.4 ‰.[17,18,26] The lowest epilimnion zooplankton δ^{15}N was defined as the baseline primary consumer of trophic level 2 (δ^{15}N primary consumer) (eq 1).

$$TL_{consumer} = ((\delta^{15}N_{consumer} - \delta^{15}N_{primary\ onsumer})/\Delta N) + 2 \quad (1)$$

Trophic magnification factors (TMFs) were estimated as the slope (b) of the lipid normalized contaminant concentration ([contaminant]$_{lw}$) regressed onto the TL (eqs 2 and 3). For the fish samples analyzed in duplicate, and the samples of zooplankton and Mysis that were considered as pseudoreplicates, the calculation of TMF was based on the mean contaminant concentration. In the statistical analyses the influence of each sample was weighted by $\sqrt{n}$ as the precision of the estimates increase with the square root of their group size (or inverse of its variance)[27] (SI Table S3). In this way, a conservative approach was applied to maintain the statistical power in the analyses.

$$[\text{contaminant}]_{lw} = ae^{bTL} \quad (2)$$

$$\text{Ln}[\text{contaminant}]\text{lw} = \text{Ln}\,a + bTL \quad (3)$$

TMFs were not calculated for D4 and D6, as too many samples had concentrations below the LOQ. For D5, the epilimnic zooplankton samples had concentrations below LOQ, but were included in the data treatment as measured because the use of uncensored data is preferable to substitution by a fixed value or random number.[17]

To compare behavior and investigate covariance with legacy contaminants, the levels of D5 were correlated with the selected benchmark chemicals (p,p′-DDE, PCBs and PBDEs), by product-moment correlation of natural logarithm transformed lipid adjusted concentrations based on unweighted influence of the different samples (n = 18).

Table 2. Trophic Magnification Factors (TMF) for D5 and Selected Benchmark Legacy Chlorinated and Brominated Contaminants with Upper and Lower 95% Confidence Intervals[a]

data set	contaminant	slope	Se	TMF	95% confidence interval	R2	*N* (Sum Of Weights)	*t* Ratio	prob > |T|
Whole Food Web									
	D5	0.83	0.30	2.28	1.22−4.29	0.33	23.07	2.78	0.0133
	PCB-153	1.59	0.22	4.90	3.06−7.85	0.76	19.15	7.14	<0.0001
	PCB-180	1.79	0.24	6.01	3.62−9.98	0.78	19.15	7.49	<0.0001
	P,P′-DDE	1.36	0.21	3.90	2.51−6.04	0.73	19.15	6.57	<0.0001
	BDE-47	1.76	0.26	5.82	3.36−10.09	0.74	19.15	6.80	<0.0001
	BDE-99	0.89	0.38	2.43	1.08−5.43	0.25	19.15	2.33	0.0331
Trout Excluded									
	D5	1.28	0.31	3.58	1.82−7.03	0.61	16.83	4.16	0.0016
	PCB-153	1.40	0.19	4.05	2.64−6.20	0.83	14.15	7.20	<0.0001
	PCB-180	1.62	0.22	5.06	3.13−8.19	0.83	14.15	7.41	<0.0001
	P,P′-DDE	1.15	0.17	3.16	2.19−4.56	0.81	14.15	6.91	<0.0001
	BDE-47	1.50	0.23	4.47	2.69−7.45	0.79	14.15	6.46	<0.0001
	BDE-99	0.32	0.28	1.38	0.74−2.58	0.10	14.15	1.12	0.2860
Smelt Excluded									
	D5	0.48	0.24	1.62	0.96−2.72	0.28	18.07	2.04	0.0658
	PCB-153	1.56	0.27	4.75	2.65−8.53	0.76	14.15	5.86	0.0001
	PCB-180	1.75	0.28	5.76	3.08−10.75	0.78	14.15	6.16	<0.0001
	P,P′-DDE	1.37	0.25	3.92	2.28−6.75	0.74	14.15	5.54	0.0001
	BDE-47	1.74	0.31	5.68	2.87−11.22	0.74	14.15	5.61	0.0001
	BDE-99	1.33	0.30	3.79	1.97−7.31	0.64	14.15	4.47	0.0009

[a]The linear regression was run on natural logarithmic transformed contaminant concentrations (lipid normalized), weighting the influence of each sample by $\sqrt{n}$ (n: the number of replicate analyses it is based on, see SI Table S3). The TMFs are highlighted in the grey field.

All statistical data treatment was carried out in JMP9.0.3 from SAS Institute 2010.

RESULTS AND DISCUSSION

QA Results. Control herring homogenates showed good agreement with previous analyses. The concentrations were 5.2 ng/g ww (RSD 2.6%) for D5 and 1.4 ng/g ww (RSD 8.9%, n = 4) for D6, compared to previous measurements of 4.9 (RSD 12%, n = 29) and 1.3 (RSD 15%, n = 14).

For D5 and D6 the total content of the field blanks was in all cases insignificant compared to the total amount of these analytes extracted from the samples (ratio >12 up to 2491, see SI Table S4). For D4 the difference between field blanks and samples was less, and in 22 of 32 samples the ratio (sample/field blank) was below 5. The amount of D4 was also below the procedural blank LOQ in 12 of the samples, including all the invertebrates. The amount of D5 was above the procedural blank LOQ in all of the samples except the four epilimnic zooplankton samples. The amount of D6 was below the procedural blank LOQ in 12 samples, including all of the invertebrate samples but one. Thus, only 22% of D4 and 63% of D6 results are above the LOQ, see SI Table S5 for details.

The mean difference in duplicates samples of the trout and vendace was 23%, 47%, and 65% for D4, D5, and D6, respectively (SI Figure S2). This difference may partly be explained by the duplicates not being taken from a homogenate, but from different pieces of the fish fillet or, in the case of vendace, from two individuals in the same jar. Homogenization was avoided because of the risk of contamination that this extra step entails. However, as the duplicate variation was less than the intraspecies variation, the mean of the duplicates was included in the data treatment and in the summary statistics.

cVMS Concentrations. D4 was quantified above the LOQ only in fish (SI Table S5), with concentrations ranging from below LOQ to 4.5 ng/g wet weight (ww). D5 was quantified above LOQ in all samples, except epilimnic zooplankton, and was the cVMS found in highest concentrations throughout the food web. The D5 concentrations showed low degree of variation among the samples of hypolimnic zooplankton (30.6−49.4 ng/g ww) and Mysis (10.8−14.6 ng/g ww), whereas the variance within the fish species was greater (vendace 45.5−214 ng/g ww, smelt 123−199 ng/g ww, trout 8.7−194.5 ng/g ww). The low variability among the zooplankton probably reflects the pseudoreplication of zooplankton and Mysis sampling, where subsamples were obtained from pooled trawls. The low variability among the samples is an indication of the high analytical reproducibility rather than low population variance of cVMS accumulation. D6 was quantified above the LOQ only in fish, and in one zooplankton sample, with low concentrations ranging from below 0.5−7.2 ng/g ww in fish.

The lipid content in the food web organisms was low, from 0.3 to 2.0% for zooplankton and Mysis, and from 0.9 to 3.9% in fish. When the contaminant concentrations were normalized to lipid weight concentrations (lw), D5 concentrations were lowest in Mysis (627 ng/g lw) and highest in smelt (18652 ± 2725 ng/g lw) (Table 1). Mysis consistently had the lowest concentrations of cVMS, whereas chlorinated and brominated contaminant concentrations in Mysis were comparable to levels in zooplankton from the epilimnion and hypolimnion (Table 1).

Although D4 and D6 had comparable lipid normalized concentrations within each fish species, D5 concentrations were from 20 to 125 times higher than D4 and D6, depending on fish species (Table 1). Similar findings were also reported in

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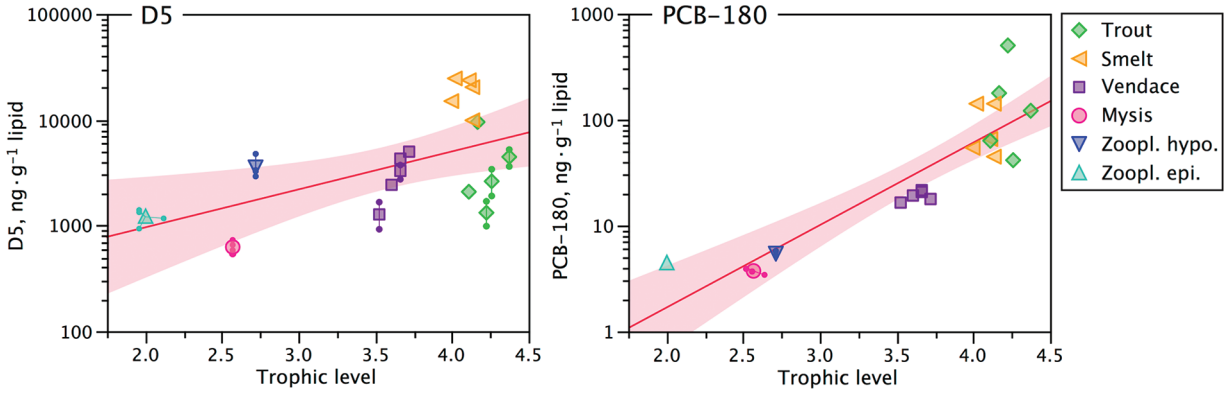

Figure 1. Relationship between lipid normalized concentrations of D5, PCB-180 and trophic level (TL). See Table 2 for details on linear regression model results such as significance levels and estimated trophic magnification factor. The zooplankton and Mysis D5 estimate consisted of the mean value of four replicate samples from the same pooled trawl, as indicated by small dots. Fish samples analyzed in duplicate for D5 are also indicated by small dots. The influence of each sample in the regressions was weighted by $\sqrt{n}$ (n: the number of replicate analyses it is based on, see SI Table S3). See SI Table S5 for individual results per sample.

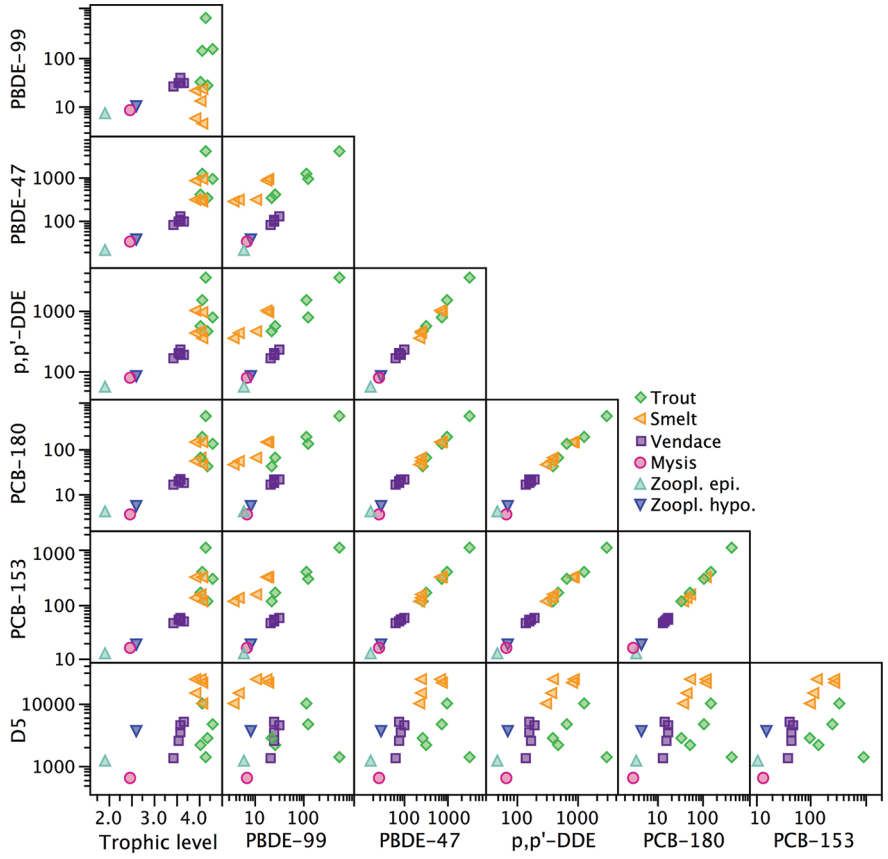

Figure 2. Scatter plot matrix for concentrations (ng/g lipid weight) of D5, benchmark legacy persistent organic pollutants, and trophic level.

other studies: relatively low levels of D4 and D6 compared to D5.[11,13,28] The cVMS concentrations varied considerably within each fish species (Table 1, SI Table S5), as has also been seen in previous studies of other marine and freshwater fish.[10,11] However, the D5 in fish were not related to their length or weight (SI Figure S3).

Comparison to Other Areas. Previously, large interlaboratory differences were reported for the analysis of cVMS. For instance, the difference in parallel samples of biota from the Oslofjord, Norway was −32% to 164% for D4, −60% to 168% for D5, and −37% to 166% for D6.[13] However, recent analytical advances such as the use of labeled surrogate standards and clean benches have increased comparability between different laboratories, as demonstrated in a recent interlaboratory study.[7] In the present study the levels of cVMS in the Lake Mjøsa food web were generally higher than reported for Arctic marine biota on Svalbard,[10] whereas they were comparable to or higher than cVMS levels from the inner Oslofjord[13] and other marine[5] and estuarine[11] areas (see Supporting Information for details). There is a need to identify the sources of cVMS to Lake Mjøsa, as the concentrations in the food web are high despite the

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relatively low population of approximately 200 000 inhabitants[29] in the Lake Mjøsa area.

Food Web Biomagnification of cVMS. The pelagic food web consisted of species ranging over 2.3 trophic levels, from epilimnic zooplankton at the lowest trophic level (2) to trout at the highest trophic level (4.3 ± 0.1), which partly overlapped with smelt (4.1 ± 0.1) (Table 1). Carbon isotopic signatures ($\delta^{13}C$) confirm that the food web was predominantly pelagic (−27.1 to −34.3‰). The findings are in accordance with the dietary information available, where trout feed predominantly on smaller smelt and some vendace.[30] The vendace and smelt of the present study were larger than the specimens fed upon by trout. Smelt feed predominantly on Mysis and zooplankton (*Daphina galeata* and *Limnocalanus macrurus*)[31] with an increased degree of cannibalism when the fish are larger than 10 cm (smelt in the present study were 20.5−23.7 cm).[32] Vendace feed on zooplankton (*D. galeata* and *L. macrurus*).[33] Among the invertebrates, Mysis feed predominantly on water fleas (e.g., *D. galeata*),[34] whereas *D. galeata* (epilimnic cladoceran) feed predominantly on algae,[35] and *L. macrurus* (hypolimnic calanoid copepod) is omnivorous, feeding on algae and zooplankton.[36]

The D5 trophic magnification factor (TMF) resulting from the regression of lipid adjusted concentrations onto estimated trophic position was significantly different from 1, with a mean value for the whole food web (TMF_{WHOLE}) of 2.28 (95% Confidence interval (CI): 1.22−4.29, p = 0.0133, R^2 = 0.33, Table 2, Figure 1). TMFs for D4 and D6 could not be evaluated due to all or most of the invertebrate samples being below the LOQ. Hence the food web biomagnification of D4 and D6 could not be assessed.

As found previously by sensitivity analysis of PCB-153 TMF in the Lake Paguchi food web leading to trout,[17] the D5 TMF was sensitive to the species that were included at the higher trophic level. The D5 TMF_{WHOLE} differed from TMF when smelt or trout was excluded (TMF_{-SMELT} and TMF_{-TROUT}, respectively) (Table 2). When smelt was excluded from the food web, the D5 TMF_{-SMELT} decreased to 1.62 (CI: 0.96−2.72, R^2 = 0.28), and was no longer significantly related to trophic position (p = 0.0658, Table 2). However, when trout was excluded, the D5 TMF_{-TROUT} increased to 3.58 (CI: 1.82−7.03, R^2 = 0.61, p = 0.0016, Table 2), with a stronger model and greater ability of trophic level to predict D5 concentration.

Legacy contaminants such as PCBs and DDT have been studied in Lake Mjøsa for years.[20−23] The food web bioaccumulation of most lipid soluble legacy contaminants is strongly intercorrelated in the food web (correlation coefficient of 0.99, Figure 2, SI Table S6). Their concentrations are also significantly positively correlated to trophic level and thus possess TMFs above 1 (Table 2).

One of the assumptions implicit in the TMF concept is that the lipid normalized concentration is a measure of the fugacity of lipid-soluble chemicals in organisms. In order for this assumption to hold across a broad range of organisms, the chemical must be primarily sequestered into lipid tissues in the organisms. Furthermore, the use of lipid normalized concentrations is dependent on a method for lipid determination that captures those kinds of lipids that are the primary repositories of the chemical in the organism. The high R^2 values of the TMFs for most of the legacy chemicals (Table 2) are in line with the theoretical foundations of the TMF concept and corroborate the suitability of the method used for lipid determination. There is more uncertainty in the application of the TMF concept to cVMS, as the tissue distribution of these chemicals in biota has been little studied.

The D5 TMF_{WHOLE} was comparable to selected legacy POPs, though in the lower range (Table 2). In particular, the D5 TMF_{WHOLE} was comparable to PBDE-99 TMF_{WHOLE}. However, for both D5 and PBDE-99, the TMF_{WHOLE}-regression model was weaker (i.e., the ability of trophic level to predict the contaminant concentration) compared to the PBDE-47, PCB-153, PCB-180, and *p,p′*-DDE, as seen by the lower R^2 (Table 2). Thus the fraction of variance in the contaminant concentrations explained by trophic level of the organism was lower for D5 and PBDE-99 than for the other investigated legacy contaminants. The weaker relationship between contaminant concentration and trophic level was reflected in the sensitivity of both the D5 and PBDE-99 TMF to species composition (Table 2). On the other hand, the TMFs of other legacy POPs (e.g., PCB-153, PCB-180) were less sensitive to the food web composition, with only minor changes in TMF when either smelt or trout were excluded (Table 2).

To understand the processes leading to an influence of food web structure in D5 and PBDE-99 TMF, correlations were investigated between the concentrations of D5 and the legacy POPs (Figure 2, SI Table S4). Whereas concentrations of most of the investigated legacy POPs correlated strongly with each other (correlation coefficient: 0.99, SI Table S6), concentrations of both D5 and PBDE-99 correlated less with the other POPs (correlation coefficient: 0.45−0.52 for D5 and 0.66−0.70 for PBDE-99, Figure 2, SI Table S6). However, D5 did not correlate with PBDE-99 (correlation coefficient: −0.05). A closer inspection of the correlation matrix and the TMF regression, revealed that D5 and PBDE-99 were both sensitive to species composition, but in opposite direction (Figure 2), that is, excluding smelt from the model resulted in lower TMF for D5 and higher TMF for PBDE-99, whereas exclusion of trout resulted in higher TMF for D5 and lower TMF for PBDE-99 (Table 2). Thus, the sensitivity of the D5 and PBDE-99 TMF to species composition is caused by different processes. Compared to PCB-180, the PBDE-99 concentration in smelt is lower than expected from the trophic level (Figure 2), indicating a higher degree of PBDE-99 metabolic elimination[37,38] in smelt compared to the other species. For trout, on the other hand, the data points of the correlation of PBDE-99 concentrations versus the other legacy contaminants fall on the same line as the rest of the food web (Figure 2). Compared with PCB-180, the concentrations of D5 in smelt were higher than expected from trophic position, and/or the concentrations in trout were lower (Figure 2). Although all representatives of the food web were collected within the same midlake area west, east and south of Helgøya in Lake Mjøsa, it cannot be ruled out that some species such as smelt may have had other sources of D5 accumulation than the rest of the food web, such as actively feeding near the wastewater treatment plant discharge. This is one conceivable explanation for the D5 concentration in smelt being higher than predicted from $\delta^{15}N$ and from other accumulated legacy contaminants (although the fact that the smelt were collected from two different locations makes this less likely). If this had been the case, the results would indicate that the bioaccumulation of D5 could not be assessed using the BMF/TMF approach applied to the legacy contaminants; additional behavioral factors of the organisms would also have to be taken into consideration.

The sensitivity of PBDE-99 TMF to food web structure can be explained by the species' different abilities to metabolize and

eliminate the contaminant, whereas the sensitivity of D5 TMF to species composition remains unexplained, although it can be deduced from the food web accumulation pattern that D5 is either eliminated comparatively rapidly by trout or its accumulation is enhanced in smelt. Biotransformation rates for D5 in fish have been estimated using models based on reported bioconcentration factors or total elimination rate constants. These values are low and on the same scale as for PCBs, but the uncertainty in these estimates are high.[39]

The finding of D5 TMF above 1 stands in contrast to previous TMF studies of a benthic freshwater food web in Lake Pepin, on the upper Mississippi[14] and in the marine benthopelagic food web of the Oslofjord, Norway,[13] both of which found TMFs below 1. These findings need not be contradictory, but may well reflect the variability in TMF values between different food webs, depending on season, species composition and site.[40,41] Such variability, together with the uncertainty and cost of the TMF determination, are obstacles to the use of TMF thresholds in chemical regulation.

The present study found that biomagnification behavior within the food web differs between the compounds, as the D5 TMF is sensitive to the food web composition, whereas PCB-180 TMF is not. Clearly, the biomagnification potential of cVMS is an issue where more studies are warranted. Future research should strive to understand the processes governing biomagnification of D5 and how the TMF is influenced by food web composition and other properties.

■ ASSOCIATED CONTENT

Supporting Information

Sample site and dates; Content of cVMS in the field blanks (ENV+ pouches); Concentration on a wet weight basis of cVMS in food web samples from Lake Mjösa; Weighting of sample means according to number of samples; Product-moment correlation coefficients (*r*: left triangular matrix) between trophic position (TL); Fish size versus D5 concentration; Detailed cVMS level comparison to other areas; role of smelt cannibalism on TMF. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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