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Office of Pollution Prevention and Toxics
U.S. Environmental Protection Agency
Attn: TSCA Section 8(e) Coordinator
Ariel Rios Building
1200 Pennsylvania Avenue, NW
Washington, DC 20004

8EHQ-10-17834

Re: TSCA Section 8(e) Notification of Substantial Risk: Octylmethylcyclotetrasiloxane, Decamethylcyclopentasiloxane and Dodecamethylcyclohexasiloxane

Dear TSCA Section 8(e) Coordinator:

In accordance with the provisions of Section 8(e) of the Toxic Substances and Control Act (TSCA), as interpreted in the TSCA Section 8(e) Policy Statement and Guidance, Fed. Reg. 33129 (June 3, 2003) and other Agency guidance, Dow Corning is submitting information from a monitoring program currently in progress on cyclic volatile methylsiloxanes (cVMS). Associated with this monitoring program, enclosed are copies of 5 final reports from studies that have been completed, and information from 3 studies currently in progress. Dow Corning has not made a determination at this time that any significant risk of injury to human health or the environment is presented by these findings. Dow Corning does not believe this information triggers reporting obligations but lacking relevant guidance from EPA, Dow Corning is submitting the information under Section 8(e) of TSCA as a precautionary measure.

Chemical Substances

556-67-2	Octylmethylcyclotetrasiloxane (D4)
541-02-6	Decamethylcyclopentasiloxane (D5)
540-97-6	Dodecamethylcyclohexasiloxane (D6)

88100000163

Summary of Results

Cyclic Methylsiloxane (cVMS) Materials in Surface Sediments and Cores for Lake Ontario

Summary
Detectable levels of cVMS were observed in sediments from Toronto Harbor, while cVMS in core samples obtained from the deep-water basins in the lake were below detectable levels.

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Trophic Dilution of Cyclic Volatile Methysiloxanes (cVMS) Materials in a Temperate Freshwater Lake

Summary
Concentrations of cVMS materials were observed in sediments, benthic invertebrates, and fish obtained from Lake Pepin. In addition, bioaccumulation metrics, biomagnifications factor (BMF) and trophic magnification factor (TMF) were calculated. The calculated BMF was greater than one for some species; however the TMF was less than one.

Analysis of Cyclic Volatile Methysiloxanes (cVMS) in Fat, Muscle, and Liver tissue of American Mink (*Mustela Vison*) Obtained from Lake Pepin Minnesota, USA

Summary
Delectable of D5 were observed in fat samples obtained from Mink living near Lake Pepin, Minnesota, USA.

Preliminary Assessment of Cyclic Methylsiloxanes (cVMS) Materials in Surface Sediments, Cores, Zooplankton, and Fish of Lake Opeongo, Ontario, Canada

Summary
Detectable levels of cVMS materials were observed in fish (cisco, perch, and lake trout). cVMS were not observed in sediments and zooplankton. The calculated BMF was greater than one for some species. It is important to note the fish (cisco, perch, and lake trout) samples from Lake Opeongo were collected by personnel that had no training for collection of samples for trace-level contaminant analysis, nor were there any documentation maintained on how the fish were collected or processed in the field.

Trophic Dilution of Cyclic Volatile Methylsiloxane (cVMS) Materials in Oslofjord.

Summary
Detectable levels of cVMS materials were observed in sediments, zooplankton, benthic invertebrates, and fish obtained from Oslofjord, Norway. In addition, bioaccumulation metrics, biomagnification factor (BMF) and trophic magnification factor (TMF) were calculated. The calculated BMF was greater than one for some species; however TMF was less than one.

Interim Study 1
Cyclic Methylsiloxanes (cVMS) Materials in Surface Sediments and Cores for Lake Pepin

Summary
Detectable levels of cVMS were observed in sediment cores obtained from 3 locations in Lake Pepin, Minnesota.

Interim Study 2
A Collaborative Assessment of Cyclic Volatile Methylsiloxane Concentrations in the Norwegian Environment

Summary
Detectable levels of cVMS were observed in sediment, shrimp, fish, and birds, while cVMS in zooplankton and seal blubber were below detectable limits.

Interim Study 3
Analysis of Cyclic Volatile Methylsiloxanes (cVMS) in Lake Trout Homogenates from Lake Superior and Ontario.

Summary
Concentrations of cVMS were observed in Lake Trout obtained from Lake Ontario and Lake Superior. Environment Canada is submitting additional samples for analysis to investigate the potential for contamination during the processing of samples.

A description of all the results is available in the enclosed reports and final reports from the studies in progress will be submitted to EPA as studies are completed. Dow Corning has not made a determination at this time that any significant risk of injury to human health or the environment is presented by these findings.

Actions
Dow Corning Corporation will notify EPA of any further relevant information that may be developed concerning these materials. If you have any questions concerning this submission, please contact me at (989) 496-8046, kathy.plotzke@dowcorning.com, or at the address provided herein.

Sincerely,

Kathleen P. Plotzke

Kathleen P. Plotzke, Ph.D.
Director, Health and Environmental Sciences
(989) 496-8046

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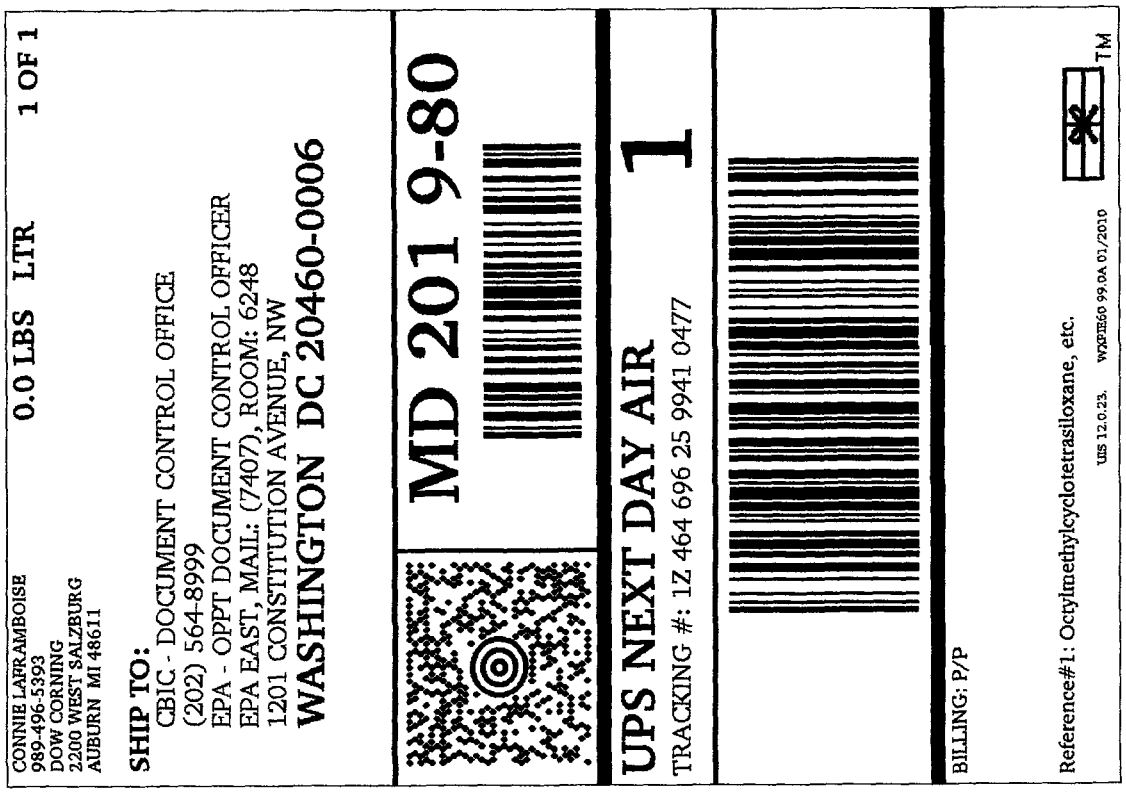

Study Title:	Bioaccumulation and Trophic Transfer of Cyclic Volatile Methylsiloxane (cVMS) Materials in the Aquatic Marine Food Webs of the Inner and Outer Oslofjord, Norway
HES Study No:	11060-108
Test Substances:	Octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2) Decamethylcyclopentasiloxane (D5; CAS No. 541-02-6) Dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6)
Author:	David E. Powell, Dow Corning Corporation
Contributing Scientists:	Jeremy Durham, Dow Corning Corporation Darren W. Huff, Dow Corning Corporation Thomas Böhmer, Evonik Goldschmidt GmbH Reinhard Gerhards, Evonik Goldschmidt GmbH Martin Koerner, Evonik Goldschmidt GmbH
Sponsor:	Centre Européen des Silicones (CES)
Testing Facility:	Health and Environmental Sciences Dow Corning Corporation 2200 West Salzburg Road Auburn, MI 48611
Date:	22 January 2010

ABSTRACT

The trophic transfer of cyclic methylsiloxane (cVMS) materials in aquatic ecosystems is an important criterion for assessing bioaccumulation and ecological risk. Trophic transfer of the three cVMS materials octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2), decamethyl-cyclopentasiloxane (D5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6) in the marine food web of the inner and outer Oslofjord were evaluated using isotopic signatures of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) as continuous variables for assessing carbon flow and relative trophic levels (TL) of consumers in the food web. Surface sediments, zooplankton, benthic macroinvertebrates, shellfish, and finfish were collected by gravity core, vertical zooplankton haul, benthic sled, and bottom trawl 12-14 November 2008 during a research cruise aboard the Norwegian research vessel F/F Trygve Braarud (University of Oslo). Samples were collected with guidance and assistance from the Norwegian Institute of Water Research (NIVA) and separated into two groups during collection for analysis by Dow Corning Corporation (Auburn, Michigan, USA) and Evonik Goldschmidt (Essen, Germany). Sediment samples were analyzed for total organic carbon and concentrations of D4, D5, and D6. Biological samples were analyzed for stable isotope fractionation ($\delta^{15}N$ and $\delta^{13}C$), whole-body lipid content, and whole-body concentrations of D4, D5, and D6.

The evaluated food web in the inner Oslofjord and the outer Oslofjord included zooplankton (200-µm net plankton), benthic macroinvertebrates (3 species, 3 genera, 3 families), shellfish (4 species 3 genera, 2 families) and finfish (14 species, 13 genera, 7 families). Food web length was about 2.6 trophic steps for inner Oslofjord and about 2.4 trophic steps for outer Oslofjord. Generally, zooplankton, benthic macroinvertebrates (worms and urchins), and blue mussel (*Mytilus edulis*) occupied the lowest trophic levels (TL ~1.5 to 2.0), northern shrimp (*Pandalus borealis*) and Atlantic herring (*Clupea harengus*) occupied the middle trophic level (TL ~3.0) and Atlantic cod (*Gadus morhua*) occupied the highest trophic level (TL ~4.0) of the two food webs. Trophic dynamics in Oslofjord were best described as a compressed food web that was defined by multiple food chains dominated by a benthipelagic food chain that was confounded by a great diversity in prey organisms and feeding relationships. In order to better define the food web in Oslofjord, species were grouped into food chains that were defined based on frequency of occurrence and the flow of carbon to consumers. The dominate food chain in the Oslofjord food web was represented by the largest number of species in the inner Oslofjord (12 of 19 species) and the outer Oslofjord (11 of 15 species). Carbon flow in the dominant food chain, which included benthic organisms at the base, was assumed to be benthic in origin.

Lipid-equivalent concentrations of the cVMS materials were greatest in the lowest trophic level species and significantly decreased up the food web, with the lowest concentrations being observed in the highest trophic level species. Trophic magnification factors (TMF values) in the dominant food chain of the food web were less than a value of 1.0 (range 0.2 to 0.6) for D4, D5, and D6, and were very consistent

between the inner and outer Oslofjord basins. The over all probability that TMF values for the cVMS materials were greater than a value of 1.0 was 0% to 4%. Predator-prey specific biomagnification factors (BMF values) ranged from 0.7 to 1.8 and were also in good agreement between the two basins. The overall probability that BMF values were greater than a value of 1.0 was 13% to 55% for D4 and D5 and 80% to 81% for D6. These results indicated that trophic dilution of the cVMS materials occurred and demonstrated with a probability of 96% to 100% that D4, D5, and D6 did not biomagnify in the aquatic marine environment of the Oslofjord. Consequently, field data from the Oslofjord demonstrated that D4, D5, and D6 were not bioaccumulative materials in aquatic marine environments.

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SIGNATURES and APPROVAL

This report consists of 40 pages with 10 tables, 3 figures, and 2 appendices. The undersigned have read and approved this report.

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Date

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INTRODUCTION

Cyclic volatile methylsiloxane (cVMS) materials are widely used in industrial and consumer applications and the wastewater stream represents a major post-use disposal route. Generally, cVMS materials are volatile (V_P > 4.5 Pa), have low water solubility ($S_W \leq 56$ µg L^{-1}), have intermediate values for the octanol/air partition coefficient (log K_{OA} > 4.2), and have high values for the octanol/water partition coefficient (log K_{OW} > 6.5) and the air/water partition coefficient (log K_{AW} > 2.7). Because of these partitioning properties, cVMS materials occupy a somewhat unique chemical space and are expected to partition primarily to air during use and after disposal to wastewater. Multimedia modeling indicates that about 50-92% of the total emission of cVMS materials (specifically D_4, D_5, and D_6) will partition to air (Powell 2008). Cyclic VMS materials that remain in the wastewater (about 8-50% of the total emission) are efficiently removed during the wastewater treatment process, with an estimated 60-78% of the mass removed by adsorption to bio-solids (i.e., sludge), 18-40% removed by volatilization to air, and < 1-4% remaining in the effluent.

In order to better understand the fate of cVMS materials in municipal wastewater effluents released to the environment, the silicone manufacturer industry associations conducted a field monitoring program on the aquatic marine ecosystem in Oslofjord, Norway. Oslofjord is a 100 km long extension of the Skagerrak strait between the southeast coast of Norway and the southwest coast of Sweden that cuts north to the city of Oslo into the most densely populated parts of Norway. Treated municipal waste water from the city of Oslo is discharged below the pycnocline in the inner Oslofjord and has caused increasing pollution problems. Because of the semi-enclosed nature of Oslofjord, chemical substances released below the pycnocline become trapped, resulting in elevated levels in the inner Oslofjord compared to the outer Oslofjord and surrounding areas.

Environmental exposure of aquatic organisms to highly lipophilic compounds may occur through both the water column and diet. Consumption of contaminated foodstuffs is thought to be the principal route of bioaccumulation for compounds with log K_{OW} values greater than about 5. Consequently, trophic transfer and magnification are important criteria for assessing bioaccumulation and ecological risk of chemicals in aquatic ecosystems. The objective of the study was to measure concentrations of octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6) in surface sediments, zooplankton, benthic macroinvertebrates, shellfish, and finfish collected from the inner and outer Oslofjord. Trophic transfer of these cVMS materials in the marine food web of the inner and outer Oslofjord were evaluated using the isotopic signatures of carbon (C; $\delta^{13}C$) and nitrogen (N; $\delta^{15}N$) as continuous variables for assessing carbon flow and relative trophic levels (TL) of consumers in the food web.

MATERIALS and METHODS

Study Area

The study area, the Oslofjord, Norway (Fig. 1), has been described in detail elsewhere (Abdullah et al. 1982; Breivik et al. 2004; Alve et al. 2009). Generally, the Oslofjord is a 100 km long extension of the Skagerrak strait between the southeast coast of Norway and the southwest coast of Sweden that cuts north to the city of Oslo into the most densely populated parts of Norway. The human population around the Oslofjord, including Oslo, is about 1.7 million persons. 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 at 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, referred to as the outer Oslofjord. A north–south oriented 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 Bunnefjorden (max depth ca 164 m) to the east and the Vestfjorden (max depth ca 160 m) to the west, which is linked to the outer fjord at Drøbak. The Oslofjord has an astronomical tidal range of about 20 cm.

The inner Oslofjord is a fairly enclosed body of water that is located within the most densely populated area of Norway. Water circulation is estuarine with a pycnocline situated at about 20 m water depth, below which salinity is about 32 to 34 ‰ and temperature is about 6 to 9 °C. Salinity above the pycnocline is mainly a function of water from the outer Oslofjord as freshwater discharge to the system is relatively small. The pycnocline 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 Vestfjorden and about 3–4 years in Bunnefjorden. Modern industrialization in the city of Oslo started in the second half of the 19th century and the Oslofjord experienced significant decreases in water and sediment quality until the middle of the 1980s when improved pollution control practices were implemented. Municipal waste water from the growing population in the city of Oslo caused increasing pollution and, particularly after the Second World War, the fjord received increasing amounts of pollutants from municipal sewage systems. Because of the semi-enclosed nature of 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. Due to governmental regulations and establishment of more modern sewage treatment plants, the fjord has experienced reduced pollution over the past few decades. Of the extensive environmental monitoring which has taken place in the Oslofjord since the late 1970s, very little has been published internationally (Alve et al. 2009).

Sample Collection

Surface sediments, bulk zooplankton, macroinvertebrates, and fish were collected from the inner and outer Oslofjord 12-14 November 2008 (Table 1). Blue mussels (Mytilus edulis) were collected from the inner Oslofjord 01 October 2008. With the exception of

blue mussels all samples were collected during a research cruise aboard the Norwegian research vessel F/F Trygve Braarud (University of Oslo) with guidance and assistance from the Norwegian Institute of Water Research (NIVA). In the field after collection, while aboard the F/F Trygve Braarud, retained samples were processed and labeled for distribution between Dow Corning Corporation (Appendix 1) and Evonik (Appendix 2), 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.

Surface Sediments: Surface sediments were collected as duplicate sediment cores from four locations in the inner Oslofjord and from three locations in the outer Oslofjord. Surface sediments were removed by extruding the cores on the deck of the ship. Only the 0-1 cm and 1-2 cm strata were retained. Sediment in direct contact with the core tube was not removed but was retained with the sample. Retained samples from the duplicate cores were distributed between Dow Corning and Evonik. Sediment samples for Dow Corning were placed directly into glass jars and capped. Sediment samples for Evonik were placed into glass centrifuge tubes, covered with water, and capped. No field quality control samples were collected or retained for sediments.

Bulk Zooplankton: Bulk zooplankton was collected using a 200-µm plankton tow (vertical hauls). Six vertical hauls were pulled from a single location in the inner Oslofjord and three vertical hauls were pulled from a single location in the outer Oslofjord. While on-site at each location the bucket contents from each vertical haul were composited into a pooled sample. Contents of the pooled sample from the outer Oslofjord were separated into jellyfish and net plankton, which were then placed into separate 4-oz jars for analysis by Dow Corning (samples were not retained for Evonik). Contents of the pooled sample from the inner Oslofjord were separated into jellyfish and net plankton, which were then placed into separate 4-oz jars for analysis by Dow Corning and by Evonik. No field quality control samples were collected or retained for bulk zooplankton.

Macroinvertebrates: With the exception of blue mussels, macroinvertebrates were collected by benthic sled or as bi-catch from bottom trawl. Blue mussels were collected by dredge from hard substrate subtidal zones in the inner Oslofjord. While on-site, macroinvertebrates were separated by species and placed into separate plastic storage bags (shrimp, mussels, urchin) or storage jars (benthic worms). Samples of benthic worms were retained for analysis by Dow Corning only. All other species were allocated for analysis between Dow Corning and Evonik. No field quality control samples were collected or retained for macroinvertebrates.

Fish: Fish were collected by bottom trawl. While on-site the contents of the trawl were emptied onto a processing table, separated by species, and placed into plastic storage bags. Retained samples of each species were allocated for analysis between Dow Corning and Evonik. Field quality control samples, which consisted of skin-off fillets of Atlantic cod from the outer Oslofjord, were collected with the fish.

Skin-off fillets were used because of potential surface contamination of the fish that may have occurred during collection and processing. Individual skin-off fillets were cut into three pieces that were used for quality control samples. One piece of the fillet was placed directly into a plastic storage bag (i.e., the field blank). A second piece of the fillet was placed into a mesh bag that was then attached to the throat of the trawl before deployment (i.e., the net blank). Upon retrieval of the trawl, the net blank was removed from the mesh bag and placed directly into a plastic storage bag. The third piece of the fillet was placed onto the processing table before the contents of the trawl was emptied onto the processing table (i.e., the process blank). The process blank was the final sample to be removed from the processing table and was placed directly into a plastic storage bag. Field quality control samples were collected from one trawl in the outer Oslofjord and from two trawls in the inner Oslofjord, and were allocated for analysis between Dow Corning and Evonik.

Shipment of Samples

Summaries of the Chain-of-Custody after collection of the samples are provided in Appendices 1 and 2. Samples for analysis by Evonik Goldschmidt were transported by car from NIVA (Oslo, Norway) to Evonik Goldschmidt (Essen, Germany) on 15 November 2008, where they were received on 16 November 2008. Samples for analysis by Dow Corning were shipped from NIVA (Oslo, Norway) to Dow Corning Corporation (Auburn, Michigan, USA) on 17 November 2008, where they were received on 25 November 2008.

Sample Preparation

Each laboratory processed samples following laboratory-specific protocols, which were not standardized or validated across the two laboratories (Appendix 1 and 2). Biological samples were processed as whole-body homogenates of individual and pooled samples. Sediment samples were processed as received from the field.

Characterization of Samples

Processed samples were characterized following laboratory-specific protocols, which were not standardized or validated across the two laboratories (Appendix 1 and 2). Sediment samples were characterized for total carbon, total inorganic carbon, total organic carbon, total water content, and total organic matter content. Biological samples were characterized for water content, lipid content, and for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$). Stable isotope abundances were expressed in per mil notation (δ) as the deviation from standards in parts per thousand (‰) according to the equation:

$$\delta X = \left[\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right] \times 1000$$

where X is ^{15}N or ^{13}C and R is the abundance ratio of the heavy to light isotope (i.e., $^{15}N/^{14}N$ or $^{13}C/^{12}C$) in the sample (R_{sample}) and the standard ($R_{standard}$). The $R_{standard}$ values were based on atmospheric nitrogen gas for ^{15}N and PeeDee Belemnite (PDB) for ^{13}C.

Analysis of Cyclic Volatile Methylsiloxane (cVMS) Materials

Processed samples were analyzed for cVMS materials (specifically D4, D5, and D6) following laboratory-specific protocols, which were not standardized or validated across the two laboratories (Appendix 1 and 2).

Quality Control

Cyclic VMS materials are widely used in consumer products and may be present in personal care products, commercial products, and lubricants. Given the significant potential for sample contamination during collection, processing, storage, and analysis for cVMS materials in environmental matrices, a quality control (QC) program was implemented to the extent possible in the field and laboratory (Table 2). Air samples were collected at the same time that aquatic samples were collected and processed to check for potential contamination that may have resulted from partitioning of airborne cVMS. Because of resource constraints and logistics, field QC samples were only collected for the bottom trawl samples. Field quality control samples (i.e., skin-off fillets of Atlantic cod from the outer Oslofjord) were collected with the bottom trawl samples as previously described under sample collection for fish. No field QC samples were obtained during collection of sediments, zooplankton, and macroinvertebrates (non by-catch specimens). Field crew refrained from using any personal care products (e.g., sun-block, sun-screen, hand lotion, etc) during collection of samples to minimize the possibility for contamination with cVMS materials. Because of the limited set of field QC samples that were collected, the extent of possible contamination resulting from collection, handling, transport, and storage could not be fully evaluated. Analysis of the air samples indicated that concentrations of D4, D5, and D6 in air were $\leq 0.3\ \mu g/m^3$ during sample collection and processing. These results indicated that the potential for sample contamination by exposure to air was not likely significant. Analysis of the field quality control samples (i.e., the field blanks, the net blanks, and the process blanks) indicated that samples were not contaminated during trawling or on-board processing.

Laboratory-specific QC programs were followed in the laboratories to evaluate detectability, bias, and precision, and to verify that samples were not potentially contaminated by laboratory processing and analysis procedures (Appendix 1 and 2).

> Detection Levels: No attempt was made to standardize methods for determination of levels of detection and quantification. As a result, levels of detection and quantification reported by the two laboratories were not defined on a uniform basis and were not directly comparable.

Bias and Precision: Standard reference materials were not available for D4, D5, or D6 in any matrix. No attempt was made to standardize methods for evaluation of bias and precision. As a result, inter-laboratory bias and precision were not defined on a uniform basis, were not consistently reported, and were not directly comparable.

Background Correction: Measured amounts of cVMS materials in the samples were corrected for background levels of cVMS using results from the reagent blanks. Results for the reagent blanks represented background levels of cVMS materials associated with extraction solvents or lab ware, as well as contamination incurred during handling, treatment (e.g. volume reduction), and analysis of the extracts. Because of the variable background encountered during analysis of samples, background correction sometimes resulted in negative values for sample concentrations that were below or near the analytical detection levels.

Units of Measure: Actual measured values provided by the contributing laboratories were combined into a single dataset that was used for all calculations. Results that were reported as negative values were omitted from the combined dataset and not further evaluated (i.e., treated as missing values). Concentrations of D4, D5, and D6 in biota and sediment were measured in wet samples and expressed on the basis of wet weight. 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 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.

Laboratory-specific summaries of the analytical results for the QC samples associated with this study are provided in Appendix 1 and 2. Detection limits between the two laboratories were not directly comparable, but appeared to be lower for analyses conducted by Dow Corning compared to analyses conducted by Evonik (Table 3). Limits of detection (LOD) during the analyses were not provided by Evonik so it was not possible to compare analytical sensitivity or background between the two laboratories.

Merging of Datasets

Analytical results for sediment (water content, carbon content, and cVMS concentrations) and biota ($\delta^{13}C$, $\delta^{15}N$, lipid content, and cVMS concentrations) were compared to determine if differences existed between results reported by Dow Corning and Evonik. Comparison of the reported results indicated that significant differences existed between the two laboratories and between species when nested within laboratory (ANOVA; $p<0.01$). The relative difference between results reported by Dow

Corning and Evonik for analyses of sediment samples (means by stratum) was -0.4% to 6.7% for water content (mean 3.0%), -16% to -1.8% for total carbon (mean -7.7%), -74% to -54% for D4 (mean -64%), -89% to -2.6% for D5 (mean -43%), and -55% to -24% for D6 (mean -40%). The relative difference between results reported by Dow Corning and Evonik for analyses of biological samples (means by species) was -2.2% to 7.2% for $\delta^{13}C$ (mean 2.8%), -2.0% to 6.9% for $\delta^{15}N$ (mean 2.5%), -49% to 81% for lipid content (mean 27%), -32% to 164% for D4 (mean 44%), -60% to 168% for D5 (mean 33%), and -37% to 166% for D6 (mean 41%). The largest relative differences between the two laboratories were generally, but not consistently associated with analytical results that were near the limits of detection.

The cause of the differences observed between results reported by Dow Corning and Evonik was not identified. Nonetheless, results from the two laboratories were combined by location into single datasets in order to increase statistical power. As a result, trophic magnification factors (TMFs) and biomagnification factors were much more variable than would have been observed had differences between the two laboratories not existed.

Statistical Analyses

Statistical analyses of the combined raw data provided by the contributing laboratories (Appendix 1 and 2) were performed using Minitab® Version 15.1.0 (Minitab 2006). A Type I error (α) of 0.05 was used to judge the significance of all statistical tests. Actual measured values were used for all calculations even if the reported results were less than the reported limits of detection. Results that were reported as negative values were omitted from the combined dataset and treated as missing values. Outliers in the combined dataset were identified using the Dixon test, the Grubbs test, and the Q-test (Gilbert 1987; Taylor 1987). Statistically significant outliers identified by at least two of the three tests were removed from the combined dataset and treated as missing values. Concentrations of the cVMS were normalized to lipid content for calculation of predator-prey specific biomagnification factors (BMF values) and trophic magnification factors (TMF values). Log transformation of concentration data was used to generate normally distributed data for regression analyses.

Paired t-tests were used to evaluate for differences between cVMS concentrations measured in the field blanks, net blanks, and process blanks that were collected as part of the trawling procedures. Analysis of variance for unbalanced designs (ANOVA; general linear model) was performed to test for differences between species and results reported by the two laboratories (species nested within laboratory) for stable isotope signatures ($\delta^{15}N$ and $\delta^{13}C$), lipid content, and concentrations of the cVMS materials in the samples. If the omnibus *F* value indicated significant differences between the mean values, a Tukey HSD multiple comparisons test (for equal sample sizes) or a Tukey-Kramer multiple comparisons test (for unequal sample sizes) was used to compare individual means (Sheskin 2000). Single-factor ANOVA with a Dunnett *a posteriori* multiple comparison test was performed to identify species that occupied common food chains in the Oslofjord food webs. The Dunnett test (Sheskin 2000) compares all

treatment group means to the mean of a single control group to identify groups whose means are significantly different from the mean of the control group. For this study, the Dunnett test was used to identify significant differences between the mean $\delta^{13}C$ signatures of a single species on a known food chain (i.e., the control group mean) to the mean $\delta^{13}C$ signatures of each species in the data set (i.e., the treatment group means).

Linear regression analysis was used to determine the slope and significance of the regression line fit to the lipid-equivalent concentrations of D4, D5, and D6 on trophic levels estimated from $\delta^{15}N$. Regression analyses were conducted using all data and using means by species. Mean values were used for the regression analysis because the number of individuals analyzed for a given species was not consistent (n = 1 to 12 individuals, depending on species) and included the analysis of pooled samples. Log transformation of concentration data was used to generate normally distributed data for the regression analyses.

Variability associated with the TMF and BMF calculations were evaluated by bootstrap analysis (Sheskin 2000) using Monte Carlo simulation with Oracle Crystal Ball software (ver 7.3.1). The principal factors of variation and uncertainty associated with the TMF calculations were assumed to be trophic level, lipid content, and concentration of the cVMS materials for each species (n= 50 assumptions for outer Oslofjord; n= 55 assumptions for inner Oslofjord). The principal factors of variation with the BMF calculations were assumed to be lipid content and concentration of the cVMS materials for each organism (n= 48 assumptions for outer Oslofjord; n= 72 assumptions for inner Oslofjord). Principal uncertainty with the BMF calculations, which were assumed to be associated with trophic level and possible omnivorous feeding by the predator species, was not evaluated. Rather, it was assumed that that predator species were feeding exclusively on prey species so that it was not necessary for BMF values to be adjusted for trophic level position or omnivorous feeding. Input distributions used for the Monte Carlo simulation were chosen on the basis of theoretical considerations because the available data were insufficient to permit distribution fitting. Lognormal distributions were used to represent lipid content and cVMS concentrations in the organisms because the measured values tended to be clustered about a minimum value and were typically right skewed. The Monte Carlo simulations were run for a total of 1000 trials across each assumption.

Separation of Food Chains

Marine ecosystems such as Oslofjord typically have very complex food web dynamics that are defined by multiple, overlapping food chains that are confounded by a great diversity in prey organisms and feeding relationships. In order to better define the food web in Oslofjord, individual species were assigned to one of four arbitrary food chains using the isotopic signature of carbon (C; $\delta^{13}C$) as a continuous variable for assessing carbon flow to consumers in the food web. The stable carbon isotope signatures of consumers reflects the sources and flow of dietary carbon within a food web (Post 2002). A Dunnett multiple comparisons test (Sheskin 2000) was used to identify

species that had $\delta^{13}C$ signatures ($\delta^{13}C_{species}$) that were significantly different from the $\delta^{13}C$ signatures for Atlantic cod (*Gadus morhua*; $\delta^{13}C_{cod}$), northern shrimp (*Pandalus borealis*; $\delta^{13}C_{shrimp}$), and Atlantic herring (*Clupea harengus*; $\delta^{13}C_{herring}$). Species with $\delta^{13}C$ signatures that were statistically less than those for cod were assigned to food chain B (7 of 22 species; included herring and zooplankton). Species with $\delta^{13}C$ signatures that were statistically greater than those for shrimp were assigned to food chain C (1 of 22 species; included only the starry skate, *Amblyraja radiata*). Species with $\delta^{13}C$ signatures that were statistically less than those for herring were assigned to food chain D (0 of 22 species). The remaining species were then assigned to food chain A (14 of 22 species; included cod, shrimp, and benthic invertebrates). Not all species in the Oslofjord food web were sampled and individual species that were sampled were assigned to only one food chain. Therefore, the individual food chains were not fully represented and assumed that omnivorous feeding occurred only within a food chain and not across the food chains. In summary, the Oslofjord food web was operationally separated into four arbitrary food chains that were defined on the basis of source and flow of dietary carbon within the food web and were identified from the $\delta^{13}C$ signature as:

- Food chain A: $\delta^{13}C_{cod} \leq \delta^{13}C_{species} \leq \delta^{13}C_{shrimp}$ (14 of 22 species)
- Food chain B: $\delta^{13}C_{herring} \leq \delta^{13}C_{species} < \delta^{13}C_{cod}$ (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)

Calculation of Bioaccumulation Metrics (TMF and BMF)

Trophic magnification factors were determined based on the relationship between the log-transformed lipid-equivalent concentrations of cVMS materials (D4, D5, and D6) and $\delta^{15}N$. Converting $\delta^{15}N$ values to relative trophic level (TL) was performed according to the following equation (Jardine et al. 2006):

$$TL = 2 + \frac{\left(\delta^{15}N_{consumer} - \delta^{15}N_{zooplankton}\right)}{\Delta^{15}N}$$

where 2 was the assumed trophic level of zooplankton and $\Delta^{15}N$ was the trophic enrichment factor constant for $\delta^{15}N$, which is between 3‰ and 4‰ per trophic level step (Post 2002). The trophic enrichment factor constant for $\delta^{15}N$ in Oslofjord was equal to 3.82 and was calculated as the slope of the regression line of $\delta^{15}N$ (Tables 4 and 5) on relative trophic positions that were assumed to be occupied by zooplankton ($\delta^{15}N$ ~9.6 ‰; trophic position = 1.0), shrimp ($\delta^{15}N$ ~12.9 ‰; trophic position = 2.0), and Atlantic cod ($\delta^{15}N$ ~17.0 ‰; trophic position = 3.0). The assumed relative trophic positions used to calculate $\Delta^{15}N$ were based on (1) the observation that Atlantic cod (*Gadus morhua*) were feeding exclusively on northern shrimp (*Pandalus borealis*) at the time of collection (i.e., cod and shrimp were separated by one trophic level step) and (2) preliminary assessment of the $\delta^{15}N$ signatures indicated that zooplankton occupied a baseline trophic level, northern shrimp occupied a middle trophic level, and Atlantic cod occupied the highest trophic level of the evaluated food web in both basins. The estimated $\Delta^{15}N$

value of 3.82‰ per trophic level step for trophic enrichment of $\delta^{15}N$ in Oslofjord was similar to the value of 3.4‰ per trophic level step that is recommended for constructing food webs without *a priori* knowledge of $\Delta^{15}N$ or the ecology of the system (Jardine et al. 2006).

Trophic magnification factors (TMF values) were calculated as the antilog of the slope (m) of the regression line of the natural log concentration (lipid-equivalent) on TL, where:

$$TMF = e^{m}$$

Predator-prey specific biomagnification factors (BMF values) were calculated by dividing the mean lipid-equivalent concentrations of cVMS materials (D4, D5, and D6) in the predator species by the mean lipid-equivalent concentrations in the prey species, using the equation:

$$BMF = \frac{C_{pred}}{C_{prey}}$$

where C_{pred} and C_{prey} were the mean lipid-equivalent concentrations of cVMS materials in the predator and prey, respectively.

RESULTS and DISCUSSION

Marine ecosystems such as Oslofjord typically have very complex food web dynamics that are defined by multiple food chains that are confounded by a great diversity in prey organisms and feeding relationships. The evaluated food web in Oslofjord (Table 1) included zooplankton (200-µm net plankton), benthic macroinvertebrates (3 species, 3 genera, 3 families), shellfish (4 species 3 genera, 2 families), and finfish (14 species, 13 genera, 7 families). Food web length was about 2.6 trophic steps for the inner Oslofjord and about 2.4 trophic steps for the outer Oslofjord. Generally, zooplankton, benthic macroinvertebrates (worms and urchins), and blue mussel (*Mytilus edulis*) occupied the lowest trophic levels (TL ~1.5 to 2.0), northern shrimp (*Pandalus borealis*) and Atlantic herring (*Clupea harengus*) occupied the middle trophic level (TL ~3.0) and Atlantic cod (*Gadus morhua*) occupied the highest trophic level (TL ~4.0) of the food web. Other mussel species occupied a trophic level range of about 2.6 to 3.1 and the remaining finfish species occupied a trophic level range of about 3.1 to 3.8.

Carbon in a complex food web may originate from multiple sources and the flow or trophic transfer of carbon may be obscured by the overlap and convergence of multiple 2-dimensional food chains that comprise the 3-dimensional food web. Stable isotope signatures in biota (Tables 4 and 5) suggested that the food web in Oslofjord was trophically compressed and confounded by overlapping food chains and omnivorous feeding (Fig. 2). Isotopic signatures indicated that zooplankton ($\delta^{15}N$ ~9.6‰; $\delta^{13}C$ ~-18.6‰) occupied a base trophic level of 2.0, that northern shrimp ($\delta^{15}N$ ~12.9‰; $\delta^{13}C$

~-16.1‰) and Atlantic herring ($\delta^{15}N$ ~13.3‰; $\delta^{13}C$ ~-19.1‰) occupied an intermediate trophic level of 3.0, and that Atlantic cod ($\delta^{15}N$ ~17.0‰; $\delta^{13}C$ ~ -17.1‰) occupied the highest trophic level of 4.0. These results for $\delta^{15}N$ suggested that Atlantic cod were the top predator species of the sampled food web in Oslofjord and were feeding on northern shrimp and Atlantic herring. However, the $\delta^{13}C$ signature for Atlantic cod was closer to that of northern shrimp, suggesting that cod were feeding primarily on shrimp rather than herring. Observation of gut contents of select Atlantic cod indicated that the fish were feeding exclusively on shrimp at the time of collection, supporting the $\delta^{15}N$ data indicating these species were separated by a single trophic level step. The NIVA field crew and local fishermen in the area indicated that shrimp were the preferred forage for Atlantic cod in Oslofjord. The $\delta^{13}C$ signatures also demonstrated that herring and shrimp were feeding on different food chains with different sources of carbon at the base. Presumably, this included a pelagic food chain (herring) and a benthic food chain (shrimp).

In order to better define the food web in Oslofjord, aquatic organisms were grouped into one of four arbitrary food chains (Table 1) based on frequency of occurrence and carbon flow to consumers. Individual species in the Oslofjord food web were assigned to the food chains based on comparison (Dunnett Test) of the $\delta^{13}C$ signatures for the species of interest ($\delta^{13}C_{species}$) to the $\delta^{13}C$ signatures for Atlantic cod ($\delta^{13}C_{cod}$), northern shrimp ($\delta^{13}C_{shrimp}$), and Atlantic herring ($\delta^{13}C_{herring}$). Food chain A was identified as the dominate food chain in the Oslofjord food web because it was represented by the largest number of species in the inner Oslofjord (12 of 19 species) and the outer Oslofjord (11 of 15 species). Food chain B was represented by 7 species in the inner Oslofjord and by 3 species in the outer Oslofjord. Food chain C was represented by only 1 species in the outer Oslofjord and food chain D was not represented in the sampled food web. This unbiased approach to isolating the food chains demonstrated that carbon flow in the food web must have originated from at least two sources. Carbon flow in food chain A, which included benthic organisms, (e.g., shrimp, mussels, and sea urchins) at the base, was assumed to be benthic in origin. Carbon flow in food chain B, which included pelagic organisms (e.g., zooplankton) at the base, was assumed to be pelagic in origin.

Overlap of the $\delta^{13}C$ signatures between species on food chains A and B increased with carbon flow up the food web (Fig. 2), which was indicative of omnivorous feeding across the two food chains. Omnivorous feeding across the food chains in the Oslofjord food web appeared to occur at $\delta^{15}N$ values that were ≥14‰ or at trophic levels above 3.1. Omnivorous feeding within the food chains at trophic levels above 3.0 was also apparent from the complete overlap of $\delta^{15}N$ values ranging from13‰ to 18‰ (Fig. 2). It was not possible to identify a distinct benthic or a distinct pelagic food chain using $\delta^{13}C$ signatures because of the overlapping and converging food chains. Therefore, it was assumed that the trophic dynamics in Oslofjord were best described as a compressed food web (omnivorous feeding within food chains) that was confounded by converging food chains (omnivorous feeding across food chains that increased with trophic level) dominated by a single benthipelagic food chain. Atlantic cod, which occupied the highest trophic level in the evaluated food web, are omnivorous predators that are

known to feed on shrimp (food chain A) and herring (food chain B) in Oslofjord. However, the $\delta^{13}C$ signatures indicated that cod were feeding primarily on food chain A and that shrimp, not herring, were the preferred forage base for Atlantic cod in Oslofjord at the time of sample collection.

Bottom sediments in Oslofjord were, presumably, the source of carbon flow in the dominant food chain A, which included benthic organisms at the base and was assumed to be benthic in origin. Because of the physical-chemical property values of very low water solubility ($S_W \leq 56$ µg L^{-1}) and very high partitioning from water to octanol (log $K_{OW} > 6.5$), cVMS materials in municipal wastewater exist in the solids phase and are released to the environment adsorbed to particulates that deposit to the bed sediments. Surface sediments in the inner Oslofjord generally had higher water content and organic carbon content than sediments from the outer Oslofjord (Tables 4 and 5). Similarly, concentrations of D4, D5, and D6 in surface sediments were considerably greater in the inner Oslofjord, relative to concentrations in the outer Oslofjord (Tables 6 and 7). When expressed on the basis of dry weight, mean concentrations in the inner Oslofjord surface sediments were 2.43 ng/g for D4 (range 0.86 to 5.07 ng/g), 412 ng/g for D5 (range 231 to 675 ng/g), and 81.5 ng/g for D6 (range 42.3 to 111 ng/g). By comparison, mean dry-weight concentrations of the cVMS materials in surface sediments of the outer Oslofjord were 0.37 ng/g for D4 (range 0.00 to 2.39 ng/g), 8.61 ng/g for D5 (range 3.57 to 19.9 ng/g), and 8.90 ng/g for D6 (range 5.17 to 16.7 ng/g). Similar differences were observed between the inner and outer Oslofjord basins when concentrations of the cVMS materials in surface sediments were expressed on the basis of wet weight and total organic carbon content (Tables 6 and 7).

The differences observed for cVMS concentrations between surface sediments in Oslofjord were indicative of the cVMS materials, which because of their hydrophobicity typically deposit to sediments in the general vicinity where they are released. Because of the semi-enclosed nature of Oslofjord, cVMS materials and other chemical substances in municipal wastewater that are 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 TOC-equivalent concentrations of the cVMS materials in the sediments, which represented the source of exposure to organisms feeding on the dominant food chain A, indicated that sediment exposure levels in the more polluted inner Oslofjord, relative to the less polluted outer Oslofjord, were about 2x higher for D4, 32x higher for D5, and 7x higher for D6.

Lipid-equivalent concentrations of D4, D5, and D6 were highly variable across species and were considerably greater in species from the inner Oslofjord, relative to concentrations in species from the outer Oslofjord (Tables 6 and 7). Similar to that observed for sediments, the observed differences in concentrations of the cVMS materials within the same species reflected the significantly higher exposure concentrations encountered in the more polluted inner Oslofjord. Lipid-equivalent concentrations of the cVMS materials were typically greatest in the lowest trophic level species (i.e., the benthic macroinvertebrates and zooplankton) and significantly

decreased up the dominant food chain A (Fig. 3). The lowest lipid-equivalent concentrations were observed in Atlantic cod, which was the highest trophic level species in the food web.

Generally, lipid-equivalent concentrations of the cVMS materials were inversely related to trophic position in the Oslofjord food webs (Table 8). Based on the mean fit of the TMF regression model (r^2 values), relative trophic level accounted for 36% to 46% of the variability observed for lipid equivalent concentrations of D5 and D6 in the dominant food chain species. In contrast for D4, relative trophic level accounted for less than 17% of the variability observed for lipid equivalent concentrations of D4 in the dominant food chain species. The general lack of fit between relative trophic level and lipid equivalent concentrations, as demonstrated by r^2 values all less than 50%, indicated that accumulation and trophic transfer of cVMS materials in Oslofjord was a complex process that was likely confounded by overlapping and convergent food chains in the food web that could not be reliably isolated.

Trophic magnification factors (TMFs) describe the average change in chemical concentration that occurs within a food web in response to carbon flow from one trophic level to the next, and are particularly useful for comparing biomagnification of chemicals within well defined food chains of a food web. Because of omnivorous feeding across food chains, trophic magnification factors (TMF values) were calculated only for the dominant food chain A in the inner Oslofjord (n = 12 species representing a food chain length of 2.3 steps) and the outer Oslofjord (n = 11 species representing a food chain length of 2.0 steps). Trophic magnification factors could not be calculated for food chains C and D because the food chains were not adequately represented by a sufficient number of species ($n \leq 1$ species). Trophic magnification factors were not calculated for food chain B because the food chain was not adequately represented by a sufficient number of species in the outer Oslofjord (n = 3 species representing a food chain length of 1.4 steps). In addition, $\delta^{13}C$ signatures suggested that a higher degree of omnivorous feeding across food chains may have existed for food chain B species in the inner Oslofjord. In contrast to omnivorous feeding within a food chain, omnivorous feeding across food chains having different sources of carbon at the base strongly influences the TMF calculation, making it especially difficult to interpret results. It is intended that additional work will be conducted with the Norwegian Institute of Water Research (located in Oslo, Norway) to better identify and isolate the food chains that characterize the Oslofjord food web so that TMF calculations can be made for all appropriate food chains.

Mean trophic magnification factors for D4, D5 and D6 in the dominant food chain A of the Oslofjord food web were all less than a value of 1.0 (range 0.2 to 0.6) and were very consistent between the inner and outer Oslofjord basins (Table 8). The over all probability that TMF values were greater than a value of 1.0 was less than 4% for D4 and equal to 0% for D5 and D6. These results for TMF indicate a 96% to 100% probability that the cVMS materials did not biomagnify in the Oslofjord.

Sensitivity analysis indicated that more than 96% of the total variability associated with mean TMF values in inner Oslofjord (Table 9) was accounted for by cVMS concentration (48% to 56%), lipid content (32% to 39%), and trophic level (7% to 12%) of the species. Similarly, more than 97% of the total variability associated with mean TMF values in outer Oslofjord (Table 10) was accounted for by cVMS concentration (58% to 72%), lipid content (15% to 29%), and trophic level (8% to 11%) of the species. Not surprisingly, the parameters having the greatest contribution to the total variability of the TMF values were cVMS concentrations and lipid content of the species that occupied the lowest and highest trophic levels (i.e., organisms at the extreme ends of the TMF regression model). Benthic worms at the base of the dominant food chain A of the inner Oslofjord accounted for 37% to 40% of the total variability whereas Atlantic cod at the top of the food chain accounted for 12% to 14%. In contrast, Atlantic cod at the top of the dominant food chain A of the outer Oslofjord accounted for 33% to 52% of the total variability and benthic worms at the base of the food chain accounted for 16% to 24%.

The high level of agreement for TMF values between the inner and outer Oslofjord food chains (Table 8) demonstrated that trophic transfer of the cVMS materials was not related to exposure. Comparison of concentrations at the base of the dominant food chain (i.e., trophic level 0; the intercept of the TMF regression, Fig. 3) indicated that biota exposure levels in the more polluted inner Oslofjord, relative to the less polluted outer Oslofjord, were about 4x for D4, 38x for D5, and 2x for D6. The differences in concentrations at the base of the dominant food chain between the inner and outer Oslofjord basins were similar to differences observed for concentrations of the cVMS materials in surface sediments (Tables 6 and 7). This similarity further supports the conclusion that sediments were the source of carbon flow and the cVMS materials in the dominant food chain A of Oslofjord.

Because of omnivorous feeding across food chains and the lack of a feeding matrix for the food web, biomagnification factors (BMF values) were calculated only for known predator-prey relationships that were separated by a single trophic level step (i.e., the cod-herring and the cod-shrimp relationships). Because the predator-prey relationships were separated by a single trophic level step, BMF values were not adjusted to correct for trophic level bias associated with omnivorous feeding within the food chain. The impact of omnivorous feeding across food chains by the predator species (Atlantic cod) was reduced, but not entirely eliminated, because the prey species in the relationships (northern shrimp and Atlantic herring) occupied the same trophic levels but on different food chains. Generally, mean predator-prey specific BMF values (cod-shrimp BMF and cod-herring BMF) were in good agreement between the inner and outer Oslofjord and were comparable to TMF values for the dominant food chain A species (Table 8). Mean predator-prey specific BMF values were 1.1 for D4 (range 1.0 to 1.4), 0.6 for D5 (range 0.2 to 0.9), and 1.4 (range 0.9 to 1.8) for D6. The over all probability that BMF values were greater than a value of 1.0 ranged from 37% to 55% for D4, from 0% to 30% for D5, and from 29% to 81% for D6. These results for BMF indicate a 20% to 100% probability that the cVMS materials did not biomagnify in the Oslofjord.

Sensitivity analysis demonstrated that biological variability had the greatest impact on the BMF values. Less than 10% of the total variability associated with the BMF values was related to analytical variability or analysis of samples having concentrations near the limits of detection. Of the total variability associated with the cod-herring BMF values for D4, D5, and D6, concentrations in cod accounted for 44% to 54%, concentrations in herring accounted for 18% to 34%, and lipid content of the fish (cod and herring) accounted for 14% to 22%. Of the total variability associated with the cod-shrimp BMF values for D4, D5, and D6, concentrations in cod accounted for 42% to 44%, concentrations in shrimp accounted for 3% to 14%, and lipid content of the fish (cod and shrimp) accounted for 12% to 31%. Atlantic cod accounted for the greatest amount of variability associated with the BMF values. About 55% to 72% of the total variability of the BMF values was from cVMS concentrations and lipid content of the Atlantic cod. In contrast, 20% to 34% of the total variability was from cVMS concentrations and lipid content of the northern shrimp or the Atlantic herring.

CONCLUSIONS

The trophic transfer of cyclic methylsiloxane (cVMS) materials in aquatic ecosystems is an important criterion for assessing bioaccumulation and ecological risk. Food web magnification of the cVMS materials (specifically D4, D5, and D6) was determined for the aquatic marine food webs in the Oslofjord, Norway, using $\delta^{15}N$ as a continuous variable for assessing trophic levels (TL). The evaluated food web included samples of zooplankton, benthic macroinvertebrates, shellfish, and finfish representing 21 species from 19 genera across 12 families. Food web length was about 2.6 trophic steps for the inner Oslofjord and about 2.4 trophic steps for the outer Oslofjord. Generally, zooplankton, benthic macroinvertebrates (worms and urchins), and blue mussel (*Mytilus edulis*) occupied the lowest trophic levels (TL ~1.5 to 2.0), northern shrimp (*Pandalus borealis*) and Atlantic herring (*Clupea harengus*) occupied the middle trophic level (TL ~3.0) and Atlantic cod (*Gadus morhua*) occupied the highest trophic level (TL ~4.0) of the food web in Oslofjord.

Concentrations of the cVMS materials were inversely related to trophic position in the Oslofjord food web. Lipid-equivalent concentrations of D4, D5, and D6 were greatest in the lowest trophic level species and significantly decreased up the food web, with the lowest concentrations being observed in the highest trophic level species. Trophic magnification factors (TMF values) in the dominant food chain of the food web were less than a value of 1.0 (range 0.2 to 0.6) for D4, D5, and D6, and were very consistent between the inner and outer Oslofjord basins. The over all probability that TMF values for the cVMS materials were greater than a value of 1.0 was 0% to 4%. Predator-prey specific biomagnification factors (BMF values) ranged from 0.7 to 1.8 and were in good agreement between two basins. Although the mean BMF values were typically greater than a value of 1.0, the over all probability that BMF values were greater than a value of 1.0 was less than 55% for D4 and D5 and less than 81% for D6. These results for TMF and BMF demonstrated that trophic dilution of the cVMS materials occurred across the dominant food chain of the Oslofjord food web. These results also indicated that trophic

transfer was not related to exposure levels, which were 2 to 38 times greater in the more polluted inner Oslofjord, relative to the less polluted outer Oslofjord.

Trophic magnification factors, which describe the change in chemical concentration from one trophic level to the other, are increasingly being used to assess bioaccumulation and biomagnification of chemicals in the environment (Muir et al. 2004; Law et al. 2006; Tomy et al. 2007; Helm et al. 2008; Houde et al. 2008). Trophic magnification factors are derived from the slope of the regression of lipid-equivalent concentrations of the chemical on trophic level (TL) of organisms of a defined food chain. As such, a TMF value represents the average increase (or decrease) in concentration of a chemical substance across the food chain rather than a single predator-prey relationship or biomagnification factor (BMF value). Consequently, TMF values are preferable to BMF values and are particularly useful for comparing trophic transfer and biomagnification of individual chemicals within well defined food chains.

Bioaccumulative substances are defined as chemical substances that biomagnify in a food web and the TMF value is considered the most conclusive evidence of the bioaccumulative nature of a chemical substance (Gobas et al. 2008, 2009; Swackhamer et al. 2009). Trophic magnification factors greater than a value of 1.0 are indicative of chemical substances, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), that biomagnify and are considered to be bioaccumulative. Ultimately, the TMF value is an expression of whether a substance undergoes trophic magnification (TMF > 1) or biodilution (TMF < 1), and field-derived TMF values less than 1.0 are considered the most conclusive evidence that a chemical substance does not biomagnify and is not bioaccumulative. Trophic magnification factors for the three cVMS materials in the dominant food chain of the Oslofjord food web were all less than a value of 1.0 (range 0.2 to 0.6). These results showed that trophic dilution of the cVMS materials occurred and demonstrated that D4, D5, and D6 did not biomagnify in the aquatic marine environment of the Oslofjord. Moreover, these results for TMF indicate a 96% to 100% probability that the cVMS materials did not biomagnify in the Oslofjord. Consequently, field data from the Oslofjord demonstrated that D4, D5, and D6 were not bioaccumulative materials in aquatic marine environments.

FUTURE WORK

This report evaluates and summarizes the biomagnification and bioaccumulation of D4, D5, and D6 in the marine aquatic food web of Oslofjord, Norway. Results from the study summarized in this report indicated that trophic transfer of cVMS materials in Oslofjord was obscured by very complex food web dynamics that were defined by multiple food chains having a great diversity in prey organisms and feeding relationships. Because of the complex food web dynamics, trophic transfer of the cVMS materials could only be evaluated for the dominant food chain in the food web, which was identified based on frequency of occurrence of species and carbon flow to consumers. It is intended that additional work will be conducted with the Norwegian Institute of Water Research (located in Oslo, Norway) to better identify and characterize

the Oslofjord food web so that TMF calculations can be made for all appropriate food chains.

ACKNOWLEDGEMENTS

Samples were collected from Oslofjord with guidance and assistance from the Norwegian Institute of Water Research (NIVA), located in Oslo, Norway. We thank the captain and crew of the Norwegian research vessel F/F Trygve Braarud (operated out of the University of Oslo) for their help and assistance with sample collection. We are especially grateful for the technical guidance and assistance provided by Merete Schøyen and Norman Green of NIVA.

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Table 1. Samples that were collected 12-14 November 2008 and used to evaluate bioaccumulation of cyclic methylsiloxane materials (cVMS; specifically, D4, D5, and D6) in the marine aquatic food webs of Oslofjord, Norway.

Code	Common Name	Family	Genus species	Collected[1] Inner	Collected[1] Outer	Food Chain[2]
SED	Sediment[1]			4	3	
WOR	Worms			1	2	A
BRL	Sea urchin	Brissidae	*Brissopsis lyrifera*		4	A
MUS (A)	Mussel (species A)[3]			2	3	A
MUS (B)	Mussel (species B)[3]			2	3	A
BMU	Blue mussel[3]	Mytilidae (mussels)	*Mytilus edulis*	5		B
ZOO (NP)	Net plankton[3]	200-µm net plankton		2	1	B
ZOO (JF)	Jellyfish[3]			2	1	
SHR	Northern shrimp[3]	Pandalidae (pandalid shrimps)	*Pandalus borealis*	6	6	A
HER	Atlantic herring	Clupeidae (herrings)	*Clupea harengus*	6		B
ACD	Atlantic cod	Gadidae (cods)	*Gadus morhua*	6	7	A
COA	Coalfish	Gadidae (cods)	*Pollachius virens*	6	6	B
EWG	European whiting	Gadidae (cods)	*Merlangius merlangus*	6		A
HAD	Haddock	Gadidae (cods)	*Melanogrammus aeglefinus*	4	12	A
NAP	North Atlantic pollock	Gadidae (cods)	*Pollachius pollachius*	6		B
NOP	Norway pout	Gadidae (cods)	*Trisopterus esmarkii*	6	10	B
PCD	Poor cod	Gadidae (cods)	*Trisopterus minutus*	6		A
EHE	European hake	Merlucciidae (hakes)	*Merluccius merluccius*	4		B
EPE	European plaice	Pleuronectidae (righteye flounders)	*Pleuronectes platessa*	6	5	A
LRD	Long rough dab	Pleuronectidae (righteye flounders)	*Hippoglossoides platessoides*	6	6	A
RAR	Starry skate	Rajidae (skates and rays)	*Amblyraja radiata*		6	C
CSE	Common sole	Soleidae (soles)	*Solea vulgaris*		6	A
VEE	Vahl's eelpout	Zoarcidae (eelpouts)	*Lycodes vahlii*	6		A

[1] For sediments, value represents the number of locations where samples were collected.

[2] Individual species in the Oslofjord food webs were assigned to food chains based on a Dunnett's test comparison of the $\delta^{13}C$ signatures for the species of interest ($\delta^{13}C_{species}$) to the $\delta^{13}C$ signatures for Atlantic cod ($\delta^{13}C_{cod}$), northern shrimp ($\delta^{13}C_{shrimp}$), and Atlantic herring ($\delta^{13}C_{herring}$). Individual species were assigned to food chains as:

- Food chain A: $\delta^{13}C_{cod} \leq \delta^{13}C_{species} \leq \delta^{13}C_{shrimp}$ (14 of 22 species)
- Food chain B: $\delta^{13}C_{herring} \leq \delta^{13}C_{species} < \delta^{13}C_{cod}$ (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)

[3] Samples were collected and analyzed as composite or pooled samples.

Table 2. Summary of the quality control (QC) program that was implemented in the field and laboratory for samples collected 12-14 Nov 2008 from Inner and Outer Oslofjord, Norway. The QC samples were collected and analyzed to evaluate detectability, bias, and precision, and to verify that samples were not contaminated by sample collection, handling, shipment, storage, and processing procedures.

QC Sample	Description	Matrices
Detection limits	• Limit of detection (LOD): The minimum level of analyte that could be detected and reported with 99% confidence that it was different from a matrix–free blank. Determined by repetitive analysis of reagent blanks. • Method detection limits (MDL): The minimum level of analyte in a sample matrix, that when processed through the complete analytical method could be measured and reported with 99% confidence that it was different from a blank. Determined by repetitive analysis of samples. • Limit of quantification (LOQ): The minimum level of analyte in a sample matrix that could be measured and reported with 99% confidence of having an estimation error no greater than 30% when based on a single measurement. Defined as 3.3 time the LOD or, preferably, as 2.5 times the MDL.	• all matrices
Reagent blanks	Extraction solvents dispensed directly into an empty extraction vial. Used to evaluate contamination from solvents, containers, and analytical operations, for blank-correction of sample data, and for calculation of limits of detection (LOD).	• all matrices
Field blanks	Reference sample having very low or non-detectable concentrations of cVMS materials that was taken into the field and processed like a field sample. Used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples.	• fish (trawl samples)
Laboratory blanks	Reference sample having very low or non-detectable concentrations of cVMS materials that was processed in the laboratory like a field sample. Used to evaluate contamination bias resulting from storage, processing, and analysis of samples in the laboratory.	• sediment • fish • mussels • shrimp
Field replicates	Replicate field samples that were processed, extracted, and analyzed as individual samples. Used to evaluate between-sample variability (precision).	• sediment • fish • mussels • shrimp

Laboratory replicates	Replicate sub-samples of a processed field sample that were extracted and analyzed as individual samples. Used to evaluate within-sample variability, for calculation of method detection limits (MDL), and to evaluate analytical precision.	• sediment • fish • mussels • shrimp
Extract replicates	Replicate analyses of a sample extract. Used to evaluate instrument precision.	• none
Field spikes	Field samples spiked in the field with known amounts of cVMS materials. Used to evaluate loss of cVMS from during collection, processing, transport, storage, and analysis of samples, and to evaluate analytical bias.	• none
Laboratory spikes	Processed field samples spiked in the laboratory with known amounts of cVMS materials. Used to evaluate analytical bias.	• sediment • fish • mussels • shrimp
Reference Samples	Control samples having known concentrations of cVMS materials (reference samples having very low or non-detectable concentrations of cVMS materials were used for field blanks and laboratory blanks). Used to evaluate contamination or loss of cVMS from samples during storage and analysis, for calculation of detection limits (MDL), and to evaluate analytical bias and precision.	• sediment • fish
Internal standards	Stable isotopes (^{13}C) of D4, D5, and D6 added to assess and correct for instrument variability.	• all matrices

Table 3. Analytical detection limits during analysis for D4, D5, and D6 in samples collected 12-14 November 2008 from Oslofjord.

	Dow Corning Analyses			Evonik Analyses		
	D4	D5	D6	D4	D5	D6
Background (ng)						
• sediment	2.07	7.95	-0.54			
• biota	0.46 to 2.49	-0.22 to 8.16	-3.08 to 1.52			
Limit of detection (LOD; ng)						
• sediment	0.08	1.63	0.47			
• biota	0.66	1.98	1.11			
Analyses less than LOD						
• sediment	0 of 6	0 of 6	0 of 6			
• biota	6 of 91	0 of 91	1 of 91			
Method detection limit (MDL; ng/g ww)[1]						
• sediment	0.41	0.30	0.42	3.7	3.7	3.7
• mussels	0.33	0.66	0.40			
• shrimp	0.21	0.24	0.39	3.3	2.7	2.7
• fish	0.38	0.22	0.43	1.5	1.1	1.9
Analyses less than MDL[2]						
• sediment	9 of 14	0 of 14	0 of 14	12 of 12	2 of 12	3 of 12
• biota	20 of 83	0 of 83	0 of 83	34 of 72	2 of 72	26 of 72

[1] Evonik MDLs for sediment represent high-biased estimates. Because of analytical challenges most of the Evonik sediment samples were consumed during analysis. Consequently, MDLs were determined on sample masses that were about 5 times less than usual, which resulted in correspondingly increased detection limits.

[2] Most (60 to 100%) of the analyses that were less than the MDL were associated with samples from the Outer Oslofjord.

Table 4. Characteristics of samples (mean and standard error; SE) collected from the Inner Oslofjord, sorted on increasing trophic level, that were used to evaluate bioaccumulation of cyclic methylsiloxane materials (cVMS; specifically, D4, D5, and D6) in the marine aquatic food webs of Oslofjord, Norway. Samples were collected 12-14 November 2008 from Inner Oslofjord with assistance from the Norwegian Institute of Water Research (NIVA).

			Water (% ww)		Lipid (% ww)[2]		$\delta^{13}C$ (ppt)		$\delta^{15}N$ (ppt)		Trophic Level	
Code	Species	N[1]	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
SED (0-1)	Sediment (0-1 cm)	8	68.2	2.4	0.86	0.06						
SED (1-2)	Sediment (1-2 cm)	8	63.8	1.7	0.95	0.04						
BMU	Blue mussel	5			0.81	0.11	-17.90	0.09	7.98	0.17	1.5	0.0
BRL	Sea urchin											
WOR	Worms	1			0.32		-16.50		8.80		1.7	
ZOO (JF)	Jellyfish	1			0.56		-17.89		9.90		2.0	
ZOO (NP)	Net plankton	1			0.74		-18.66		9.90		2.0	
MUS (B)	Mussel (species B)	2			0.90	0.31	-16.27	0.01	11.79	0.16	2.6	0.0
MUS (A)	Mussel (species A)	2			0.76	0.28	-16.72	0.11	12.70	0.20	2.8	0.1
HER	Atlantic herring	6			8.83	0.29	-19.06	0.25	13.29	0.08	3.0	0.0
SHR	Northern shrimp	6			3.01	0.43	-16.02	0.05	13.30	0.06	3.0	0.0
EPE	European plaice	6			4.97	0.42	-17.05	0.30	13.50	0.24	3.1	0.1
COA	Coalfish	6			2.30	0.10	-18.56	0.27	14.23	0.16	3.3	0.0
CSE	Common sole											
NOP	Norway pout	6			8.83	0.52	-17.94	0.12	14.44	0.20	3.3	0.1
EHE	European hake	4			2.41	0.55	-17.73	0.07	14.61	0.20	3.4	0.1
RAR	Starry skate											
HAD	Haddock	4			4.68	0.36	-17.00	0.10	15.99	0.34	3.8	0.1
EWG	European whiting	6			1.25	0.15	-17.51	0.05	16.07	0.25	3.8	0.1
LRD	Long rough dab	6			2.40	0.49	-17.02	0.15	16.08	0.22	3.8	0.1
VEE	Vahl's eelpout	6			1.03	0.13	-17.05	0.21	16.18	0.28	3.8	0.1
NAP	North Atlantic pollock	6			3.94	0.43	-17.66	0.11	16.19	0.28	3.8	0.1
PCD	Poor cod	6			2.73	0.59	-16.88	0.09	16.21	0.17	3.8	0.1
ACD	Atlantic cod	6			2.31	0.32	-16.75	0.10	16.79	0.22	4.0	0.1

[1] N is the number of samples analyzed

[2] For sediment samples, % total organic carbon (TOC, % ww) is reported rather than lipid content.

Table 5. Characteristics of samples (mean and standard error; SE) collected from the Outer Oslofjord, sorted on increasing trophic level, that were used to evaluate bioaccumulation of cyclic methylsiloxane materials (cVMS; specifically, D4, D5, and D6) in the marine aquatic food webs of Oslofjord, Norway. Samples were collected 12-14 November 2008 from Outer Oslofjord with assistance from the Norwegian Institute of Water Research (NIVA).

			Water (% ww)		Lipid (% ww)[2]		$\delta^{13}C$ (ppt)		$\delta^{15}N$ (ppt)		Trophic Level	
Code	Species	N[1]	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
SED (0-1)	Sediment (0-1 cm)	6	62.5	2.6	0.71	0.04						
SED (1-2)	Sediment (1-2 cm)	6	60.1	1.3	0.75	0.03						
BMU	Blue mussel											
BRL	Sea urchin	3			0.32	0.00	-16.50	0.00	8.80	0.00	2.1	0.0
WOR	Worms	1			0.32		-16.50		8.80		2.1	
ZOO (JF)	Jellyfish	1			0.58		-17.79		9.27		2.2	
ZOO (NP)	Net plankton	1			1.09		-18.56		9.27		2.2	
MUS (B)	Mussel (species B)	3			0.81	0.06	-16.90	0.00	12.50	0.06	3.0	0.0
SHR	Northern shrimp	6			3.30	0.51	-16.17	0.09	12.58	0.03	3.0	0.0
MUS (A)	Mussel (species A)	3			1.38	0.09	-16.58	0.06	13.00	0.15	3.1	0.0
HER	Atlantic herring											
EPE	European plaice	5			2.59	0.57	-16.41	0.32	14.14	0.31	3.4	0.1
CSE	Common sole	3			5.72	1.55	-16.47	0.19	14.30	0.50	3.4	0.1
NOP	Norway pout	10			7.10	0.57	-18.04	0.14	14.53	0.22	3.5	0.1
EHE	European hake											
RAR	Starry skate	3			2.56	0.23	-15.13	0.09	14.73	0.13	3.5	0.0
COA	Coalfish	6			5.23	0.57	-18.51	0.26	15.14	0.22	3.6	0.1
LRD	Long rough dab	6			2.30	0.10	-17.31	0.17	15.17	0.33	3.6	0.1
HAD	Haddock	12			3.64	0.30	-17.66	0.13	15.42	0.17	3.7	0.0
EWG	European whiting											
VEE	Vahl's eelpout											
NAP	North Atlantic pollock											
PCD	Poor cod											
ACD	Atlantic cod	6			2.63	0.52	-17.40	0.21	17.29	0.16	4.1	0.0

[1] N is the number of samples analyzed

[2] For sediment samples, % total organic carbon (TOC, % ww) is reported rather than lipid content.

Table 6. Concentrations (mean and standard error; SE) of cVMS materials (D4, D5, and D6) measured in samples from the Inner Oslofjord food web, sorted on increasing trophic level. Samples were collected 12-14 November 2008 from Inner Oslofjord, Norway with assistance from the Norwegian Institute of Water Research (NIVA).

				D4 (ng/g ww)		D5 (ng/g ww)		D6 (ng/g ww)		D4 (ng/g lipid)[2]		D5 (ng/g lipid)[2]		D6 (ng/g lipid)[2]	
Code	Species	TL	N[1]	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
SED (0-1)	Sediment (0-1 cm)		7	0.8	0.2	149.3	27.3	29.3	3.4	86	20	16930	2390	3423	256
SED (1-2)	Sediment (1-2 cm)		8	0.9	0.2	137.1	20.8	25.7	3.1	98	19	14510	2300	2744	365
BMU	Blue mussel	1.5	5	0.3	0.2	68.9	33.2	1.5	0.7	18	3	5333	1303	120	25
BRL	Sea urchin														
WOR	Worms	1.7	1	8.6		552.9		20.1		2687		172777		6266	
ZOO (JF)	Jellyfish	2.0	1	0.1		6.7		0.4		2		1195		71	
ZOO (NP)	Net plankton	2.0	1	2.8		367.8		2.9		379		49594		397	
MUS (B)	Mussel (species B)	2.6	2	0.2	0.0	39.3	11.5	1.9	0.5	21	4	4468	277	213	16
MUS (A)	Mussel (species A)	2.8	2	0.3	0.0	208.1	43.7	7.7	1.0	36	8	34137	18322	1118	282
HER	Atlantic herring	3.0	6	10.2	2.2	1407.3	347.0	18.7	3.3	115	22	18379	3113	241	30
SHR	Northern shrimp	3.0	6	2.7	0.0	107.2	11.1	3.2	0.5	100	14	3723	319	104	5
EPE	European plaice	3.1	6	22.1	5.8	1435.4	237.2	26.6	3.6	414	77	28136	2936	543	79
COA	Coalfish	3.3	6	11.8	1.6	114.5	31.9	18.6	1.5	504	48	4799	1208	809	52
CSE	Common sole														
NOP	Norway pout	3.3	6	26.8	2.0	710.0	141.1	15.4	1.5	303	15	8951	996	181	6
EHE	European hake	3.4	4	6.9	2.4	783.9	387.2	12.9	6.3	271	53	25832	10098	428	163
RAR	Starry skate														
HAD	Haddock	3.8	4	4.2	0.7	214.2	51.4	22.5	3.4	98	5	4429	882	413	36
EWG	European whiting	3.8	6	2.3	0.4	87.5	16.3	2.3	0.5	192	7	7105	839	185	22
LRD	Long rough dab	3.8	6	12.2	2.8	386.3	82.2	13.5	2.9	715	140	19806	4664	794	247
VEE	Vahl's eelpout	3.8	6	1.7	0.2	31.7	8.7	3.1	0.9	174	22	3121	612	362	132
NAP	North Atlantic pollock	3.8	6	11.9	4.3	1158.7	487.4	24.0	6.3	278	81	26106	9645	576	124
PCD	Poor cod	3.8	6	1.7	0.4	43.4	14.1	3.9	1.0	71	7	1455	176	96	12
ACD	Atlantic cod	4.0	6	2.6	0.8	61.7	19.5	4.2	1.3	100	19	2026	265	137	15

[1] N is the number of samples analyzed

[2] For sediment samples, TOC (total organic carbon) equivalent concentrations are reported rather than lipid-equivalent concentrations.

Table 7. Concentrations (mean and standard error; SE) of cVMS materials (D4, D5, and D6) measured in samples from the Outer Oslofjord food web, sorted on increasing trophic level. Samples were collected 12-14 November 2008 from Outer Oslofjord, Norway with assistance from the Norwegian Institute of Water Research (NIVA).

				D4 (ng/g ww)		D5 (ng/g ww)		D6 (ng/g ww)		D4 (ng/g lipid)[2]		D5 (ng/g lipid)[2]		D6 (ng/g lipid)[2]	
Code	Species	TL	N[1]	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
SED (0-1)	Sediment (0-1 cm)		5	0.3	0.2	3.7	1.1	3.5	0.8	45	27	525	130	492	91
SED (1-2)	Sediment (1-2 cm)		6	0.0	0.2	2.9	0.4	3.4	0.3	1	25	394	62	450	40
BMU	Blue mussel														
BRL	Sea urchin	2.1	3	0.5	0.1	13.3	2.4	10.1	2.2	154	17	4159	761	3156	675
WOR	Worms	2.1	1	0.1		4.0		1.3		16		1254		405	
ZOO (JF)	Jellyfish	2.2	1	0.0		0.4		0.1		2		65		13	
ZOO (NP)	Net plankton	2.2	1	0.2		10.1		0.6		15		928		55	
MUS (B)	Mussel (species B)	3.0	3	-0.3	0.0	4.3	0.1	1.2	0.2			537	50	118	5
SHR	Northern shrimp	3.0	6	0.3	0.0	17.7	5.6	1.0	0.2	10	2	495	105	29	1
MUS (A)	Mussel (species A)	3.1	3	0.2	0.0	14.1	0.2	4.2	0.2	14	2	1029	55	306	13
HER	Atlantic herring														
EPE	European plaice	3.4	5	3.2	0.6	49.0	14.5	7.5	1.3	141	3	1884	402	261	45
CSE	Common sole	3.4	3	2.9	0.3	28.8	7.4	2.9	0.8	61	18	531	84	54	10
NOP	Norway pout	3.5	10	1.4	0.2	22.3	3.4	2.5	0.2	22	2	308	32	37	3
EHE	European hake														
RAR	Starry skate	3.5	3	0.5	0.7	27.6	11.1	1.2	0.4	69		1020	366	46	12
COA	Coalfish	3.6	6	0.8	0.3	9.7	3.2	2.8	0.4	20	4	156	15	53	7
LRD	Long rough dab	3.6	6	0.5	0.3	7.8	1.0	1.9	0.6	40	7	304	28	58	13
HAD	Haddock	3.7	12	0.4	0.1	5.3	1.3	4.5	0.7	12	2	159	30	132	15
EWG	European whiting														
VEE	Vahl's eelpout														
NAP	North Atlantic pollock														
PCD	Poor cod														
ACD	Atlantic cod	4.1	6	0.2	0.2	11.5	5.4	1.1	0.3	17	3	223	62	41	5

[1] N is the number of samples analyzed

[2] For sediment samples, TOC (total organic carbon) equivalent concentrations are reported rather than lipid-equivalent concentrations.

Table 8. Summary of bioaccumulation metrics for cyclic methylsiloxane materials in the aquatic marine food web of Oslofjord, Norway. Mean values, 95% confidence intervals, and probabilities were obtained using Monte Carlo simulation (n=1000 trials). Samples were collected 12-14 November 2008 from the inner and outer Oslofjord with assistance from the Norwegian Institute of Water Research (NIVA).

Bioaccumulation Metric	Inner Oslofjord	Outer Oslofjord
Food Chain A Trophic Magnification Factor (TMF)		
• D4		
o Mean TMF	0.6	0.5
o 95% confidence interval	0.3 to 1.0	0.2 to 1.1
o Probability of TMF > 1.0	1.6%	3.5%
o Mean fit of TMF regression model (r^2)	9.2%	16%
• D5		
o Mean TMF	0.3	0.4
o 95% confidence interval	0.1 to 0.4	0.2 to 0.7
o Probability of TMF > 1.0	0.0%	0.0%
o Mean fit of TMF regression model (r^2)	45%	41%
• D6		
o Mean TMF	0.4	0.2
o 95% confidence interval	0.2 to 0.6	0.2 to 0.4
o Probability of TMF > 1.0	0.0%	0.0%
o Mean fit of TMF regression model (r^2)	36%	46%
Cod-Shrimp Biomagnification Factor (BMF)		
• D4		
o Mean BMF	1.0	1.4
o 95% confidence interval	0.4 to 2.1	0.4 to 4.2
o Probability of BMF > 1.0	37%	55%
• D5		
o Mean BMF	0.7	0.9
o 95% confidence interval	0.3 to 1.5	0.2 to 2.8
o Probability of BMF > 1.0	13%	30%
• D6		
o Mean BMF	1.7	1.8
o 95% confidence interval	0.6 to 3.6	0.6 to 4.9
o Probability of BMF > 1.0	80%	81%
Cod-Herring Biomagnification Factor (BMF)		
• D4		
o Mean BMF	1.0	
o 95% confidence interval	0.4 to 2.0	
o Probability of BMF > 1.0	39%	
• D5		
o Mean BMF	0.2	
o 95% confidence interval	0.1 to 0.4	
o Probability of BMF > 1.0	0%	
• D6		
o Mean BMF	0.9	
o 95% confidence interval	0.4 to 2.0	
o Probability of BMF > 1.0	29%	

Table 9. Sensitivity of TMF results to concentration, lipid content, and trophic level for food chain A species in the inner Oslofjord. Values are sorted on mean trophic level (by species) and reported as the % contribution of each parameter to the total variance of the mean TMF value.

Species	Trophic Level	Contribution to Total Variance of Mean TMF Value			
		Concentration	Lipid Content	Trophic Level	Total
D4 TMF Results					
• Wor	1.7	22.2%	17.5%	0.6%	40.3%
• MUS (B)	2.6	0.9%	5.7%	1.1%	7.7%
• MUS (A)	2.8	0.4%	1.8%	2.1%	4.3%
• SHR	3.0	0.1%	1.4%	0.0%	1.5%
• EPE	3.1	1.5%	0.0%	0.1%	1.6%
• HAD	3.8	0.9%	0.3%	0.2%	1.4%
• EWG	3.8	2.6%	1.8%	1.6%	6.0%
• LRD	3.8	4.9%	2.5%	2.7%	10.1%
• VEE	3.8	0.4%	1.6%	1.9%	3.9%
• PCD	3.8	3.8%	2.5%	0.2%	6.6%
• ACD	4.0	9.7%	3.8%	0.4%	14.0%
	Total:	47.5%	39.1%	10.9%	97.5%
D5 TMF Results					
• Wor	1.7	22.4%	14.1%	0.8%	37.4%
• MUS (B)	2.6	1.6%	5.2%	0.8%	7.5%
• MUS (A)	2.8	0.0%	2.2%	0.2%	2.4%
• SHR	3.0	0.1%	0.2%	0.0%	0.3%
• EPE	3.1	1.0%	0.4%	0.2%	1.6%
• HAD	3.8	1.5%	0.1%	0.9%	2.5%
• EWG	3.8	1.0%	1.7%	2.6%	5.3%
• LRD	3.8	2.7%	2.0%	4.9%	9.6%
• VEE	3.8	5.7%	1.3%	0.7%	7.7%
• PCD	3.8	7.0%	3.8%	0.3%	11.1%
• ACD	4.0	9.7%	1.5%	0.6%	11.8%
	Total:	52.7%	32.5%	12.1%	97.3%
D6 TMF Results					
• Wor	1.7	24.2%	13.3%	0.2%	37.7%
• MUS (B)	2.6	3.1%	7.8%	1.4%	12.3%
• MUS (A)	2.8	0.2%	1.9%	0.0%	2.2%
• SHR	3.0	0.4%	0.4%	0.1%	1.0%
• EPE	3.1	0.1%	0.0%	0.4%	0.5%
• HAD	3.8	0.3%	0.3%	2.4%	3.0%
• EWG	3.8	1.9%	1.2%	0.2%	3.3%
• LRD	3.8	3.3%	0.5%	1.8%	5.6%
• VEE	3.8	7.3%	2.3%	0.7%	10.3%
• PCD	3.8	4.7%	2.5%	0.0%	7.2%
• ACD	4.0	10.9%	2.4%	0.3%	13.6%
	Total:	56.5%	32.6%	7.4%	96.6%

Table 10. Sensitivity of TMF results to concentration, lipid content, and trophic level for food chain A species in the outer Oslofjord. Values are sorted on mean trophic level (by species) and reported as the % contribution of each parameter to the total variance of the mean TMF value.

Species	Trophic Level	Contribution to Total Variance of Mean TMF Value			
		Concentration	Lipid Content	Trophic Level	Total
D4 TMF Results					
• Wor	2.1	10.6%	2.8%	2.6%	16.1%
• BRL	2.1	1.7%	2.7%	0.7%	5.1%
• MUS (B)	3.0	0.9%	0.0%	0.0%	1.0%
• SHR	3.0	0.3%	0.2%	0.0%	0.5%
• MUS (A)	3.1	0.0%	0.0%	0.0%	0.0%
• EPE	3.4	0.1%	0.6%	3.0%	3.6%
• CSE	3.4	0.0%	1.6%	3.7%	5.4%
• LRD	3.6	5.0%	0.1%	0.0%	5.2%
• HAD	3.7	7.7%	0.6%	0.0%	8.3%
• ACD	4.1	45.8%	6.5%	0.0%	52.3%
	Total:	72.2%	15.2%	10.1%	97.5%
D5 TMF Results					
• Wor	2.1	11.9%	3.8%	2.1%	17.7%
• BRL	2.1	4.0%	5.0%	0.2%	9.1%
• MUS (B)	3.0	0.0%	0.1%	0.1%	0.1%
• SHR	3.0	0.1%	0.4%	0.1%	0.6%
• MUS (A)	3.1	0.1%	0.1%	0.1%	0.4%
• EPE	3.4	1.9%	0.9%	3.6%	6.4%
• CSE	3.4	0.0%	1.6%	0.6%	2.2%
• LRD	3.6	1.6%	0.0%	0.3%	1.9%
• HAD	3.7	7.7%	0.9%	0.2%	8.8%
• ACD	4.1	42.6%	7.0%	0.8%	50.4%
	Total:	69.9%	19.8%	8.0%	97.7%
D6 TMF Results					
• Wor	2.1	12.8%	7.6%	3.7%	24.1%
• BRL	2.1	10.3%	4.7%	0.0%	14.9%
• MUS (B)	3.0	0.0%	0.2%	0.0%	0.2%
• SHR	3.0	1.1%	0.0%	0.1%	1.2%
• MUS (A)	3.1	0.0%	0.0%	0.3%	0.4%
• EPE	3.4	1.9%	0.5%	2.8%	5.2%
• CSE	3.4	2.1%	1.4%	0.4%	3.9%
• LRD	3.6	6.9%	0.0%	0.4%	7.4%
• HAD	3.7	4.8%	0.3%	2.5%	7.6%
• ACD	4.1	17.6%	14.5%	0.7%	32.9%
	Total:	57.6%	29.3%	11.0%	97.9%

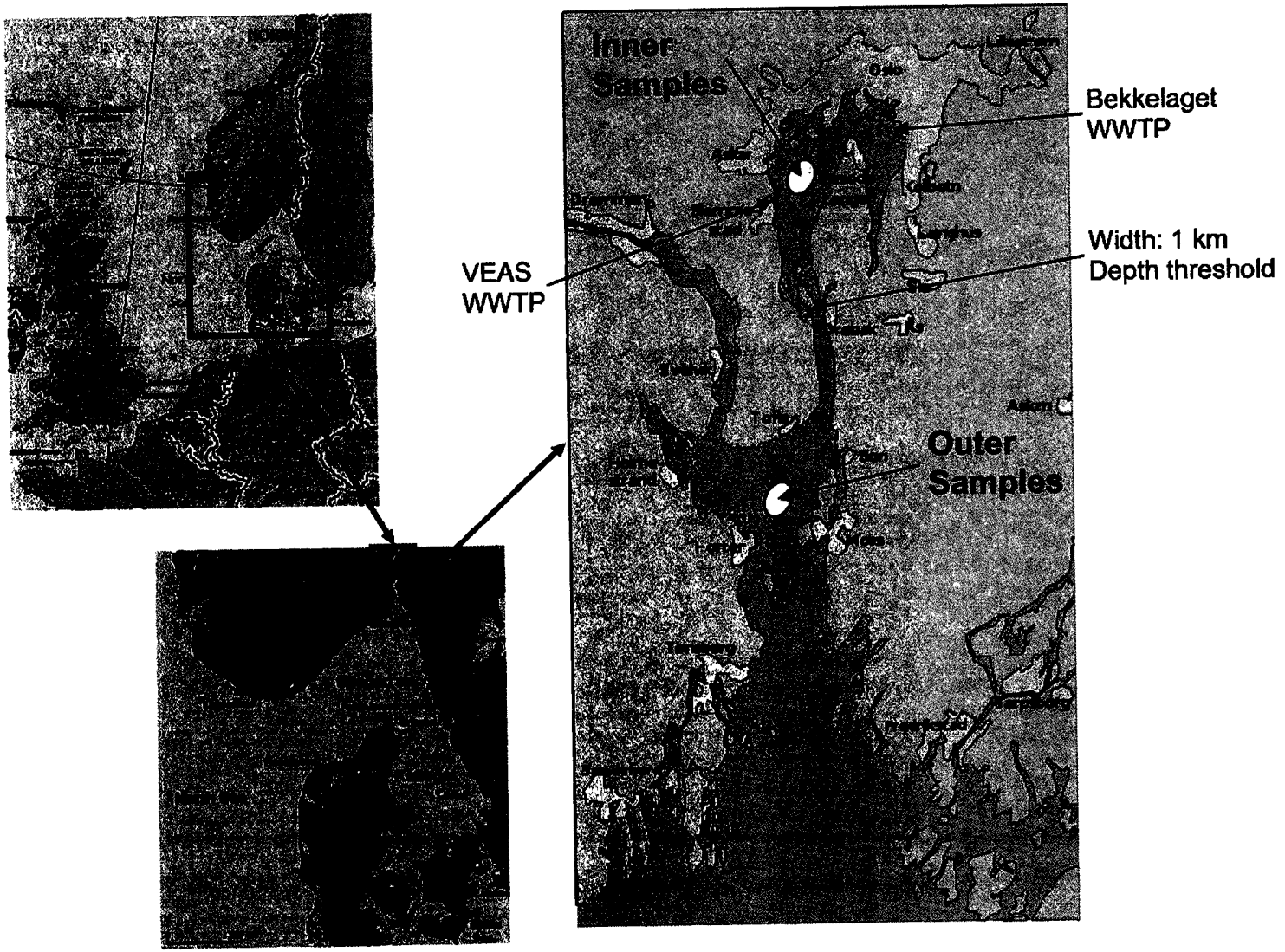

Figure 1. Map of Oslofjord, Norway, showing were samples were collected. Samples were collected from the inner and outer Oslofjord 12-14 November 2008.

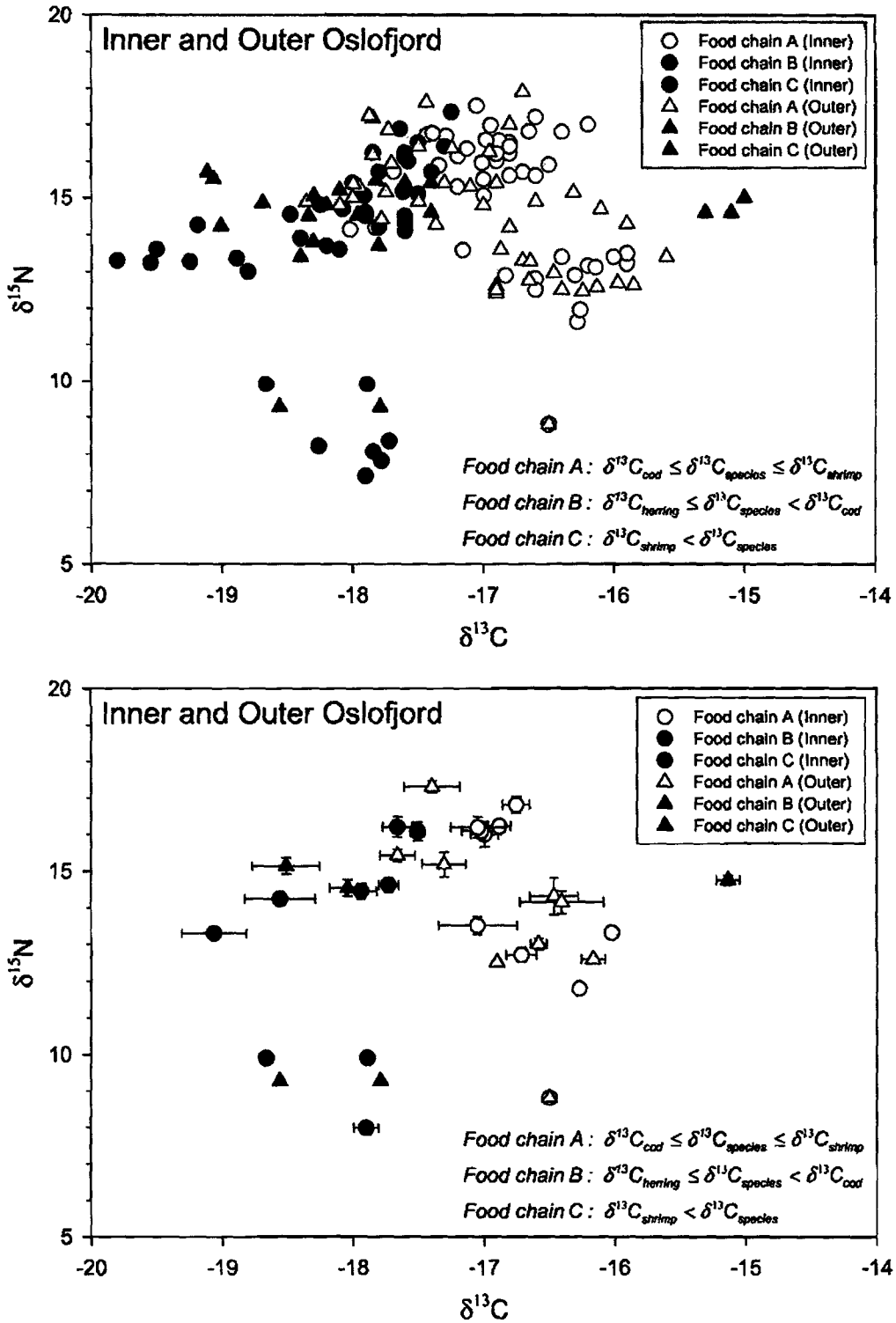

Figure 2. Food web diagram for the inner and outer Oslofjord, based on stable isotope analysis of samples collected 12-14 November 2008. Error bars represent the standard error of the mean isotopic ratios by individual species.

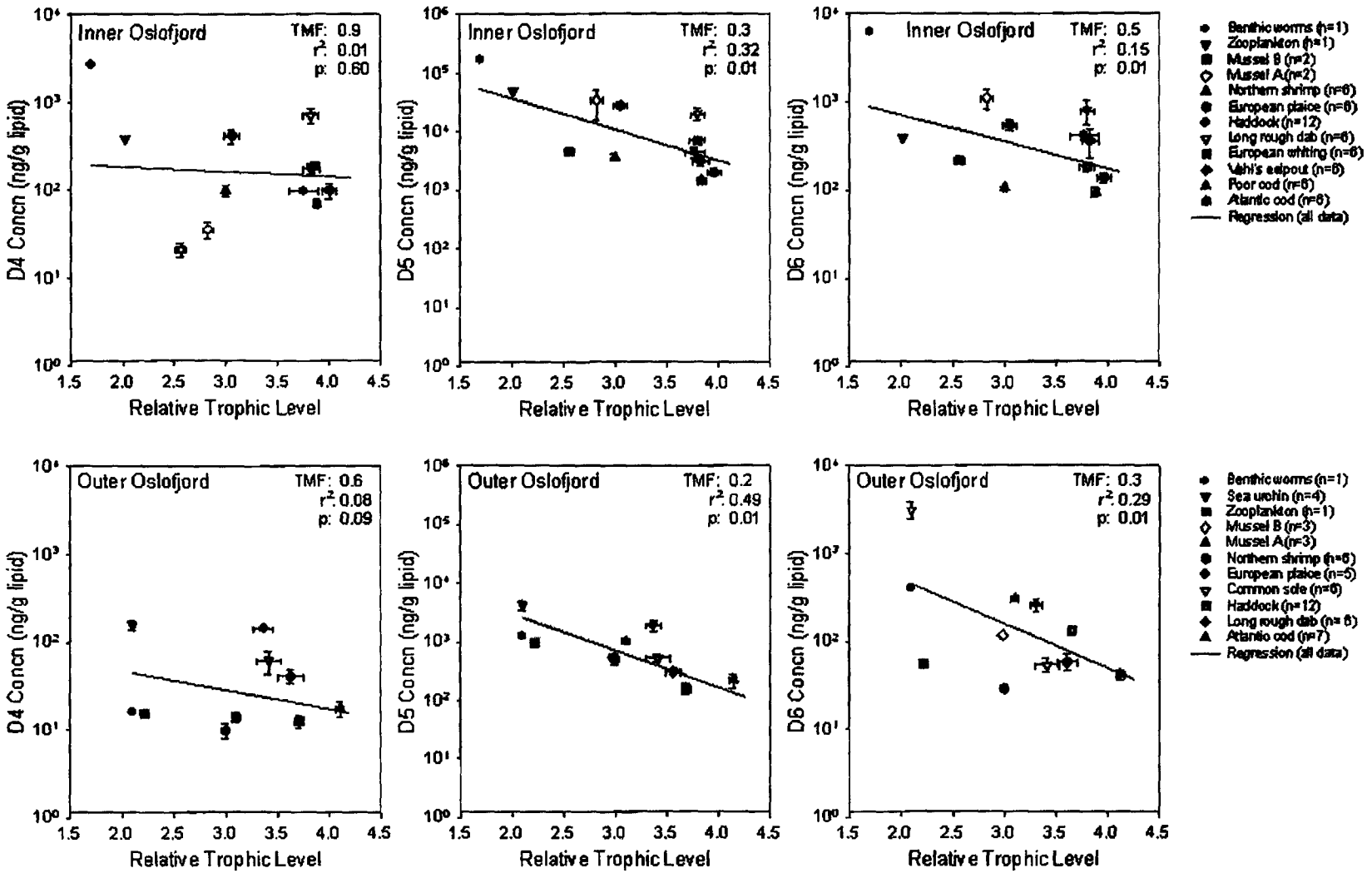

Figure 3. Trophic magnification factors for the aquatic food web species collected from the inner and outer Oslofjord 12-14 November 2008. Trophic magnification factors were calculated based on regression analysis across all samples for the dominant food chain in the food web.

APPENDIX 1: Contributing Scientist Report. Dow Corning Corporation

Analytical results for volatile methyl siloxanes (VMS) in biota and sediment obtained from Oslofjord, Norway

Goldschmidt Analytik

EVONIK INDUSTRIES

Measurements of food-web related data on cVMS distribution in environmental samples collected in Oslo Fjord

(part of a joint project with Dow Corning Corporation, Midland, MI, USA)

A study carried out by:

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Essen, November 11, 2009

1. Objective

As part of a joint project with Dow Corning Corporation, Midland, Mi, environmental samples - have been analysed for their content of cyclic volatile methyl siloxanes (cVMS) (D_4, D_5 and D_6). For biological samples in addition the lipid content and stable isotope measurements of $^{12}C/^{13}C$ and $^{14}N/^{15}N$ were carried out. The intend of these measurements was to generate data allowing to follow cVMS distribution in different trophic levels of the food webs existing in the environments the samples were taken from.

2. Samples

The samples analysed were collected in cooperation with NILU (Norwegian Institute of Air Research) and NIVA (Norwegian Institute of Water Research), who thankfully agreed on our participation in their sampling campaign planned for November 2008 in Oslo Fjord. So it was possible to have experts from Dow Corning and Evonik on the ship, who have a long-time experience in sample collection and in trace analysis for cVMS.

On November 12th samples were collected in the outer Oslo fjord, on November 13thand 14th samples sampling was done in the inner Oslo fjord.

Sediment samples were collected with the help of a core probe sampler which allowed obtaining different sediment layers (0-1 cm; 1-2 cm). The sediment samples were transferred from the sampler into pre-cleaned glass jars and then covered with sea water. The containers then were screw- capped with a gas-tight sealing and kept at 4°C until analysis.

Marine animals were caught by a trawl net. Immediately after trawling the individuals were identified, separated, packed in plastic bags and frozen in a freezer. Shrimp samples were pooled at four to eight individuals and packed in a plastic bag. Fish samples were measured by length, weighed and individually packed in plastic bags. All biota samples were kept frozen until analysis.

In order to evaluate potential contaminations from the trawling or the sample handling onboard field blank samples were prepared and implemented in the sampling process:
Three atlantic cods caught at the first day of trawl in the outer Oslo fjord were filleted. The fillets of each cod were split into six subsamples. Two of them used as "pure blank", two of them were deployed in the net during trawl catching and two of them were retained on the boat and added to the catch in the collection bucket after trawling.
The procedure was applied at three different turns resulting in 18 different quality control blanks which were separated into two groups of nine samples for the two laboratories.

In order to check a potential contamination of the samples by air-transported VMS five air samples were collected at the two days of trawling. Samples were collected both at the outer backmost deck (trawl handling) and in the inner wet lab by drawing approximately 5 liters air over a pre-cleaned TENAX adsorption tube with a flow of 50 to 100 ml/min. The samples were stored in air tight glass-container at ambient conditions and transported into the lab together with the fish samples.

The samples arrived in the laboratory on November 16. The fish were transferred into a freezer set to a temperature of -20 °C.

2.1. *Sample Preparations*

2.1.1. Fish

As agreed for this project, cVMS concentrations of the biota samples should represent an average whole-body concentration. For the stable-isotope measurements planned, however, it was necessary to use well defined muscle tissue.

Accordingly the fish were defrosted and a small sample of fillet (~ 1 g) above the lateral line right behind the operculum were removed with the help of a scalpel. The fillet samples were carefully separated from the skin, transferred into small glass vials and refrozen until analysis.

Subsequently the fish were cut into small pieces with the help of knives and a hatchet. The pieces were ground and homogenized in a threefold repeated procedure in a meat grinder using punched disks with decreasing hole-diameters. Depending on the size of the fish a 10g - 200g portion of the resulting homogenous paste was transferred into pre-cleaned glass vials and refrozen until final analysis. For lipid analysis in addition samples of 5-50g of the homogenate were transferred into other glass vials and refrozen until analysis. The exceeding quantities of the whole-body homogenates produced were disposed.

2.1.2. Shrimp

The pooled shrimp samples were defrosted and depending on their size, four to eight individuals were ground and homogenized in a repeated procedure in a small hand-driven meat grinder using punched disks with decreasing hole-diameters.

One 5g portion of the resulting homogenous paste was transferred into a pre-cleaned glass vial and used for cVMS analysis. Two additional 5g portions of the resulting homogenous paste was transferred into a glass vials and retained for fat analysis and stable Isotope determination

2.1.3. Mussels

The mussel samples were defrosted and depending on their size, three to four individuals were pooled for VMS and fat analysis using the entire core material.

2.1.4. Sediment samples

Sediment samples were used for analysis as delivered to the laboratory.

3. Analysis

3.1. Analyses carried out by contract laboratories

For stable isotope analysis and lipid content analysis, which both are well standardised technologies; two experienced contract laboratories were used:

Stable Isotope Analysis were performed at TÜV Rheinland Agroisolab GmbH, Prof.-Rehm-Str. 6, 52428 Jülich, Germany , while lipid content analysis were performed via extraction according to the German standard § 35 LMBG L 17.00-4 at Technische Lebensmittel- und Umweltanalytik GmbH, Fischkai 1, 27572 Bremerhaven, Germany.

The data of both determinations are integrated in the result section of this report.

3.2. cVMS analysis

3.2.1. Reference Article Information

Reference article characterization was done in our own laboratory by GLC/FID analysis.

- Identification: Octamethylcyclotetrasiloxane (D_4)
- Purity: 99.8 % by GC-FID
-
- Identification: Decamethylcyclopentasiloxane (D_5)
- Purity: 99.5 % by GC-FID
-
- Identification: Dodecamethylcyclohexasiloxane (D_6)
- Purity: 99.5 % by GC-FID

^{13}C-labelled material of D4, D5 and D6 to be used as internal standard was gratefully made available by Dow Corning Corporation.

3.2.2. Sample Processing and Analysis

3.2.2.1. Calibration

The analysis was based upon the principle of calibrating a gas chromatograph with mass selective detection (GC-MS).Six solvent standards were prepared from pentane spiked with various concentrations of D_4, D_5, and D_6 and an equal concentration of ^{13}C-D_4, ^{13}C-D_5 and ^{13}C-D_6 as internal standards. From these samples a linear calibration function was established for each VMS. The pentane extracts of the samples were evaluated using the calibration curves obtained independently.

The solvent standard concentrations ranges validated were adapted to the desired working range and ranged from 4 ng/ml to 100 ng/ml.

The experimental conditions for the GC-MS measurements are compiled in the following tables

Parameter	Setting
Instrument/Software	HP6890 Series Gas Chromatograph HP5973 Mass Selective Detector HP ChemStation version E 01.01.
Inlet conditions	1 µl Pulsed Splitless ; 96 kPa, 0,2 min at 170°C
Carrier	Helium, constant Pressure 48 kPa
Column	Agilent 19091F-115 (FFAP) 50m * 0.32 mm * 0,50µm
Oven Program	40°C (hold 1 min); 40 °C to 150°C at 6°C/min; post run 5 min al 230 °C
Transfer line	180 °C

Acquisition Mode: Single Ion Detection			
	Retention time	**Quantifier**	**Qualifier**
D4	5.8 min.	281 amu	265, 249 amu
D5	8.9 min.	355 amu	267,251 amu
D6	12.9 min.	341 amu	429, 147 amu
^{13}C-D4	5.8 min.	285 amu	268, 252 amu
^{13}C-D5	8.9 min.	360 amu	270, 253 amu
^{13}C-D6	12.9 min.	345 amu	435, 150 amu

Peak responses from the GC-MS system (peak area) were evaluated by automatic electronic integration either by using integration parameters in the software or by drawing a baseline manually in the software for the peak. If the baselines were drawn manually, this was indicated on the chromatogram printout in the study file. Detailed records of the GC-MS system and data system software used can be found in the study file.

A linear regression analysis was performed relating the concentration of the calibration standards to the relative chromatographic response ratio (test article/internal standard).

As a low, but considerable amount of the individual cVMS was found in blank solutions – currently unavoidable contaminations from solvents and analytical devices used- all peak area ratios in the calibration samples were corrected by the corresponding peak area ratios of a calibration blank. The resulting data pairs area ratio vs. concentration ratio were used for a linear regression calibration function (y = a * x).

The linearity parameters; slopes, and correlation coefficients, were determined for each of the cVMS to be analysed. The minimum acceptance criterion for the linearity of a standard curve was a regression coefficient (R2) of 0.995.

Calibration curves were determined from linear regression analysis of the data using Microsoft Excel Version 2003.

3.2.2.2. Analysis

3.2.2.2.1. biological tissue samples:

Extraction:

Extraction of the ground and homogenized sample was performed using a 6:1 solvent to sample ratio of pentane (e.g. 30 ml pentane vs.5 g tissue sample). The sample was weighed into a pre-cleaned screw cap centrifuge glass vial. Subsequently an appropriate amount of internal standard (representing approx. 270 ng/g) solution and a measured volume of pentane extraction solvent were added. The samples were homogenised under cooling (ice/water bath) with the help of an Ultra-Turrax device for 1 minute. The samples were then centrifuged for 5 minutes at a setting of 3000 RPM's. The extract from each sample was transferred into a separate vial.

Pre-cleaning and drying of the raw extract

The raw extract was cleaned by column chromatography. As sorbent 0.8 g of pre-cleaned Florisil (activated at 550°C) were filled into a 5 cm glass column and covered with 100 mg of $MgSO_4$ (pre-treated at 540 °C). 4 ml of the raw extract were transferred onto the $MgSO_4$ layer. Subsequently the cVMS were eluted from the column with additional 5 ml of petrol-ether: MTBE [99:1]. The eluate was carefully reduced by volume to 0.5 ml by a gentle stream of nitrogen at 25 °C and analysed by GC/MS.

3.2.2.2.2. Sediment samples:

Extraction:

Prior to extraction, the water-covered sediment samples were centrifuged at 2000 rpm for five minutes in order to ensure a reproducible solid content of the sediment. After centrifugation the upper water layer was carefully removed by from the sediment and stored apart.

One gram of the remaining sediment then was weighed into a pre-cleaned 15 ml ground stoppered centrifuge glass vial. Subsequently 1 ml of acetonitrile, an appropriate amount of internal standard solution and 2 ml of pentane extraction solvent were added. The sample was extracted by shaking 30 minutes on a vertical shaker. The samples were then centrifuged for 5 minutes at a setting of 3000 RPM's. The extract was transferred into a separate vial. Subsequently two times 2 ml portions of pentane were added and the extraction procedure was repeated twice. The combined extracts were used for pre-cleaning.

Solid content:

For determination of the solid content another 1 g portion of the precipitated sediment was weighed onto a pre-weighed aluminium dish. The solid content was determined by dfferential weighing after 2 h drying at 105°C in an oven.

Pre-cleaning and drying of the sediment raw-extracts

The combined raw extracts were cleaned by column chromatography. As sorbent 0.8 g of pre-cleaned Florisil (activated at 550°C) were filled into a 5 cm glass column and covered with 100 mg of $MgSO_4$ (pre-treated at 540 °C). The combined raw extract was transferred onto the $MgSO_4$ layer. Subsequently the cVMS were eluted from the column with additional 5 ml of petrolether : MTBE [99:1]. The eluate was carefully reduced by volume to 0.5 ml by a gentle stream of nitrogen at 25 °C and analysed by GC/MS.

3.2.2.2.3. QC- samples

3.2.2.2.3.1. QC fish fillet sample

The QC fillets were analysed in the same way as the biological tissue samples.

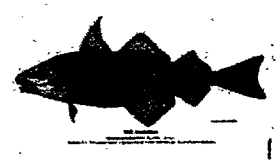
3.2.2.2.3.2. Air monitoring samples

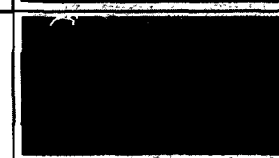
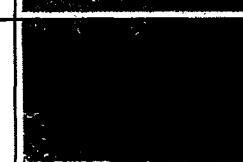
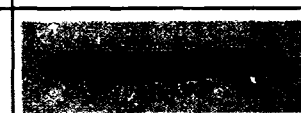
Samples were analysed according to the method described in CES Report: "Presence of volatile siloxanes in ambient air" of 2001 (CES Project 2000/4). The TENAX tubes were analysed by TDS-GC/MS coupling. cVMS were quantified against calibration reference samples spiked on TENAX tubes.

4. Results

4.1. Biota samples

The biota analysed in this study are compiled in table 1. The abbreviations introduced in the first column are used to identify the nature of the samples in the result tables.

Abbreviation	English name	Scientific name	
MUS	Pectinidae Blue Mussel	Pectinidae Mytilus edulis	
SHR	Shrimps		
NOP	Norway Pout	Trisopterus esmarkii	
EPE	European Plaice	Pleuronectes platessa	[redacted]
HAD	Haddock	Melanogrammus aeglefinus	
COA	Coalfish	Pollachius virens	[redacted]
ACD	Atlantic Cod	Gadus morhua	
RAR	Starry Skate	Raja Radiata	[redacted]
BRL	Sea Urchins	Bryopsis Lyrifea	[redacted]

CSE	Common Sole	Solea solea	
LRD	Long rough dab	Hippoglossoides plates-soides	
NAP	North atlantic pollok	Pollachius pollachius	
HER	Herring	Clupea harengus	
PCD	Poor Cod	Trisopterus minutus	
VEE	Vahls Eelpout	Lycodes vahlii	
EHE	European Hake	Merluccius merluccius	

Tab.1. biota analysed

4.1.1. Results Stable Isotope Index and Lipid Analysis

The stable isotope ratio information δ for carbon and nitrogen results from the measured concentrations of the stable isotopes $^{13}C/^{12}C$ and $^{15}N/^{14}N$. δ-values are not absolute isotope abundances but using differences between sample readings and natural abundance standards which are considered δ = zero (e.g. air for nitrogen or Pee Dee Belemnite for carbon). For practical work IAEA-certified reference material is used. Thus for example $\delta^{13}C$ is calculated according to:

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1 \right) * 1000 \ (^{0}/_{00})$$

The precision of the determination of the δ-values is in the order of 0.1 units. In table 2 and 3 the $\delta^{13}C$ and $\delta^{15}N$ values determined for the biota samples analysed are compiled together with information on the carbon and nitrogen content of the samples. These data were obtained from the small filet samples taken for stable isotope analysis, while the lipid concentration, also given in table 2 (Outer Oslo Fjord samples) and table 3 (Inner Oslo Fjord samples), was determined from the homogenisate of the whole bodies (without the small sample taken out before for isotope analysis).

	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	C (%)	N (%)	lipid (%)
	Filet	Filet	Filet	Filet	Whole body homogenisate
ACD 002	-16.8	17.0	43.2	13.9	4.1
ACD 004	-16.7	17.9	43.6	14.1	1.3
COA 002	-17.6	15.4	45.2	14.4	6.5
COA 004	-18.1	15.2	44.8	14.5	5.2
COA 006	-18.2	14.8	44.3	14.4	3.7
CSE 002	-16.6	14.9	39.6	12.7	7.8
CSE 004	-16.1	14.7	43.5	13.8	6.6
CSE 006	-16.7	13.3	46.2	14.7	2.7
EPE 002	-15.6	13.4	44.9	14.4	1.8
EPE 004	-15.9	14.3	44.5	14.2	3.2
HAD 002	-17.0	14.8	45.6	14.4	4.4
HAD 004	-16.9	15.4	44.8	14.4	4.2
HAD 006	-17.5	16.4	42.7	13.3	3.2
HAD 008	-18.0	15.0	40.4	12.9	4.5
HAD 10	-18.1	14.8	45.3	14.4	2.9
HAD 012	-17.3	15.4	44.5	14.6	1.5
LRD 002	-16.8	14.2	46.3	14.6	3.4
LRD 004	-17.1	15.3	43.9	14.3	2.1
LRD 006	-17.5	14.9	44.0	14.2	2.5
NOP 002	-18.3	13.8	45.1	14.6	5.3
NOP 004	-17.8	13.7	45.4	14.8	6.6
NOP 006	-18.4	13.4	44.5	14.4	5.3
NOP 008	-17.4	14.6	44.8	14.5	5.8
NOP 010	-17.4	15.4	44.7	14.5	6.9
RAR 002	-15.0	15.0	42.3	15.8	2.8
RAR 004	-15.1	14.6	42.8	15.9	2.8
RAR 006	-15.3	14.6	40.5	15.3	2.1
MUS 2	-16.9	12.5	31.7	9.9	0.7
MUS 4	-16.9	12.4	32.1	9.9	0.9
MUS 6	-16.9	12.6	30.3	9.3	0.8
SHR 2	-16.4	12.5	38.5	11.5	1.7
SHR 6	-16.4	12.6	36.5	11.0	1.8
BRL	-16.5	8.8	4.9	0.8	0.3

Tab.2. stable isotope analysis data and carbon, nitrogen and lipid content in samples collected in the outer Oslo Fjord

	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	C (%)	N (%)	lipid (%)
	Filet	Filet	Filet	Filet	Whole body homogenisate
ACD 022	-16.4	16.8	45.6	14.6	1.7
ACD 024	-16.8	16.5	37.0	11.9	1.6
ACD 026	-16.6	17.2	43.1	13.9	1.6
COA 022	-17.9	14.6	42.8	14.0	2.7
COA 024	-17.9	14.5	43.5	14.3	1.9
COA 025	-18.4	13.9	45.2	14.6	2.4
COA 026	-19.5	13.6	43.8	14.3	0.8
EHE 002	-17.6	14.5	46.1	14.9	1.4
EHE 004	-17.8	14.2	45.1	14.5	1.6
EPE 022	-16.3	12.9	43.7	13.8	4.6
EPE 024	-16.4	13.4	45.7	14.2	6.1
EPE 026	-16.6	12.8	44.6	14.0	4.0
EWG 002	-17.5	15.1	44.3	14.4	0.7
EWG 004	-17.3	16.4	42.7	13.9	1.1
EWG 006	-17.4	15.7	39.6	12.8	1.0
HAD 022	-16.8	16.2	43.7	13.8	3.8
HAD 024	-16.9	16.0	45.6	14.5	4.5
HER 002	-19.8	13.3	45.6	14.5	9.6
HER 004	-18.1	13.6	43.2	14.1	9.8
HER 006	-18.8	13.0	45.2	14.6	8.6
LRD 022	-16.8	15.6	45.2	14.4	0.9
LRD 024	-16.7	15.7	44.9	14.3	3.9
LRD 026	-16.6	15.6	42.9	13.9	1.3
NAP 002	-18.0	15.4	43.6	14.1	4.9
NAP 004	-17.5	16.5	37.7	12.2	3.0
NAP 006	-17.8	15.7	43.8	14.2	4.7
NOP 022	-18.2	13.7	45.4	14.0	8.0
NOP 024	-17.6	14.3	45.8	14.4	8.3
NOP 026	-17.6	14.1	45.1	14.4	8.1
PCD 002	-17.0	15.5	43.3	13.8	1.0
PCD 004	-16.5	15.9	44.7	14.2	3.1
PCD 006	-16.8	16.4	47.0	14.9	1.6
VEE 002	-17.2	15.3	42.7	13.5	1.4
VEE 004	-16.2	17.0	42.9	13.6	1.1
VEE 006	-16.9	16.2	45.6	14.5	1.3
MUS22	-16.6	12.5	33.4	9.6	0.5
SHR 22	-16.0	13.4	32.8	10.0	2.0
SHR 24	-16.0	13.4	34.3	10.3	2.0
SHR 26	-15.9	13.5	39.6	11.9	2.2

Tab.3. stable isotope analysis data and carbon, nitrogen and lipid content in samples collected in the inner Oslo Fjord

4.1.2. Results cVMS Analysis

The data of the cVMS analyses are compiled in table 4 (outer Oslo Fjord) and 5 (inner Oslo Fjord).

	D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	D4/lipid (ng/g)	D5/lipid (ng/g)	D6/lipid (ng/g)
	Whole body homogenisate					
ACD 002	-0.2	17.1	1.7	-5	416	42
ACD 004	-0.2	0.7	0.3	-17	51	24
COA 002	1.0	24.4	3.7	15	373	56
COA 004	1.2	6.3	3.3	23	122	65
COA 006	-0.3	7.3	2.8	-8	195	75
CSE 002	2.6	28.6	2.6	33	365	34
CSE 004	3.6	41.6	4.3	55	630	65
CSE 006	2.5	16.1	1.7	94	598	63
EPE 002	2.3	26.8	3.4	133	1516	190
EPE 004	4.8	77.7	10.5	150	2435	329
HAD 002	-0.5	0.7	4.0	-11	15	91
HAD 004	0.0	4.9	9.1	0	119	220
HAD 006	0.3	1.4	1.4	10	45	43
HAD 008	0.3	5.1	4.6	6	114	102
HAD 10	1.3	1.1	2.3	44	38	80
HAD 012	0.1	4.9	2.4	10	330	160
LRD 002	0.8	7.5	0.5	23	225	16
LRD 004	-0.3	7.8	4.5	-15	370	212
LRD 006	-0.1	8.3	1.2	-6	333	48
NOP 002	1.6	18.5	1.8	31	348	33
NOP 004	1.2	24.1	2.4	18	364	36
NOP 006	0.0	10.2	2.8	-1	191	53
NOP 008	1.8	12.4	2.5	31	213	42
NOP 010	1.2	23.1	1.9	18	334	28
RAR 002	-0.2	28.4	0.7	-7	1026	26
RAR 004	1.9	46.4	1.9	69	1652	67
RAR 006	-0.1	8.0	1.0	-7	383	46
MUS 2	-0.3	4.4	1.5	-46	632	219
MUS 4	-0.3	4.1	1.1	-36	460	122
MUS 6	-0.3	4.4	1.0	-37	520	113
SHR 2	0.3	6.8	0.5	15	399	28
SHR 6	0.3	5.1	0.5	18	289	26
BRL	0.5	9.2	7.1	144	2872	2225

Tab.4. cVMS concentrations in biota (whole body) of biota collected in the outer Oslo Fjord

	D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	D4/lipid (ng/g)	D5/lipid (ng/g)	D6/lipid (ng/g)
	Whole body homogenisate					
ACD 022	0.8	20.1	1.5	48	1219	89
ACD 024	0.8	28.1	2.3	51	1792	149
ACD 026	1.7	45.8	2.2	108	2844	135
COA 022	17.3	193.9	20.6	652	7316	778
COA 024	7.8	44.0	12.9	406	2302	674
COA 025	15.5	231.3	22.1	643	9599	918
COA 026	11.4	62.3	15.9	1373	7508	1911
EHE 002	4.2	134.8	2.7	313	9983	199
EHE 004	2.2	119.0	1.7	139	7533	107
EPE 022	11.1	1120.4	36.8	242	24463	804
EPE 024	40.1	2271.6	28.7	661	37484	473
EPE 026	9.4	866.1	15.3	235	21761	385
EWG 002	0.7	56.1	1.5	100	7580	200
EWG 004	2.1	90.3	2.5	190	8284	231
EWG 006	2.0	66.2	1.1	208	6757	109
HAD 022	2.2	83.9	17.2	59	2238	457
HAD 024	4.8	215.0	31.7	107	4821	710
HER 002	5.1	327.5	7.0	54	3412	73
HER 004	19.6	2810.7	26.3	200	28681	269
HER 006	7.1	826.9	11.8	83	9637	138
LRD 022	6.7	213.5	14.6	757	24261	1662
LRD 024	5.2	179.1	4.5	133	4604	117
LRD 026	9.9	360.0	12.8	770	28122	998
NAP 002	30.1	3272.1	41.7	613	66642	849
NAP 004	4.7	472.4	19.4	156	15590	641
NAP 006	6.3	561.1	14.3	135	11964	304
NOP 022	28.2	591.8	13.7	351	7361	170
NOP 024	25.1	888.2	13.6	301	10650	163
NOP 026	24.4	805.6	15.6	300	9921	192
PCD 002	-0.3	14.0	8.2	-25	1347	788
PCD 004	2.5	53.3	4.1	80	1742	133
PCD 006	1.5	19.5	1.0	94	1202	59
VEE 002	2.3	72.8	3.0	165	5162	214
VEE 004	1.6	14.4	0.3	142	1263	27
VEE 006	1.2	18.7	1.4	92	1436	105
MUS 022	0.2	251.8	6.7	44	52458	1400
SHR 022	2.5	71.1	2.1	125	3487	101
SHR 024	2.9	98.0	2.2	144	4926	113
SHR 026	2.6	87.2	1.9	121	4001	86

Tab.5. cVMS concentrations in biota (whole body) of biota collected in the inner Oslo Fjord

4.2. Sediment Sample Screening

Because only small quantities of sediment were available, the analyses could be carried out only with samples of approximately 1 g, which is about five times less than we usually use for this kind of analyses. For the samples SED-005 and SED-015 there was not enough material at all left to do the analyses. According to the lower quantities analysed the detection limits in this case are expected to be higher than usually. They are expected in the 10 ng/g range (dry weight) for the cVMS.

Taking into account that only small quantities of the sediments were available for analysis, also some homogeneity issues should be considered. However, in this case of a more screening effort, the data show the big difference in cVMS concentrations in the inner and outer Oslo Fjord.

Study Area	Field/Lab Code	D4 (ng/g) /dw	D5 (ng/g) / dw	D6 (ng/g) /dw
Outer Oslo Fjord	SED-001 (0-1 cm)	1.71	19.94	16.73
Outer Oslo Fjord	SED-002 (1-2 cm)	-1.15	6.26	10.71
Outer Oslo Fjord	SED-005 (0-1 cm)			
Outer Oslo Fjord	SED-006 (1-2 cm)	-1.06	5.53	8.34
Outer Oslo Fjord	SED-009 (0-1 cm)	2.39	10.03	6.94
Outer Oslo Fjord	SED-010 (1-2 cm)	2.02	10.62	9.41
Inner Oslo Fjord	SED-015 (0-1 cm)			
Inner Oslo Fjord	SED-016 (1-2 cm)	3.84	230.88	42.28
Inner Oslo Fjord	SED-017 (0-1 cm)	4.55	670.91	111.49
Inner Oslo Fjord	SED-018 (1-2 cm)	5.07	674.57	111.45
Inner Oslo Fjord	SED-023 (0-1 cm)	3.24	633.13	103.96
Inner Oslo Fjord	SED-024 (1-2 cm)	2.98	489.74	77.80
Inner Oslo Fjord	SED-027 (0-1 cm)	0.86	351.74	107.10
Inner Oslo Fjord	SED-028 (1-2 cm)	2.32	357.03	107.55

Tab.6. cVMS concentrations in sediments collected in the outer and inner Oslo Fjord

5. Quality Control

5.1. Detection Limits and Limits of Quantification

Since in this study the expected concentrations in the fish were far above detection limits only repeated analysis of a blank cod and a blank shrimp sample and the observed data scatter was used to estimate the detection limits. Thus the derived detection limits are something in-between instrument detection limit (without using a matrix sample) and method detection limit (MDL), which would also include the sample preparation starting from a material containing 5-10 times of the respective cVMS detection limits). Experience shows that MDLs would be approximately twice as high as the LoDs determined here (table 7)

		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
Cod homogenisate	LoD	0.76	0.53	0.97
	LoQ (3*LoD)	2.28	1.60	2.92
	LoQ (5*LoD)	3.80	2.67	4.87
Shrimp homogenisate	LoD	1.65	1.34	1.35
	LoQ (3*LoD)	4.95	4.01	4.06
	LoQ (5*LoD)	8.25	6.69	6.76

Tab.7. Detection limits estimations for fish and shrimp

5.2. QC Samples

The concentrations analysed in the cod filets used for quality control purposes show that no contamination took place during the trawl (deployed in the net) or during processing of the catch on board of the ship (retained sample) in comparison to the original sample (field blank):.

QC set 1: used 12.11.08; outer Oslo fjord 3rd trawl

	sample		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
COD 1	QC 2	Deployed in the net	0.26	0.96	-0.28
	QC 4	field bank	0.22	1.04	-0.30
	QC 6	retained sample	0.04	0.63	-0.28

QC set 2: used 13.11.08; inner Oslo fjord 2rnd trawl

	sample		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
COD 2	QC 8	deployed in the net	-0.12	0.05	-0.41
	QC 10	field bank	-0.05	0.33	0.16
	QC 12	retained sample	0.12	0.28	0.00

QC set 3: used 13.11.08; inner Oslo fjord 3rd trawl

	sample		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
COD 3	QC 14	deployed in the net	-0.06	1.50	-0.05
	QC 16	field bank	0.33	2.57	0.11
	QC 18	retained sample	0.14	2.23	0.06

5.3. *Air Monitoring Samples*

Air samples taken during the trawls indicate that there is no contamination to be expected by contact of the samples with the air during the period until freezing:

	sample	sample	D4 (µg/m³)	D5 (µg/m³)	D6 (µg/m³)
OSLO 1 12.11.08	backmost deck	14:00-14:40	< 0.2	< 0.2	< 0.2
OSLO 2 12.11.08	wetlab	14:45-15:27	< 0.2	< 0.2	< 0.2
OSLO 3 13.11.08	wetlab	13:51-14:38	< 0.2	< 0.2	< 0.2
OSLO 4 13.11.08	backmost deck	14:41-15:39	< 0.2	< 0.2	< 0.2
OSLO 6 14.11.08	backmost deck	9:06-11:45	< 0.2	0.3	< 0.2

Study Title:	Contributing Scientist Report: Analytical results Cyclic Volatile Methylsiloxanes (cVMS) in biota and sediment obtained from Oslofjord, Norway
HES Study No:	11060-108
Test Substances:	Octamethylcyclotetrasiloxane (D_4) Decamethylcyclopentasiloxane (D_5) Dodecamethylcyclohexasiloxane (D_6)
Author:	Jeremy A. Durham David E. Powell
Study Personnel:	Jeremy A. Durham Darren W Huff
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Testing Facility:	Dow Corning Corporation Health & Environmental Sciences (HES) 2200 West Salzburg Road Auburn, MI 48611
HES Group Supervisor:	Debra A. McNett
Study Completion Date:	23 December 2009

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ABSTRACT

This report describes the quantitation of Cyclic Volatile Methylsiloxanes (cVMS) D_4, D_5 and D_6 in biota and sediment collected from the inner and outer Oslofjord in Norway. The samples received were collected in October - November 2008 through NIVA (Norwegian Institute for Water Research). Samples were shipped to Dow Corning on November 17th 2008 and were received on November 25th 2008 in a frozen state (except for sediment, zooplankton and benthic worms). Biota and fish samples were stored frozen and sediment samples stored refrigerated until analysis. The ng/g amounts of cVMS found in the samples varied widely from below limit of detection to a high of 1888 ng/g D_5 in a fish species. The limits of detection for biota samples analyzed using tetrahydrofuran solvent were 0.66, 1.98 and 1.11 ng for D_4, D_5 and D_6, respectively. The limits of detection for biota and sediment samples using hexane solvents were 0.08, 1.63, 0.47 ng for D_4, D_5 and D_6, respectively. The method detection limits determined for fish, mussel, sediment and shrimp were consistent with one another and ranged 0.21-0.41, 0.22-0.66, and 0.39-0.43 ng/g for D_4, D_5 and D_6, respectively.

SIGNATURES AND APPROVAL

This report consists of 40 pages with 1 figure, 14 tables, and 1 appendix. The undersigned have read and approved this report.

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23 December 2009
Date

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I. OBJECTIVE

In collaboration with NIVA (Norwegian Institute for Water Research) and Evonik Industries AG, a set of biota and sediment samples were collected as part of a food web study in Oslofjord, Norway and were analyzed for Cyclic Volatile Methylsiloxanes (cVMS) (D_4, D_5 and D_6).

II. TEST SYSTEM

The test systems for this study consisted of a variety environmental samples consisting of fish, mussels, shrimp, sea urchin, benthic worms, zooplankton, and sediment collected from Norway during October and November 2008.

III. REFERENCE ARTICLE INFORMATION

Reference article characterization was done in compliance with the EPA Toxic Substances Control Act (TSCA), Good Laboratory Practice Regulations (40CFR Part 792).

A. Reference Article 1

- Identification: Octamethylcyclotetrasiloxane (D_4)
- CAS Number: 556-67-2
- Lot Number: LL084732 (supplied as Dow Corning™ 244 Fluid)
- Expiration Date: June 17, 2011
- Purity: 99.77 % by GC-FID

B. Reference Article 2

- Identification: Decamethylcyclopentasiloxane (D_5)
- CAS Number: 541-02-6
- Lot Number: 0000341832 (supplied as Dow Corning™ 1693 Fluid)
- Expiration Date: December 31, 2010
- Purity: 99.16 % by GC-FID

C. Reference Article 3

- Identification: Dodecamethylcyclohexasiloxane (D_6)
- CAS Number: 540-97-6
- Lot Number: LL114030(supplied as Dow Corning™ 246 Fluid)
- Expiration Date: June 8, 2009
- Purity: 99.54 % by GC-FID

IV. SAMPLE PROCESSING AND ANALYSIS

The environmental samples were shipped to Dow Corning in frozen condition from NIVA on November 17, 2008. The biota samples were received on November 25, 2008 in a frozen condition (except for sediment, benthic and zooplankton samples) and stored frozen upon receipt at –20±10° C. The sediment

samples were stored refrigerated at 5±4° C. A list of the types and number of samples received from Norway is shown in **Table 1**.

The processing of samples varied depending on matrix. Care was taken during the processing to limit laboratory contamination. Individuals working with samples were not allowed to apply any personal care products known to contain siloxanes on the days samples were processed.

Fish samples were removed from frozen storage and placed in a refrigerator the morning of processing. Before processing, the fish were measured for fresh weight and total length and a small piece of skin-free dorsal muscle (about 3 g) was removed from behind the pectoral fin above the lateral line for analysis of stable isotope signatures. The partially frozen fish samples were prepared by cutting up whole, individual fish into small sections using stainless steel knives, with the cut sections being passed three times through a Hobart model 4822 meat grinder having a 13-mm cutting plate. The ground fish was collected into a stainless steel bowl and mixed by hand using a stainless steel spoon after each pass through the grinder. The ground fish was then homogenized by passing through the grinder a fourth time using a 3.2-mm cutting plate.

An alternative hand grinder was used for fish weighing approximately 100 grams or less as well as for the on board field controls. The hand grinder was Universal model 400 meat and food chopper having a 4-mm cutting plate. The thawed samples were passed two-three times through the hand meat grinder. The ground sample was collected into a stainless steel bowl and mixed by hand using a stainless steel spoon after each pass through the grinder.

Aliquots of the homogenates were removed and placed into pre-weighed glass containers for immediate extraction. An additional small quantity (about 3 g) of the homogenized sample was removed for analysis of lipid content. The remaining whole-body fish homogenate was then transferred, depending on size of fish, to a 0.1 to 4-L glass jar with Teflon-lined lid for frozen storage at -20°C.

A composite of shrimp was removed from frozen storage and immediately passed four times through the Hobart grinder with 13-mm cutting plate. The composite consisted of 300- 400 grams of shrimp. The ground shrimp was collected into a stainless steel bowl and mixed by hand using a stainless steel spoon after each pass through the grinder. The ground shrimp homogenate was then transferred to an appropriate size glass jar with Teflon-lined lid for frozen storage at -20°C. Prior to storage, aliquots were removed and placed into pre-weighed glass containers for immediate extraction.

Mussel samples were removed from frozen storage and immediately opened with a scalpel and the entire inside contents removed. In order to have sufficient sample for analysis, a composite was made with several samples n = (2-10), depending on size of mussel and availability. The composite was homogenized with stainless steel scissors. The homogenized mussel was then transferred to an appropriate size glass jar with Teflon-lined lid for frozen storage at -20°C. Prior to storage, aliquots were removed and placed into pre-weighed glass containers for immediate extraction.

Sea urchin samples were removed from frozen storage and immediately opened with a scalpel and the entire inside contents removed and placed into pre-weighed glass containers for immediate extraction.

Zooplankton and benthic worm samples were removed from frozen storage and allowed to come to refrigerated temperature. The samples were mixed with a stainless steel spatula and aliquots were removed and placed into pre-weighed glass containers for immediate extraction. The zooplankton and worm samples were processed and analyzed even though during shipping it appears that significant

degradation of the zooplankton and worms occurred as the package containing the samples did not remain in a refrigerated state during shipping. The collection container was placed back into frozen storage at -20°C.

Sediment samples were removed from refrigerated storage and mixed thoroughly; aliquots were removed and placed into pre-weighed glass containers for immediate cVMS extraction. Two additional samples were prepared by combining a portion of each (n = 6) inner Oslofjord sample to form a composite samples as well as combining a portion of each (n = 8) outer Oslofjord sample to form an additional composite that could be used for MDL determinations. Additional sub-samples were collected for characterization analyses: sediment samples to be analyzed for water, total organic carbon, and organic matter content were weighed into containers with screw-cap lids. Sediment samples to be analyzed for water and organic matter content were shipped under blue ice from Dow Corning to the University of Minnesota on April 29th 2009. Samples were received in good condition at the University of Minnesota on May 4th 2009, and placed into refrigerated storage at about 4°C in the dark until processed for analysis. The original collection container was placed back into refrigerated storage.

The analysis of fish, mussel, shrimp and sea urchin was based upon the principle of calibrating a gas chromatograph-mass spectrometry with mass selective detection (GC-MS) using solvent standards of tetrahydrofuran (THF) spiked with various concentrations of D_4, D_5, and D_6 and ^{13}C-D_4, ^{13}C-D_5 and ^{13}C-D_6 as internal standards, and then analyzing THF extracts of the homogenates against the calibration curves. Extractions were performed by using 2:1 solvent to sample ratio of THF containing the internal standards. After addition of a weighed amount of THF containing internal standard the samples were vortex mixed for 30 minutes using a bed vortex mixer set on high. The samples were then centrifuged for 5 minutes at a setting of 2000 revolutions per minute. The extract from each sample was transferred to a separate vial. A second extraction was performed using THF without internal standard. The sample was vortex mixed for 30 minutes and centrifuged for 5 minutes. The extract from each sample was transferred to the vial containing the first extract and dried using $MgSO_4$ (~ 250 mg).

The analysis of sediment was based upon the principle of calibrating a GC-MS using solvent standards of hexane spiked with various concentrations of D_4, D_5, and D_6 and ^{13}C-D_4, ^{13}C-D_5 and ^{13}C-D_6 as internal standards, and then analyzing hexane extracts of the homogenates against the calibration curves. For extraction of cVMS materials from sediment, a 6-g sub-sample of wet sediment was weighed into a single-use borosilicate glass vial, followed by addition of 6 mL of acetonitrile. After brief manual agitation, 12 mL of hexanes was added to the vial. For extraction of cVMS materials from zooplankton and worms a portion of sample was weighed into a glass vial, followed by the addition of 12 mL of hexanes was added to the vial. The hexanes solvent contained known concentrations of isotopically labeled ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6 to serve as internal standard surrogates. The vial with sample was re-weighed after each solvent addition so that accurate internal standard amounts could be determined. Capped vials were placed on a vortex mixer for 30 min, followed by brief centrifugation to facilitate separation of the phases. The upper hexane layer was removed to a round-bottom glass tube containing anhydrous magnesium sulfate (ca. 0.25 g) for drying the extract. A second portion of hexanes without the internal standards was added to the extraction vial. The extraction process was repeated and the hexanes were combined in the glass tube. The extract volume in each tube, for sediment only, was reduced in volume to approximately 1-2 mL under a stream of high purity nitrogen in a 25 °C bath. A portion of the resulting concentrated extract was transferred to a crimp-cap vial for GC-MS analysis

The amounts of cVMS materials in each extract were determined from the resulting $1/(\text{peak area})^2$-weighted linear regression calibration functions. The linearity parameters; y – intercepts, slopes, and correlation coefficients, were determined for each of the standard curves. The solvent standard

concentration ranges validated were approximately 0.2 to 1200 ng/g for D_4, D_5 and D_6 in THF and approximately 5 to 11,000 ng/g for D_4, D_5 and D_6 in hexane. The minimum acceptance criterion for the linearity of a standard curve was a regression coefficient (R^2) of 0.99.

Peak responses from the GC-MS system were quantitated by automatic electronic integration either by using integration parameters in the software or by drawing a baseline manually using the software utility for the peak. If the baselines were drawn manually, this was indicated on the chromatogram printout. Calibration curves were determined from linear regression analysis of the data using Microsoft Excel Version 9 and Sigma Plot 2001.

A. Characterization of Sediments

Sediment composition and characterization analyses were determined by the Limnological Research Center at the University of Minnesota in Minneapolis. Small aliquots (about 1 g) of each sediment sample were weighed into individual glass containers and shipped under blue ice from Dow Corning to the University of Minnesota on April 29th 2009. Samples were received in good condition at the University of Minnesota on May 5th 2009, and placed into refrigerated storage at about 4°C in the dark until processed for analysis. Sediment samples (sediment core strata and surface sediment samples) were analyzed by *carbon coulometry* (total carbon, total inorganic carbon, and total organic carbon) and *loss-on-ignition* (total water content and total organic matter content).

Carbon Coulometry Analyses: Organic carbon and carbonate mineral content were determined on freeze-dried and ground samples by coulometric titration (Engleman *et al.* 1985), using a UIC model 5011 CO_2 coulometer. Results were obtained as total carbon (%TC) and total inorganic carbon (%TIC); with total organic carbon (%TOC) calculated by difference.

Loss-on-Ignition Analyses: A small quantity (about 3 cm^3) of sediment from each sample was used to determine sediment composition by analysis of weight loss on ignition if the sample (Heiri *et al.* 2001). The entire sediment sample was vigorously stirred until homogenized, then sub-sampled with a spatula into a pre-weighed ceramic crucible and weighed again. Samples were oven-dried at 100°C overnight, cooled completely, and weighed to determine water content. Samples were then ignited in a muffle furnace at 550°C for four hours, cooled, and weighed to determine organic matter content. Samples were finally burned at 1000°C for two hours, cooled, and weighed to determine $CaCO_3$ content. The sample mass remaining after the 1000°C burn was considered the "inorganic" content, i.e., silicate minerals, oxides, and silicate algal (diatom) remains.

B. Characterization of Biota

Biological samples were analyzed for water content, lipid content and for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) by the Biogeochemistry and Paleoproteomics Laboratory at Michigan State University in East Lansing. Isotopic signatures were determined on skin-free dorsal muscle (fish) or whole-body homogenate (zooplankton and macroinvertebrates). Water and lipid contents of all samples were determined on the whole-body homogenates. Small aliquots (about 3 g) of each sample were weighed into individual glass containers and were transported by car in a cooler containing blue ice from Dow Corning to Michigan State University. Upon arrival samples were immediately placed into refrigerated storage at about 4°C in the dark until processed for analysis.

Water and lipid content: Water and lipid contents were determined on whole-body homogenates of individual fish and homogenized composite samples of zooplankton and macroinvertebrates. Water content was determined as weight loss during lyophilization to a constant weight. The remaining lyophilized material was then extracted with chloroform:methanol (87:13) and lipid content determined gravimetrically and expressed on both dry and wet weight basis. The precision (± standard deviation) for this technique, based on replicate analyses of a laboratory standard (rainbow trout, *Oncorhynchus mykiss*), was 0.2 % for water content and 1.25% for lipid content.

Stable isotope analysis: Isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) of the zooplankton and macroinvertebrates were determined on whole-body homogenates of composite samples. Isotopic signatures of the fish were determined on skinless dorsal muscle tissue that was collected from posterior to the pectoral fin above the lateral line of each individual specimen. Samples were lyophilized to a constant weight, extracted with chloroform:methanol (87:13) to remove the lipids, dried in a vacuum oven, and homogenized to a fine powder with a mechanical mill. Samples (about 1.0 mg in tin capsules) were then combusted with O_2 and Cr_2O_2 at about 1030°C in an elemental analyzer (Eurovector). NOx products were reduced with Cu at 650°C. The combustion products N_2, CO_2, and H_2O were separated on a packed column and the $^{15}N/^{14}N$ or $^{13}C/^{12}C$ isotopic ratios determined using an interfaced isotope ratio mass spectrometer (Elementar Americas, Inc). Stable isotope abundances were expressed in per mil notation (δ) as the deviation from standards in parts per thousand (‰) according to the equation:

$$\delta X = \left[\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right] \times 1000$$

where X was ^{15}N or ^{13}C and R was the abundance ratio of the heavy to light isotope (i.e., $^{15}N/^{14}N$ or $^{13}C/^{12}C$) in the sample (R_{sample}) and the standard ($R_{standard}$). The $R_{standard}$ values were based on atmospheric nitrogen gas for ^{15}N and PeeDee Belemnite (PDB) for ^{13}C. The precision (± standard deviation) for this technique, based on replicate analyses of laboratory standard (Atlantic salmon; *Salmo salar*), was ≤ 0.2 ‰ for ^{15}N and ^{13}C.

V. QUALITY CONTROL

Rainbow trout control fish were obtained from Rainbow Ranch Trout Farm in Tawas City, Michigan USA. The control fish was transferred to Dow Corning and stored frozen -80 °C until time of analysis. The control trout was removed from frozen storage and placed in a refrigerator the morning of processing. The control fish was then processed in the same manner as study samples. This homogenate was used as control tissue to evaluate matrix effects and check for possible contamination during the processing of fish study samples.

Reference fish (rainbow trout obtained from Rainbow Ranch Trout Farm in Tawas City, Michigan USA) were dosed with D_4, D_5 and D_6, at Dow Corning, this dosing was completed under (Durham). The fish was sacrificed and stored frozen -80 °C until time of analysis. The reference trout was removed from frozen storage and placed in a refrigerator the morning of processing. The reference fish was then processed in the same manner as samples. This reference sample was used to evaluate loss as well as storage stability of homogenates stored at -20 °C.

Shrimp were obtained from a local grocery store. The shrimp were stored frozen at -20 °C until time of analysis. A composite of control shrimp (~400 grams) was created by homogenizing the shrimp by passing through a Hobart grinder three times using a 13-mm cutting plate. This homogenate was used as control tissue to evaluate matrix effects during the processing of shrimp study samples.

Blue mussels were obtained from a local grocery store. The mussels were stored frozen at -20 °C until time of analysis. A composite of control mussels was created by cutting the shucked mussels into pieces with a stainless steel scissors to form a homogenate. This control sample was used as laboratory control matrix to evaluate matrix effects during the processing of mussel study samples.

Sediment was obtained from Sanford Lake, Michigan USA. Blank sediment along with reference sediment spiked with D_4, D_5 and D_6 were prepared and processed in the same manner as study samples. These samples were used to evaluate matrix effects during the processing of sediment study samples.

Procedural solvent blanks were completed for every analysis day to determine day to day variability that occurs from the instrument, extraction process as well as laboratory contamination.

On board field controls were prepared and implemented in the sampling process, in order to evaluate potential contaminations from the trawling or the sample handling. Three Atlantic cod fish caught at the first day of trawl in the outer Oslofjord were filleted. The fillets of each cod were split into six subsamples. Two of them used as "pure blank", two of them were deployed in the net during trawl catching and two of them were retained on the boat and added to the catch in the collection bucket after trawling as well as any surface the fish touched prior to being placed in storage bags. The procedure was applied at three different turns resulting in 18 different quality control blanks which were separated into two groups of nine samples for the two laboratories conducting cVMS analysis.

Air monitoring quality controls were prepared in order to check a potential contamination of the samples by air-transported cVMS. Five air samples were collected at the two days of trawling. Charcoal tube samples were analyzed according to Dow Corning internal air monitoring methods for D_4, D_5, and D_6. Charcoal tubes sections were extracted in 2 mL of carbon disulfide, and the vials were capped and shaken on a mechanical shaker for 30 minutes. Aliquots of the extracts were analyzed by GC/FID, along with analytical calibration standards and sorbent-based quality control samples.

Extractions of procedural solvent blanks, matrix spikes, matrix controls, field controls, study sample replicates as well as spike addition to samples were processed the same way as samples for a particular set of analysis. In this manner, an assessment of accuracy could be made, and the limit of detection (LOD) and method detection limits (MDL) could be determined. These aspects of the method that were assessed can be collectively referred to as figures of merit. The target analytical concentration for the biota matrix spikes was ~80 ng D_4, D_5 and D_6 and ~133 ng D_4, D_5 and D_6 for the sediment. The spike additions were completed by spiking a known amount by volume using a gas-tight syringe into the solvent layer prior to the first 30 minute vortex. This method was developed based on the methodology developed for the extraction and analysis of D_4 from biological samples (Varaprath *et al.* 1998; and Varaprath *et al.* 2000).

Peak responses from the GC-MS system were quantitated by automatic electronic integration either by using integration parameters in the software or by drawing a baseline manually in the software for the peak. If the baselines were drawn manually, this was indicated on the chromatogram printout in the study file. Calibration curves were determined from linear regression analysis of the data using Microsoft Excel Version 9 and Sigma Plot 2001.

VI. UNITS OF MEASURE

For field monitoring, a measurement that is less than a specified detection level (DL) may be: 1) reported as "below detection", 2) reported as zero, 3) reported as less than (<) the value of the DL, 4) reported as some value between zero and the DL, for example one-half the DL, or 5) reported as the actual value (positive or negative), whether or not it is below the DL. The last option, the reporting of the actual value, is the recommended procedure (Clarke 1998; Frome and Wambach 2005; Antweiler and Taylor 2008); otherwise the data is considered to be "censored". For this project, measured concentrations that were less than the MDL or LOD were reported as the measured concentration (i.e., uncensored value).

Concentrations of D_4, D_5, and D_6 in biota and sediment were measured in wet samples and expressed on the basis of wet weight. Concentrations of D_4, D_5, and D_6 that are 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 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 D_4, D_5, and D_6 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.

VII. DETERMINATION OF LIMITS OF DETECTION AND METHOD DETECTION LIMIT

Detection Levels:
For the purpose of this study, detection levels as defined by APHA (1999) were used since they were frequently identified in the field monitoring literature. Although the terminology may differ from that provided in more definitive sources (ASTM 2003; IUPAC 1995, 2002) the definitions are analogous. Methods for determining detection levels are available in various publications (Analytical Methods Committee 1987; Taylor 1987; Kateman and Buydens 1993; IUPAC 1995; Berger et al. 1996; Smith 1997; Eurachem 1998; APHA 1999; IUPAC 2002). Of the different detection levels that are defined, the limit of detection (LOD) and the method detection level (MDL) are the most valuable for field monitoring. The LOD and MDL are similar in concept to the signal-to-noise ratio, and were defined as:

- LOD: The minimum level of target analyte that can be measured and reported with 99% confidence that the level of analyte is greater than zero. The LOD is based on the ability to distinguish between signal and noise of the instrument and is determined by repetitive analysis of matrix-free blanks.

- MDL: The minimum level of target analyte in a specified matrix that can be measured and reported with 99% confidence that the level of analyte in the matrix is greater than zero. The MDL is a measure of a methods ability to quantify an analyte in a sample matrix and is determined by repetitive analysis of a sample matrix having a small, but measurable amount of analyte (2-5 times the MDL). The MDL will be greater than the LOD because of additional background noise resulting from the sample matrix and variability introduced through processing the sample for analysis.

Detection limits (DL) were determined as a function of the variance associated with replicate analyses of matrix-free blanks (LOD) and replicate analyses of samples containing a small, but measurable amount of cVMS materials (MDL). The DL (LOD or MDL) at 99% confidence were then defined as:

$$DL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses.

For this study, the LOD was calculated using non-background corrected amounts of D_4, D_5, and D_6 measured in reagent blanks that were carried through the entire analytical procedure. The MDL was calculated using non-background corrected amounts and concentrations of D_4, D_5, and D_6 measured in replicate samples. A highly variable instrumental blank response that could be minimized, but not eliminated or stabilized, was always present for D_4, D_5, and D_6, which made determination of levels of detection and quantification of the cVMS materials difficult in most samples. Comparison of analytical results for the THF reagent blanks (n=40 blanks analyzed across 9 separate days) indicated highly significant differences (ANOVA; $p < 0.01$) for D_4, D_5 and D_6 between analytical batches of samples. Therefore, the overall LOD during the analysis of biological samples was calculated using the pooled standard deviation across analysis date for all THF reagent blanks. In contrast to the biological samples, the sediment samples were processed and analyzed as a single batch of samples. Hence, the overall LOD during the analysis of sediment samples was calculated using the sample standard deviation for all hexane reagent blanks.

Background Correction:
Measured amounts of cVMS materials in the samples were corrected for background levels of cVMS on a daily basis, using results from the reagent blanks. Results for the reagent blanks represented background levels of cVMS materials associated with extraction solvents or lab ware, as well as contamination incurred during handling, treatment (e.g. volume reduction), and analysis of the extracts. Because of the variable background, measured amounts of cVMS materials in the samples were corrected for background levels of cVMS using results from reagent blanks that were analyzed on the day that samples were analyzed. Supporting information for Limits of Detection and Method Detection Limits is attached in **Appendix 1**.

VIII. RESULTS AND DISCUSSION

A. Study Samples

The ng/g amounts of D_4, D_5 and D_6 found for the environmental samples are presented in **Table 2-4**. The limit of detection for fish, shrimp, sea urchin and mussel samples (THF extracts) were determined to be 0.66 ng D_4, 1.98 ng D_5 and 1.13 ng D_6. The limit of detection for sediment, zooplankton, and worm samples (Hexane extracts) were determined to be 0.08 ng D_4, 1.63 ng D_5 and 0.47 ng D_6. These limits of detection were determined on solvent blanks summarized in **Table 5**. Method detection limit (MDL) was determined by replicate analysis for fish, mussel, sediment and shrimp. The MDL ranged from 0.21-0.41 ng/g-wet-weight (ww) D_4, 0.22-0.66 ng/g-ww D_5, and 0.39-0.43 ng/g-ww D_6 and is presented in **Table 5**

B. Quality control

Quality control (QC) samples were prepared and analyzed in conjunction with the samples. The QC samples included solvent blanks, control matrix, and spike addition to control matrix and field collected samples. The nominal spike level and the results for quantifying D_4, D_5 and D_6 are presented in **Table 6-8**. A single spike concentration level was prepared and used to spike triplicate samples. The amount spiked into the control tissue or field sample was approximately 80ng for biota samples and approximately 130 ng for sediment samples. Additionally a sample of spiked control sediment, at a concentration of approximately 65 ng/g was analyzed. This sample was spiked directly into the

sediment water slurry and was stored since preparation in May 2008 under the same conditions as the field collected samples. While the spiked sample was stored for a longer time than the samples it should be noted that the recovery is much lower than the spike additions at time of analysis. This is unlike the storage of biota samples stored frozen at -20°C where no loss appears to be occurring as indicated with method development (Durham) as well as the reference samples that were carried throughout the analysis and are summarized in **Table 9**. The method produced acceptable accuracies for all of the samples. The concentrations analysed in the field control cod fillets used for quality control purposes show that no contamination took place during the trawl (deployed in the net) or during processing of the catch on board of the ship (retained sample) in comparison to the original sample (field blank) and are summarized in **Table 10**. Air samples taken during the trawls indicate that there is no contamination to be expected by contact of the samples with the air during the period until freezing as summarized in **Table 11**. An example of the solvent standard accuracy and standard curves obtained from the analysis are presented in **Table 12** and **Figure 1**, respectively. The solvent standards were separated into two ranges for D_4, D_5 and D_6 in order to accommodate a wide range of concentrations. In all cases, the correlation coefficient (R^2) value was greater than 0.99. The GC-MS conditions are listed in **Table 13**.

C. Sediment and Biota Characteristics

A summary of the sediment characteristics collected in the Oslofjord is contained in **Table 14**. In addition to individual samples analyzed, a composite of outer Oslofjord (Sample numbers 3-12) and inner Oslofjord (Sample numbers 13-26) were also analyzed. A summary of the biota characteristics (lipid and Stable Isotope data) from the biota collected in the Oslofjord is summarized within the sample data table.

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TABLES

Table 1. Organization of Test Samples

Location	Matrix Type	Abbreviation	Collection Date	Number of Samples
Outer Oslofjord	Atlantic Cod	ACD	11/12/2008	5
Inner Oslofjord	Atlantic Cod	ACD	11/13/2008	3
Outer Oslofjord	Coal Fish	COA	11/12/2008	3
Inner Oslofjord	Coal Fish	COA	11/13/2008	2
Outer Oslofjord	European Plaice	EPE	11/12/2008	3
Inner Oslofjord	European Plaice	EPE	11/13/2008	3
Outer Oslofjord	Haddock	HAD	11/12/2008	6
Inner Oslofjord	Haddock	HAD	11/13/2008	2
Outer Oslofjord	Long Rough Dab	LRD	11/12/2008	3
Inner Oslofjord	Long Rough Dab	LRD	11/13/2008	3
Outer Oslofjord	Norway Pout	NOP	11/12/2008	5
Inner Oslofjord	Norway Pout	NOP	11/13/2008	3
Inner Oslofjord	European Hake	EHE	11/13/2008	2
Inner Oslofjord	European Whiting	EWE	11/13/2008	3
Inner Oslofjord	Atlantic Herring	HER	11/13/2008	3
Inner Oslofjord	North Atlantic Pollock	NAP	11/13/2008	3
Inner Oslofjord	Poor Cod	PCD	11/13/2008	3
Inner Oslofjord	Vahls ellpout	VEE	11/13/2008	3
Outer Oslofjord	Sediment	SED	11/12/2008	6
Inner Oslofjord	Sediment	SED	11/13/2008	2
Inner Oslofjord	Sediment	SED	11/14/2008	6
Outer Oslofjord	Shrimp	SHR	11/12/2008	4
Inner Oslofjord	Shrimp	SHR	11/13/2008	3
Outer Oslofjord	Mussel	MUS-sp-a	11/12/2008	3
Inner Oslofjord	Mussel	MUS-sp-a	11/13/2008	1
Inner Oslofjord	Mussel	MUS-sp-b	11/13/2008	2
Inner Oslofjord	Mussel	BMU	10/1/2008	5
Outer Oslofjord	Zooplankton	ZOO	11/12/2008	2
Inner Oslofjord	Zooplankton	ZOO	11/14/2008	2
Outer Oslofjord	Worms	BEN	11/12/2008	1
Inner Oslofjord	Worms	BEN	11/14/2008	1
Outer Oslofjord	Sea Urchin	BRL	11/12/2008	2

Table 2. Summary of D_4, D_5 and D_6 concentrations, lipid content and stable isotope analysis of biota samples collected from outer Oslofjord

ID (Abbreviation)	Weight (g)	% Water	% Lipid d/w	% Lipid w/w	Bkg-Corr cVMS Concentration (ww) D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	Lipid Normalized Concentration D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	$\delta^{15}N$	$\delta^{13}C$
ACD-003	5.7854	79.36%	17.60%	3.63%	0.87	35.64	1.24	24	981	34	16.85	-17.73
ACD-005	5.4459	80.15%	9.36%	1.86%	0.19 b	2.69	0.73	10	145	39	17.60	-17.44
ACD-006	5.7345	81.35%	7.18%	1.34%	0.29 b	2.94	0.71	22	220	53	17.17	-17.85
ACD-007	5.6195	78.36%	16.32%	3.53%	0.45	9.97	1.92	13	282	54	17.23	-17.87
COA-001	5.4557	73.42%	24.78%	6.59%	0.73	10.62	2.04	11	161	31	15.50	-19.06
COA-003	5.1962	78.40%	15.74%	3.40%	0.22 b	1.18	1.12	6	35	33	14.22	-19.01
COA-005	5.5218	74.16%	23.18%	5.98%	1.85	8.71	3.59	31	146	60	15.69	-19.11
EPE-001	5.4147	79.12%	13.33%	2.78%	3.94	88.00	9.67	141	3161	347	13.59	-16.87
EPE-003	5.4368	78.31%	19.57%	4.24%	3.79	39.43	7.61	89	929	179	14.27	-17.37
EPE-005	5.7888	85.00%	6.30%	0.94%	1.33	13.01	6.40	141	1378	678	15.15	-16.31
HAD-001	5.4062	76.35%	17.36%	4.10%	0.59	6.00	3.61	14	146	88	16.16	-17.85
HAD-003	5.5411	76.94%	21.14%	4.88%	0.56	9.22	9.04	11	189	185	16.34	-17.24
HAD-005	5.3335	74.99%	18.63%	4.66%	1.04	16.98	5.53	22	364	119	14.88	-18.36
HAD-007	5.2930	77.26%	18.93%	4.30%	0.38	2.72	4.78	9	63	111	15.28	-17.95
HAD-009	5.4691	79.92%	10.36%	2.08%	0.37 b	4.19	3.16	18	201	152	15.38	-18.00
HAD-011	5.3239	79.47%	10.45%	2.15%	0.34 b	5.82	4.47	16	271	208	15.15	-17.75
LRD-001	5.3023	80.92%	10.30%	1.97%	0.61	4.94	1.29	31	252	65	15.93	-17.70
LRD-003	5.1671	79.50%	12.87%	2.64%	0.94	5.89	1.34	36	223	51	14.42	-17.78
LRD-005	5.4098	81.20%	12.63%	2.37%	1.45	12.08	2.41	61	509	101	16.25	-16.95
NOP-001	4.9990	72.73%	30.05%	8.20%	1.59	28.83	3.05	19	352	37	14.50	-18.34
NOP-003	4.3546	74.27%	20.92%	5.38%	1.26	17.02	2.71	23	316	50	16.47	-17.96
NOP-005	5.2424	68.19%	44.43%	14.13%	2.54	45.34	3.21	18	321	23	15.05	-18.30
NOP-007	5.0198	70.57%	36.59%	10.77%	1.65	31.67	2.81	15	294	26	14.86	-18.69
NOP-009	5.7427	72.25%	28.20%	7.82%	1.14	12.33	1.98	15	158	25	15.46	-17.82
MUS-001 (sp A)	3.5369	85.79%	10.92%	1.55%	0.20 b	14.42	4.51	13	929	290	12.75	-16.65
MUS-003 (sp A)	2.4394	86.47%	9.29%	1.26%	0.21 b	14.05	4.16	17	1118	332	12.96	-16.46
MUS-005 (sp A)	3.3815	88.81%	11.69%	1.33%	0.11 b	13.85	3.94	9	1041	296	13.28	-16.64
SHR-001	5.3814	74.93%	17.73%	4.44%	0.31	40.83	1.34	7	919	30	12.63	-15.85
SHR-003	5.5688	77.09%	17.06%	3.91%	0.24	27.40	1.24	6	701	32	12.69	-15.97
SHR-004	5.3119	76.52%	15.91%	3.74%	0.26	13.58	1.08	7	363	29	12.46	-16.24
SHR-005	5.0778	76.32%	17.95%	4.25%	0.28	12.74	1.14	7	300	27	13.16	-16.13
BRL-001	5.3561	Insufficient Sample			0.42	13.12	8.88		Insufficient Sample			
BRL-003	4.2453	Insufficient Sample			0.60	17.62	14.30		Insufficient Sample			
BEN-01	1.4740	Insufficient Sample			0.28 b	4.01	1.30		Insufficient Sample			
ZOO-01	6.2084	96.97%	19.06%	0.58%	0.02 b	0.38	0.07 a	3	65	13	*too low*	-17.79
ZOO-02	5.9931	93.98%	18.08%	1.09%	0.17	10.10	0.60	15	928	55	*too low*	-18.56

a) less than LOD
b) less than MDL

Table 3. Summary of D_4, D_5 and D_6 concentrations, lipid content, and stable isotope analysis of biota samples collected from inner Oslofjord

ID (Abbreviation)	Weight (g)	% Water	% Lipid d/w	% Lipid w/w	Bkg-Corr cVMS Concentration (ww) D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	Lipid Normalized Concentration D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	$\delta^{15}N$	$\delta^{13}C$
ACD-021	5.5456	79.20%	14.92%	3.10%	3.81	66.47	5.67	123	2142	183	16.81	-16.65
ACD-023	5.3704	80.37%	13.71%	2.69%	2.59	57.46	3.52	96	2135	131	15.94	-17.01
ACD-025	5.3115	76.75%	15.22%	3.23%	5.58	152.35	9.92	173	4711	307	17.51	-17.05
COA-021	5.7775	79.40%	11.23%	2.31%	8.94	84.27	16.42	387	3643	796	14.26	-19.19
COA-023	5.6178	79.27%	10.66%	2.21%	9.76	71.22	22.02	442	3222	996	14.54	-18.48
EHE-001	5.4799	80.11%	17.05%	3.39%	8.40	1631.65	26.62	248	48129	785	15.15	-17.62
EHE-003	5.6016	80.95%	17.41%	3.32%	12.82	1250.12	20.62	387	37684	622	14.59	-17.90
EPE-021	5.4130	78.07%	19.25%	4.22%	12.12	859.52	17.38	287	20362	412	14.19	-17.83
EPE-023	5.5638	76.62%	19.32%	4.52%	20.57	1607.40	34.88	455	35595	772	13.58	-17.16
EPE-025	5.3661	75.33%	26.25%	6.48%	39.16	1887.52	26.49	605	29149	409	14.14	-18.02
EWG-001	5.3767	82.91%	7.80%	1.33%	2.27	80.82	2.06	171	6063	155	16.22	-17.60
EWG-003	5.2600	82.35%	9.37%	1.65%	2.99	165.34	2.66	181	9996	161	16.87	-17.64
EWG-005	5.3734	82.08%	9.36%	1.68%	3.49	66.23	4.28	208	3951	255	16.10	-17.60
HAD-021	5.4287	76.93%	23.20%	5.35%	5.17	222.31	23.54	97	4153	440	15.06	-18.37
HAD-023	5.5334	76.35%	21.81%	5.16%	4.73	335.46	17.67	92	6504	343	16.68	-17.29
HER-001	5.2215	73.52%	32.98%	8.73%	8.96	1731.77	27.88	103	19831	319	13.26	-19.24
HER-003	5.6361	73.44%	30.63%	8.14%	12.86	1248.21	20.38	158	15343	251	13.36	-18.89
HER-005	5.4880	73.85%	31.15%	8.15%	7.53	1498.83	18.61	93	18401	228	13.24	-19.55
LRD-021	5.2919	79.92%	14.40%	2.89%	11.54	329.13	8.69	399	11363	300	16.71	-17.43
LRD-023	5.2907	78.27%	15.84%	3.44%	15.92	522.25	15.23	462	15165	442	16.76	-17.39
LRD-025	5.1175	81.23%	10.78%	2.02%	23.98	714.06	25.21	1185	35302	1246	16.13	-17.20
NAP-001	5.7714	77.23%	19.34%	4.40%	19.06	1857.80	42.98	433	42201	976	16.23	-17.85
NAP-003	5.4973	80.41%	11.55%	2.26%	3.46	98.30	4.60	153	4343	203	17.34	-17.24
NAP-005	5.8208	77.84%	19.59%	4.34%	7.70	690.18	20.90	177	15894	481	16.00	-17.58
NOP-021	5.2683	72.08%	34.42%	9.61%	32.04	564.32	18.46	333	5873	192	14.81	-18.25
NOP-023	5.7050	71.17%	38.50%	11.10%	31.70	1215.55	20.60	286	10952	186	15.05	-17.91
NOP-025	5.1684	75.74%	32.03%	7.77%	19.25	194.52	10.38	248	2503	134	14.70	-18.07
PCD-001	5.6083	77.15%	21.18%	4.84%	2.79	105.71	4.93	58	2184	102	16.57	-16.98
PCD-003	5.5937	78.60%	17.99%	3.85%	2.07	47.92	3.67	54	1245	95	16.56	-17.75
PCD-005	5.6872	81.14%	10.59%	2.00%	1.40	20.19	1.60	70	1010	90	16.33	-17.13
VEE-001	5.6579	83.28%	5.72%	0.96%	1.88	34.08	3.53	197	3563	369	16.97	-16.94
VEE-003	5.4976	82.24%	3.53%	0.63%	1.34	23.65	3.51	214	3767	560	15.88	-17.34
VEE-005	5.5173	81.97%	4.13%	0.74%	1.76	28.34	6.67	237	3535	895	15.71	-17.69
BMU-301	3.7895	88.84%	10.88%	1.21%	1.24	199.88	4.17	102	16457	343	8.22	-18.26
BMU-304	3.1509	91.08%	6.92%	0.62%	0.12 a	41.20	0.65	20	6672	104	8.06	-17.84
BMU-306	3.4549	92.75%	9.88%	0.72%	0.11 a	16.69	0.58	16	2331	81	7.83	-17.78
BMU-307	3.8250	88.46%	5.24%	0.60%	0.15 b	49.47	1.16	24	8187	192	7.41	-16.89
BMU-A30	3.6799	94.03%	15.03%	0.90%	0.10 a	37.19	0.91	12	4142	101	8.36	-17.72
MUS-021 (sp A)	3.4625	89.48%	9.88%	1.04%	0.29 b	164.35	8.69	28	15815	836	12.89	-16.83
MUS-021 (sp B)	3.6703	91.54%	14.32%	1.21%	0.21 b	50.77	2.39	18	4190	197	11.62	-16.28
MUS-031 (sp B)	3.8289	92.04%	7.37%	0.59%	0.15 b	27.84	1.35	25	4745	230	11.95	-16.26
SHR-021	5.1080	75.35%	14.54%	3.58%	2.74	146.98	4.33	77	4102	121	13.22	-15.9
SHR-023	5.1026	74.97%	17.31%	4.33%	2.69	123.01	4.23	62	2840	98	13.16	-16.2
SHR-025	5.5082	74.31%	15.26%	3.92%	2.79	117.05	4.21	71	2985	107	13.12	-16.14
BEN-03	5.4175	Insufficient Sample			8.60	552.89	20.05		Insufficient Sample			
ZOO-21	4.2776	Insufficient Sample			2.81	367.81	2.94		Insufficient Sample			
ZOO-22	6.1463	96.94%	18.26%	0.56%	0.02 b	6.68	0.40	4	1195	71	*too low*	-17.89

a) less than LOD
b) less than MDL

Table 4. Summary of D_4, D_5 and D_6 concentrations in sediment samples collected from inner and outer Oslofjord

Study Area	ID (Abbreviation)	Weight (g)	% Water	Bkg-Corr cVMS Concentrationn (ww) D4 (ng/g)	D5 (ng/g)	D6 (ng/g)	Bkg-Corr cVMS Concentrationn (dw) D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
Outer	SED-03 (0-1cm)	6.1727	72.7%	0.02 b	2.49	2.67	0.04	9.12	9.78
Outer	SED-04 (1-2 cm)	6.6632	54.2%	0.08 b	3.65	3.55	0.02	7.98	7.76
Outer	SED-07 (0-1cm)	6.6244	66.7%	0.04 b	2.39	2.71	0.03	7.16	8.13
Outer	SED-08 (1-2 cm)	6.6898	64.4%	0.06 b	3.67	3.33	0.03	10.30	9.36
Outer	SED-11 (0-1cm)	6.0497	54.1%	0.06 b	1.90	2.56	0.03	4.13	5.59
Outer	SED-12 (1-2 cm)	6.1626	61.2%	0.09 b	1.39	2.01	0.03	3.57	5.17
Inner	SED-13 (0-1cm)	6.1972	74.1%	0.40 b	82.75	20.57	1.56	319.24	79.36
Inner	SED-14 (1-2 cm)	6.0739	64.8%	0.57	100.25	20.23	1.61	284.80	57.47
Inner	SED-19 (0-1cm)	6.2783	63.5%	0.69	128.33	22.38	1.88	351.62	61.33
Inner	SED-20 (1-2 cm)	7.0044	55.9%	0.73	112.36	18.72	1.66	254.73	42.45
Inner	SED-21 (0-1cm)	5.9734	61.3%	1.03	202.91	34.37	2.67	524.43	88.82
Inner	SED-22 (1-2 cm)	6.3063	62.2%	0.81	173.66	26.64	2.15	459.68	70.51
Inner	SED-25 (0-1cm)	6.6661	82.1%	0.20 b	56.00	16.78	1.11	311.99	93.51
Inner	SED-26 (1-2 cm)	6.7559	72.2%	0.26 b	74.98	18.74	0.95	269.61	67.40

a) less than LOD
b) less than MDL

Table 5. Limits of Detection

Matrix	MDL_{reg} (ng/g ww)		
	D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
Fish	0.38	0.22	0.43
Mussel	0.33	0.66	0.40
Sediment	0.41	0.30	0.42
Shrimp	0.21	0.24	0.39

	D4 (ng)	D5 (ng)	D6 (ng)
Biota THF Extracts LOD:	0.66	1.98	1.11
Sediment Hexane Extracts LOD:	0.08	1.63	0.47

Table 6. Quality Control results for D_4

QC ID	Expected [D4] ng	Recovered [D4] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
Shrimp matrix (3-10-09)					
qc 0-1	0	0.93			
qc 0-2	0	0.26			
qc 0-3	0	0.20			
QC spike 1	77.4	77.2	0%	-1%	1%
QC spike 2	77.4	75.4	-3%		
QC spike 3	77.4	76.6	-1%		
Spike addition 3a	77.4	78.6	1%	-1%	2%
Spike addition 3b	77.4	75.5	-2%		
Spike addition 3c	77.4	76.0	-2%		
Blue Mussel matrix (3-12-09)					
qc 0-1	0	0.539			
qc 0-2	0	0.264			
qc 0-3	0	0.548			
QC spike 1	77.4	76.5	-1%	-1%	1%
QC spike 2	77.4	75.8	-2%		
QC spike 3	77.4	76.5	-1%		
Spike addition 5a	77.4	74.6	-4%	-3%	0%
Spike addition 5b	77.4	75.0	-3%		
Spike addition 5c	77.4	74.5	-4%		
fish matrix (3-17-09)					
qc 0-1	0	1.75			
qc 0-2	0	2.23			
qc 0-3	0	2.14			
QC spike 1	77.4	76.7	-1%	-2%	1%
QC spike 2	77.4	75.6	-2%		
QC spike 3	77.4	75.0	-3%		
fish matrix (3-19-09)					
QC 0-1	0	10.33			
QC 0-2	0	2.68			
QC 0-3	0	2.57			
QC spike 1	77.4	75.8	-2%	-2%	1%
QC spike 2	77.4	75.7	-2%		
QC spike 3	77.4	76.5	-1%		
Spike addition EPE3a	77.4	77.3	0%	0%	2%
Spike addition EPE3b	77.4	78.2	1%		
Spike addition EPE3c	77.4	75.8	-2%		
fish fillet matrix (3-23-09)					
QC 0-1	0	2.77			
QC 0-2	0	1.64			
QC 0-3	0	1.25			
QC spike 1	77.4	76.3	-1%	-2%	1%
QC spike 2	77.4	74.9	-3%		
QC spike 3	77.4	76.4	-1%		

Table 6 continued. Quality Control results for D_4

QC ID	Expected [D4] ng	Recovered [D4] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
		fish matrix (3-26-09)			
qc 0-1	0	2.66			
qc 0-2	0	2.78			
qc 0-3	0	2.66			
QC spike 1	77.4	75.1	-3%	-4%	1%
QC spike 2	77.4	73.9	-5%		
QC spike 3	77.4	74.1	-4%		
		fish matrix (3-31-09)			
qc 0-1	0	2.68			
qc 0-2	0	2.56			
qc 0-3	0	1.84			
QC spike 1	77.4	74.2	-4%	-4%	0%
QC spike 2	77.4	74.0	-4%		
QC spike 3	77.4	74.6	-4%		
		fish matrix (4-02-09)			
qc 0-1	0	2.80			
qc 0-2	0	2.35			
qc 0-3	0	2.75			
QC spike 1	77.4	71.2	-8%	-7%	1%
QC spike 2	77.4	72.4	-6%		
QC spike 3	77.4	73.0	-6%		
		fish matrix (4-06-09)			
qc 0-1	0	1.45			
qc 0-2	0	1.88			
qc 0-3	0	1.96			
QC spike 1	77.4	71.7	-7%	-6%	1%
QC spike 2	77.4	73.6	-5%		
QC spike 3	77.4	73.0	-6%		
		sediment matrix (4-16-09)			
FB-4	0	0.75			
FB-5	0	0.97			
FB-6	0	0.89			
RS-4 units = ng/g	60.4	41.5	-31%	-33%	7%
RS-5 units = ng/g	62.2	44.4	-29%		
RS-6 units = ng/g	63.2	39.0	-38%		
Spike addition 3-12a	130	145	11%	12%	0%
Spike addition 3-12b	130	145	11%		
Spike addition 3-12c	130	146	12%		

Table 7. Quality Control results for D5

QC ID	Expected [D5] ng	Recovered [D5] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
Shrimp matrix (3-10-09)					
qc 0-1	0	2.63			
qc 0-2	0	2.33			
qc 0-3	0	1.76			
QC spike 1	80.3	78.4	-2%	1%	4%
QC spike 2	80.3	80.7	1%		
QC spike 3	80.3	85.1	6%		
Spike addition 3a	80.3	83.0	3%	1%	2%
Spike addition 3b	80.3	79.3	-1%		
Spike addition 3c	80.3	82.0	2%		
Blue Mussel matrix (3-12-09)					
qc 0-1	0	10.2			
qc 0-2	0	10.1			
qc 0-3	0	14.8			
QC spike 1	80.3	79.4	-1%	2%	3%
QC spike 2	80.3	82.4	3%		
QC spike 3	80.3	83.7	4%		
Spike addition 5a	80.3	78.7	-2%	-2%	0%
Spike addition 5b	80.3	79.0	-2%		
Spike addition 5c	80.3	79.2	-1%		
fish matrix (3-17-09)					
qc 0-1	0	5.53			
qc 0-2	0	7.06			
qc 0-3	0	5.84			
QC spike 1	80.3	78.3	-3%	-3%	2%
QC spike 2	80.3	75.5	-6%		
QC spike 3	80.3	78.8	-2%		
fish matrix (3-19-09)					
QC 0-1	0	7.97			
QC 0-2	0	5.89			
QC 0-3	0	5.07			
QC spike 1	80.3	78.2	-3%	-1%	2%
QC spike 2	80.3	81.6	2%		
QC spike 3	80.3	79.8	-1%		
Spike addition EPE3a	80.3	87.1	9%	7%	5%
Spike addition EPE3b	80.3	81.2	1%		
Spike addition EPE3c	80.3	88.8	11%		
fish fillet matrix (3-23-09)					
QC 0-1	0	13.6			
QC 0-2	0	9.68			
QC 0-3	0	8.24			
QC spike 1	80.3	81.3	1%	0%	2%
QC spike 2	80.3	78.2	-3%		
QC spike 3	80.3	81.4	1%		

Table 7 continued. Quality Control results for D_5

QC ID	Expected [D5] ng	Recovered |D5| ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
		fish matrix (3-26-09)			
qc 0-1	0	5.50			
qc 0-2	0	5.28			
qc 0-3	0	5.92			
QC spike 1	80.3	76.5	-5%	-7%	3%
QC spike 2	80.3	72.2	-10%		
QC spike 3	80.3	75.5	-6%		
		fish matrix (3-31-09)			
qc 0-1	0	8.39			
qc 0-2	0	11.45			
qc 0-3	0	5.81			
QC spike 1	80.3	77.2	-4%	-3%	0%
QC spike 2	80.3	77.7	-3%		
QC spike 3	80.3	78.0	-3%		
		fish matrix (4-02-09)			
qc 0-1	0	10.71			
qc 0-2	0	7.44			
qc 0-3	0	8.36			
QC spike 1	80.3	73.0	-9%	-9%	1%
QC spike 2	80.3	72.9	-9%		
QC spike 3	80.3	74.4	-7%		
		fish matrix (4-06-09)			
qc 0-1	0	6.58			
qc 0-2	0	7.03			
qc 0-3	0	7.51			
QC spike 1	80.3	77.9	-3%	-3%	2%
QC spike 2	80.3	76.8	-4%		
QC spike 3	80.3	79.2	-1%		
		sediment matrix (4-16-09)			
FB-4	0	8.07			
FB-5	0	9.52			
FB-6	0	9.44			
RS-4 units = ng/g	71.2	62.7	-12%	-15%	4%
RS-5 units = ng/g	73.3	62.2	-15%		
RS-6 units = ng/g	74.5	60.4	-19%		
Spike addition 3-12a	133	149	12%	12%	1%
Spike addition 3-12b	133	148	11%		
Spike addition 3-12c	133	150	13%		

Table 8. Quality Control results for D_6

QC ID	Expected [D6] ng	Recovered [D6] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
Shrimp matrix (3-10-09)					
qc 0-1	0	1.76			
qc 0-2	0	1.13			
qc 0-3	0	1.24			
QC spike 1	82.1	88.4	8%	7%	1%
QC spike 2	82.1	86.6	5%		
QC spike 3	82.1	88.2	7%		
Spike addition 3a	82.1	88.2	7%	5%	2%
Spike addition 3b	82.1	85.5	4%		
Spike addition 3c	82.1	85.4	4%		
Blue Mussel matrix (3-12-09)					
qc 0-1	0	3.73			
qc 0-2	0	3.39			
qc 0-3	0	4.28			
QC spike 1	82.1	84.3	3%	4%	1%
QC spike 2	82.1	84.8	3%		
QC spike 3	82.1	86.2	5%		
Spike addition 5a	82.1	84.2	3%	2%	1%
Spike addition 5b	82.1	82.7	1%		
Spike addition 5c	82.1	84.5	3%		
fish matrix (3-17-09)					
qc 0-1	0	3.05			
qc 0-2	0	2.33			
qc 0-3	0	2.46			
QC spike 1	82.1	83.6	2%	3%	1%
QC spike 2	82.1	85.6	4%		
QC spike 3	82.1	84.9	3%		
fish matrix (3-19-09)					
QC 0-1	0	1.77			
QC 0-2	0	2.45			
QC 0-3	0	0.97			
QC spike 1	82.1	85.2	4%	4%	1%
QC spike 2	82.1	85.5	4%		
QC spike 3	82.1	86.4	5%		
Spike addition EPE3a	82.1	92.5	13%	12%	2%
Spike addition EPE3b	82.1	93.3	14%		
Spike addition EPE3c	82.1	89.8	9%		
fish fillet matrix (3-23-09)					
QC 0-1	0	2.14			
QC 0-2	0	2.34			
QC 0-3	0	2.11			
QC spike 1	82.1	86.0	5%	5%	2%
QC spike 2	82.1	87.7	7%		
QC spike 3	82.1	83.8	2%		

Table 8 continued. Quality Control results for D_6

QC ID	Expected [D6] ng	Recovered [D6] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
		fish matrix (3-26-09)			
qc 0-1	0	2.30			
qc 0-2	0	1.35			
qc 0-3	0	1.81			
QC spike 1	82.1	80.3	-2%	-3%	1%
QC spike 2	82.1	79.4	-3%		
QC spike 3	82.1	79.5	-3%		
		fish matrix (3-31-09)			
qc 0-1	0	3.79			
qc 0-2	0	3.08			
qc 0-3	0	2.01			
QC spike 1	82.1	84.8	3%	2%	2%
QC spike 2	82.1	82.2	0%		
QC spike 3	82.1	84.3	3%		
		fish matrix (4-02-09)			
qc 0-1	0	1.89			
qc 0-2	0	1.61			
qc 0-3	0	1.76			
QC spike 1	82.1	79.7	-3%	-2%	1%
QC spike 2	82.1	79.5	-3%		
QC spike 3	82.1	81.3	-1%		
		fish matrix (4-06-09)			
qc 0-1	0	2.03			
qc 0-2	0	2.02			
qc 0-3	0	2.42			
QC spike 1	82.1	81.6	-1%	0%	0%
QC spike 2	82.1	82.1	0%		
QC spike 3	82.1	81.7	0%		
		sediment matrix (4-16-09)			
FB-4	0	3.36			
FB-5	0	3.95			
FB-6	0	3.50			
RS-4 units = ng/g	59.2	53.4	-10%	-14%	4%
RS-5 units – ng/g	61.0	50.8	-17%		
RS-6 units = ng/g	61.9	52.7	-15%		
Spike addition 3-12a	138	153	11%	11%	0%
Spike addition 3-12b	138	153	11%		
Spike addition 3-12c	138	154	11%		

Table 9. Quality Control Reference fish analysis

QC ID	Date of analysis	1-27-09 initial [D4] ng/g	Recovered [D4] ng/g	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)
		Rainbow Trout Matrix			
ref-1		402.6	390.8	-3%	-6%
ref-2	17-Mar-09	402.6	364.7	-9%	
ref-3		402.6	344.7	-14%	-13%
ref-4	19-Mar-09	402.6	355.7	-12%	
ref-5		402.6	356.3	-12%	-9%
ref-6	26-Mar-09	402.6	374.2	-7%	
ref-7		402.6	334.6	-17%	-15%
ref-8	31-Mar-09	402.6	353.7	-12%	
ref-9		402.6	346.4	-14%	-15%
ref-10	2-Apr-09	402.6	341.6	-15%	
ref-11		402.6	406.4	1%	-3%
ref-12	6-Apr-09	402.6	374.9	-7%	

QC ID	Date of analysis	1-27-09 initial [D5] ng/g	Recovered [D5] ng/g	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)
		Rainbow Trout Matrix			
ref-1		317.0	298.2	-6%	-9%
ref-2	17-Mar-09	317.0	280.9	-11%	
ref-3		317.0	274.5	-13%	-8%
ref-4	19-Mar-09	317.0	308.5	-3%	
ref-5		317.0	293.2	-8%	-9%
ref-6	26-Mar-09	317.0	285.0	-10%	
ref-7		317.0	262.9	-17%	-13%
ref-8	31-Mar-09	317.0	286.0	-10%	
ref-9		317.0	270.3	-15%	-14%
ref-10	2-Apr-09	317.0	274.5	-13%	
ref-11		317.0	317.8	0%	-4%
ref-12	6-Apr-09	317.0	292.6	-8%	

QC ID	Date of analysis	1-27-09 initial [D6] ng/g	Recovered [D6] ng/g	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)
		Rainbow Trout Matrix			
ref-1		220.2	236.6	7%	6%
ref-2	17-Mar-09	220.2	231.2	5%	
ref-3		220.2	224.3	2%	9%
ref-4	19-Mar-09	220.2	257.2	17%	
ref-5		220.2	231.1	5%	4%
ref-6	26-Mar-09	220.2	225.5	2%	
ref-7		220.2	202.8	-8%	-4%
ref-8	31-Mar-09	220.2	221.3	1%	
ref-9		220.2	205.8	-6%	-5%
ref-10	2-Apr-09	220.2	213.9	-3%	
ref-11		220.2	247.9	13%	8%
ref-12	6-Apr-09	220.2	227.9	4%	

Table 10. Quality Control Fillet analysis

QC set 1: used November 12, 2008; outer Oslo fjord 3rd trawl

	sample		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
COD 1	QC 1	Deployed in the net	0.73	5.95	1.16
	QC 3	field bank	0.40	5.28	1.15
	QC 5	retained sample	0.67	8.05	3.00

QC set 2: used November 13, 2008; inner Oslo fjord 2nd trawl

	sample		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
COD 2	QC 7	deployed in the net	0.10	1.19	0.56
	QC 9	field bank	0.05	1.86	0.58
	QC 11	retained sample	0.06	0.65	0.55

QC set 3: used November 13, 2008; inner Oslo fjord 3rd trawl

	sample		D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
COD 3	QC 13	deployed in the net	0.80	14.25	1.70
	QC 15	field bank	0.45	14.95	1.40
	QC 17	retained sample	0.49	14.48	4.08

Table 11. Air Monitoring during field collections

Sample Name	Collection Date	Air Volume (L)	µg D4	µg D5	µg D6	D4 Conc. (ug/m^3)	D5 Conc. (ug/m^3)	D6 Conc. (ug/m^3)
OOF-1	11/12/08	439	<RL	0.313	<RL	< 0.55	0.71	< 0.55
OOF-2	11/12/08	511	<RL	<RL	<RL	< 0.47	< 0.47	< 0.47
IOF-1	11/13/08	532	<RL	<RL	<RL	< 0.43	< 0.43	< 0.43
IOF-2	11/13/08	531	<RL	<RL	<RL	< 0.43	< 0.43	< 0.43
IOF-3	11/14/08	345	<RL	<RL	<RL	< 0.70	< 0.70	< 0.70
IOF-4	11/14/08	344	<RL	<RL	<RL	< 0.70	< 0.70	< 0.70
	Reporting Limit (µg) =		0.24	0.24	0.24			

Sample Name	Sample Description
OOF-1	Personal sample worn by individual during sample collection on the ship
OOF-2	Area sample located on the bow of the ship away from all workers
IOF-1	Area sample located on starboard side of deck near live-well tank and sample collection area
IOF-2	Area sample located on side of freezer on upper level of ship near exhaust vent
IOF-3	Area sample located on starboard side of deck near live-well tank and sample collection area
IOF-4	Area sample on countertop in wet lab

Table 12. Method Results for Solvent Standards

Example Standard Curve 3-10-2009

Standard ID	Expected $[D_4]$ ng	$[D_4]$ found ng	%Relative Error (Accuracy)
STD 0.2	1.59	1.61	1.4
STD 0.4	3.40	3.33	2.0
STD 0.8	6.92	6.84	1.1
STD 1.7	14.2	14.0	1.1
STD 3.5	29.3	28.8	1.9
STD 7	59.3	59.0	0.5
STD 15	124	124	0.1
STD 30	248	250	0.8
STD 60	493	501	1.5
STD 125	1161	1176	1.3
STD 250	2172	2208	1.7
STD 500	4411	4435	0.5
STD 1000	9854	9851	0.0

Standard ID	Expected $[D_5]$ ng	$[D_5]$ found ng	%Relative Error (Accuracy)
STD 0.2	1.67	1.58	5.0
STD 0.4	3.57	3.98	11.4
STD 0.8	7.26	7.14	1.7
STD 1.7	14.9	14.66	1.5
STD 3.5	30.8	28.6	7.2
STD 7	62.3	60.3	3.2
STD 15	131	133	1.7
STD 30	260	262	0.8
STD 60	518	524	1.2
STD 125	1219	1241	1.7
STD 250	2281	2346	2.9
STD 500	4632	4710	1.7
STD 1000	10349	10366	0.2

Standard ID	Expected $[D_6]$ ng	$[D_6]$ found ng	%Relative Error (Accuracy)
STD 0.2	1.84	2.0	7.5
STD 0.4	3.94	3.63	7.9
STD 0.8	8.01	7.75	3.3
STD 1.7	16.4	16.93	3.1
STD 3.5	34.0	34.4	1.2
STD 7	68.7	70.17	2.2
STD 15	144	151	4.6
STD 30	287	290	1.0
STD 60	572	583	2.0
STD 125	1345	1361	1.2
STD 250	2516	2482	1.4
STD 500	5109	4794	6.2
STD 1000	11414	Standard Not used	

Table 13. GC Conditions

Parameter	Setting
Instrument/Software	**HP6890 Series Gas Chromatograph** **HP5973 Mass Selective Detector** **HP ChemStation version D.03.00**
Inlet conditions	**Pulsed-Split 5:1, Split Flow 7ml/min Total Flow 11.7ml/min, Pulse pressure 20psi, pulse time 1min** **1 µL injection; Merlin Microseal, Temp: 150 °C**
Carrier	**Helium, 1 mL/min constant flow**
Column	**DB-WAXetr, 30m x 0.25mm, 0.25 mm film thickness**
Oven Program	**40 °C (hold 3 min) to 190°C at 25°C/min, to 240°C at 40 °C/ min**
Transfer line	**280 °C**
MSD	**Selective ion monitoring, m/z D_4-281, 13C-D_4-285, D_5-355, 13C-D_5-360, D_6-429, 13C-D_6-435; 100 ms dwell time**

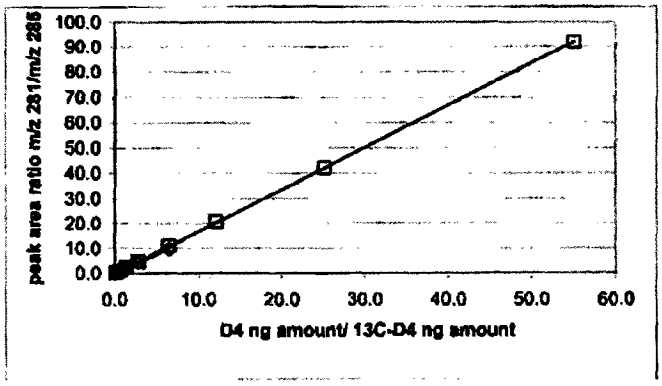
Table 14. Sediment Characteristics

	coulometry			loss-on-ignition							
Sample ID	%TC	%TIC	%TOC	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	%H2O	% Organic	% CaCO3	% Inorg.
3	2.33	0.34	2.00	1.19	0.32	0.27	0.03	72.7	11.6	9.5	78.9
4	2.27	0.32	1.95	1.37	0.63	0.46	0.04	54.2	9.8	6.4	83.8
7	2.27	0.40	1.87	1.24	0.41	0.33	0.03	66.7	10.2	9.2	80.6
8	2.22	0.35	1.87	1.26	0.45	0.36	0.04	64.4	9.9	8.2	81.9
11	2.19	0.40	1.79	1.37	0.63	0.46	0.04	54.1	8.9	7.5	83.6
12	2.21	0.40	1.80	1.32	0.55	0.41	0.04	58.6	9.2	7.0	83.8
3-12	2.19	0.38	1.81	1.27	0.46	0.36	0.03	63.7	8.4	9.3	82.3
13	3.14	0.29	2.84	1.18	0.30	0.26	0.04	74.1	13.5	9.9	76.6
14	3.13	0.35	2.78	1.25	0.44	0.35	0.04	64.8	12.4	7.1	80.5
19	2.75	0.23	2.52	1.27	0.46	0.36	0.04	63.5	10.6	7.6	81.7
20	2.83	0.31	2.51	1.35	0.59	0.44	0.04	55.9	10.0	7.2	82.9
21	2.97	0.28	2.69	1.29	0.50	0.39	0.04	61.3	11.5	7.2	81.3
22	2.69	0.19	2.49	1.28	0.48	0.38	0.04	62.2	10.4	7.3	82.3
25	3.13	0.32	2.81	1.11	0.20	0.18	0.03	82.1	14.0	18.0	68.0
26	3.22	0.28	2.94	1.15	0.26	0.22	0.03	77.6	13.5	13.1	73.5
13-26	2.85	0.23	2.61	1.24	0.41	0.33	0.04	66.8	10.6	9.5	79.8

Figures

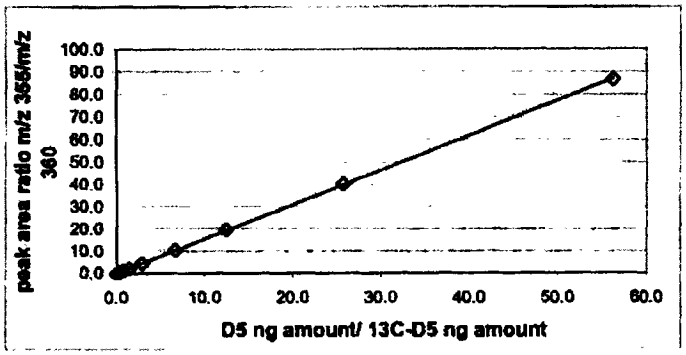
Figure 1. Tetrahydrofuran Standard Curves from analysis for cVMS

D_4 Curve



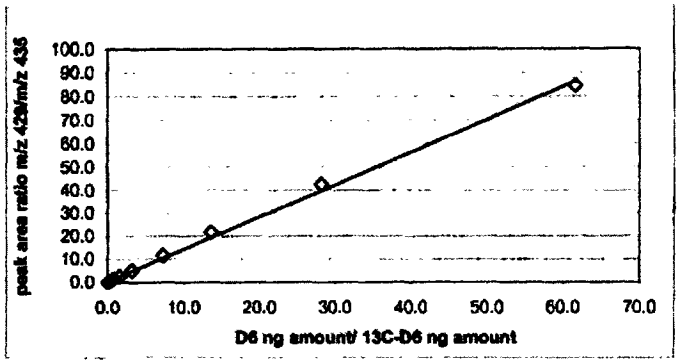
Slope = 1.6708 Y - Intercept = -0.00090 R^2 = 0.9998

D_5 Curve



Slope = 1.5424 Y - Intercept = 0.0226 R^2 = 0.9986

D_6 Curve



Slope = 1.6171 Y - Intercept = 0.0092 R^2 = 0.9981

Note: Peak area ratios are corrected for background amounts as well as contributions from internal standard for D_4 and D_5, peak area ratios are corrected for background amounts for D_6.

Appendix 1. Detection limit supplemental information

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
10-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	1.65	-0.12	-2.07			
10-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	1.91	-0.73	-2.08			
10-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	1.59	-0.34	-2.11			
10-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	1.72	0.30	-2.11			
					mean:	1.72	-0.22	-2.09			
					sd:	0.14	0.43	0.02	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	0.63	1.96	0.10	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
12-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	1.26	0.38	-1.24			
12-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	1.44	0.64	-0.01			
12-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	1.26	3.13	0.12			
12-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	1.27	2.35	-0.23			
					mean:	1.31	1.62	-0.34			
					sd:	0.08	1.33	0.62	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	0.39	6.04	2.80	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
17-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	1.45	6.45	1.45			
17-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	1.74	6.24	1.45			
17-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	1.93	5.82	1.44			
17-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	2.04	6.54	1.44			
					mean:	1.79	6.26	1.44			
					sd:	0.26	0.32	0.01	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	1.17	1.46	0.03	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
19-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	2.50	5.07	0.59			
19-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	2.44	5.78	0.59			
19-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	2.75	6.88	2.32			
19-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	2.30	6.90	2.59			
					mean:	2.50	6.16	1.52			
					sd:	0.19	0.89	1.08	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	0.86	4.05	4.91	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
23-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	1.18	7.82	-0.62			
23-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	1.31	8.52	-0.63			
23-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	1.18	8.50	-0.61			
23-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	1.28	7.81	-0.62			
					mean:	1.24	8.16	-0.62			
					sd:	0.07	0.40	0.01	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	0.31	1.83	0.04	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
26-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	0.49	3.73	-1.00			
26-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	0.42	2.86	-1.03			
26-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	0.39	3.62	-0.99			
26-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	0.56	2.01	-1.00			
					mean:	0.46	3.06	-1.00			
					sd:	0.08	0.80	0.02	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	0.35	3.63	0.07	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
31-Mar-09	Lab	pb-1	PB THF	Solvent	0.0000	0.69	1.69	-3.02			
31-Mar-09	Lab	pb-2	PB THF	Solvent	0.0000	0.71	2.20	-3.10			
31-Mar-09	Lab	pb-3	PB THF	Solvent	0.0000	1.09	3.29	-3.11			
31-Mar-09	Lab	pb-4	PB THF	Solvent	0.0000	0.84	2.55	-3.09			
					mean:	0.83	2.48	-3.08			
					sd:	0.18	0.60	0.04	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	0.82	2.72	0.18	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
02-Apr-09	Lab	pb-1	PB THF	Solvent	0.0000	1.38	3.88	-2.27			
02-Apr-09	Lab	pb-2	PB THF	Solvent	0.0000	1.99	3.12	-2.21			
02-Apr-09	Lab	pb-3	PB THF	Solvent	0.0000	1.50	3.18	-2.27			
02-Apr-09	Lab	pb-4	PB THF	Solvent	0.0000	1.89	3.71	-2.25			
02-Apr-09	Lab	pb-5	PB THF	Solvent	0.0000	0.94	1.31	-1.33			
02-Apr-09	Lab	pb-6	PB THF	Solvent	0.0000	0.98	1.58	-1.33			
02-Apr-09	Lab	pb-7	PB THF	Solvent	0.0000	0.82	1.50	-1.35			
02-Apr-09	Lab	pb-8	PB THF	Solvent	0.0000	0.80	1.46	-1.22			
					mean:	1.29	2.47	-1.78			
					sd:	0.48	1.11	0.50	0.27	0.82	0.46
					n:	8.00	8.00	8.00	40.00	40.00	40.00
					t:	3.00	3.00	3.00	2.43	2.43	2.43
					LOD:	1.43	3.32	1.51	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)	Pooled Results (Minitab) D4 (ng)	D5 (ng)	D6 (ng)
07-Apr-09	Lab	pb-1	PB THF	Solvent	0.0000	1.03	5.03	-1.06			
07-Apr-09	Lab	pb-2	PB THF	Solvent	0.0000	1.52	4.93	-1.06			
07-Apr-09	Lab	pb-3	PB THF	Solvent	0.0000	1.26	5.37	-1.05			
07-Apr-09	Lab	pb-4	PB THF	Solvent	0.0000	1.52	5.19	-1.05			
					mean:	1.33	5.13	-1.05			
					sd:	0.24	0.19	0.01	0.27	0.82	0.46
					n:	4.00	4.00	4.00	40.00	40.00	40.00
					t:	4.54	4.54	4.54	2.43	2.43	2.43
					LOD:	1.07	0.86	0.04	0.66	1.98	1.11

Analysis Date	Study Area	IDNO	QC Code	Matrix	Weight (g)	Measured cVMS Mass (ng) D4 (ng)	D5 (ng)	D6 (ng)
16-Apr-09	Lab	pb-1	PB Hexane	Solvent	0.0000	2.11	8.75	-0.57
16-Apr-09	Lab	pb-2	PB Hexane	Solvent	0.0000	2.06	7.33	-0.37
16-Apr-09	Lab	pb-3	PB Hexane	Solvent	0.0000	2.05	8.04	-0.39
16-Apr-09	Lab	pb-4	PB Hexane	Solvent	0.0000	2.05	7.66	-0.71
16-Apr-09	Lab	pb-5	PB Hexane	Solvent	0.0000	2.06	7.82	-0.60
16-Apr-09	Lab	pb-6	PB Hexane	Solvent	0.0000	2.08	8.12	-0.64
					mean:	2.07	7.95	-0.54
					sd:	0.02	0.48	0.14
					n:	6.00	6.00	6.00
					t:	3.36	3.36	3.36
					LOD:	0.08	1.63	0.47

Field/Lab Code	QC Code	Sample Type	Matrix	Weight (g)	Measured cVMS Mass (ng)			Bkg-Corr cVMS Concn (ng/g ww)		
					D4 (ng)	D5 (ng)	D6 (ng)	D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
QC-Fish (RBT)	QC	Blank	Fish	5.3373	3.54	11.79	4.49	0.33	1.04	0.57
QC-Fish (RBT)	QC	Blank	Fish	5.6508	4.02	13.32	3.78	0.40	1.25	0.41
QC-Fish (RBT)	QC	Blank	Fish	5.4872	3.93	12.11	3.91	0.39	1.06	0.45
QC-Fish (RBT)	QC	Blank	Fish	5.4072	12.83	14.13	3.29	1.91	1.47	0.33
QC-Fish (RBT)	QC	Blank	Fish	5.5407	5.17	12.05	3.97	0.48	1.06	0.44
QC-Fish (RBT)	QC	Blank	Fish	5.6473	5.06	11.23	2.49	0.45	0.90	0.87
QC-Fish (RBT)	QC	Blank	Fish	5.2764	3.12	8.56	1.30	0.50	1.04	0.44
QC-Fish (RBT)	QC	Blank	Fish	5.1847	3.24	8.34	0.34	0.54	1.02	0.26
QC-Fish (RBT)	QC	Blank	Fish	5.8076	3.12	8.98	0.80	0.46	1.02	0.31
QC-Fish (RBT)	QC	Blank	Fish	5.5131	3.51	10.87	0.70	0.49	1.52	0.69
QC-Fish (RBT)	QC	Blank	Fish	5.0580	3.39	13.93	0.00	0.51	2.26	0.61
QC-Fish (RBT)	QC	Blank	Fish	5.2405	2.67	8.29	-1.08	0.35	1.11	0.38
QC-Fish (RBT)	QC	Blank	Fish	5.8603	4.49	14.18	-0.36	0.55	2.00	0.24
QC-Fish (RBT)	QC	Blank	Fish	6.0382	4.04	10.92	-0.64	0.46	1.40	0.19
QC-Fish (RBT)	QC	Blank	Fish	5.8265	4.45	11.84	-0.49	0.54	1.61	0.22
QC-Fish (RBT)	QC	Blank	Fish	5.2008	2.79	11.71	0.98	0.28	1.27	0.39
QC-Fish (RBT)	QC	Blank	Fish	5.1696	3.21	12.18	0.97	0.38	1.36	0.39
QC-Fish (RBT)	QC	Blank	Fish	5.8065	3.30	12.84	1.36	0.34	1.29	0.42
				mean:	4.22	11.50	1.43	0.52	1.32	0.42
				sd:	2.27	1.91	1.78	0.36	0.36	0.17
				count:	18.00	18.00	18.00	18.00	18.00	18.00
				$t_{n-1,0.99}$:	2.57	2.57	2.57	2.57	2.57	2.57
				MDL:	5.82	4.91	4.58	0.92	0.92	0.44
				mean/MDL:	0.72	2.34	0.31	0.57	1.42	0.95
QC-Fish (RBT)	QC	Spike	Fish	5.2027	80.41	90.36	87.54	15.11	16.16	16.55
QC-Fish (RBT)	QC	Spike	Fish	5.2730	79.31	87.64	89.59	14.70	15.43	16.72
QC-Fish (RBT)	QC	Spike	Fish	4.9530	78.64	90.64	88.70	15.52	17.03	17.62
QC-Fish (RBT)	QC	Spike	Fish	5.2556	80.75	90.35	88.38	14.89	16.02	16.53
QC-Fish (RBT)	QC	Spike	Fish	5.8606	80.95	94.46	88.82	13.39	15.07	14.90
QC-Fish (RBT)	QC	Spike	Fish	5.1150	81.41	91.79	89.48	15.43	16.74	17.20
QC-Fish (RBT)	QC	Spike	Fish	5.2879	78.20	84.96	81.03	14.70	15.49	15.51
QC-Fish (RBT)	QC	Spike	Fish	5.7453	77.19	81.18	80.33	13.35	13.59	14.16
QC-Fish (RBT)	QC	Spike	Fish	6.2996	77.72	85.00	80.57	12.26	13.01	12.95
QC-Fish (RBT)	QC	Spike	Fish	5.2834	77.40	88.27	84.58	14.49	16.24	16.61
QC-Fish (RBT)	QC	Spike	Fish	5.8626	77.47	89.74	82.40	13.07	14.88	14.58
QC-Fish (RBT)	QC	Spike	Fish	5.1042	77.67	88.73	84.05	15.05	16.90	17.07
QC-Fish (RBT)	QC	Spike	Fish	5.8899	75.47	85.32	79.19	12.60	14.07	13.75
QC-Fish (RBT)	QC	Spike	Fish	5.5909	78.56	84.77	78.90	13.46	14.72	14.43
QC-Fish (RBT)	QC	Spike	Fish	5.3046	77.07	85.80	80.60	14.29	15.71	15.53
QC-Fish (RBT)	QC	Spike	Fish	5.6630	74.90	90.45	82.77	12.99	15.07	14.80
QC-Fish (RBT)	QC	Spike	Fish	5.9130	78.88	89.63	83.41	12.78	14.29	14.28
QC-Fish (RBT)	QC	Spike	Fish	5.3971	76.06	91.35	82.80	13.85	15.98	15.54
				mean:	78.00	88.36	84.07	14.00	15.36	15.48
				sd:	1.90	3.28	3.75	1.04	1.13	1.34
				count:	18.00	18.00	18.00	18.00	18.00	18.00
				$t_{n-1,0.99}$:	2.57	2.57	2.57	2.57	2.57	2.57
				MDL:	4.87	8.42	9.63	2.68	2.90	3.43
				mean/MDL:	16.01	10.49	8.73	5.26	5.29	4.51
QC-Ref (RBT)	QC	Ref	Fish	5.0705	1981.69	1512.12	1199.45	390.47	298.98	236.27
QC-Ref (RBT)	QC	Ref	Fish	5.3284	1943.47	1496.85	1232.12	364.40	279.74	230.97
QC-Ref (RBT)	QC	Ref	Fish	5.4174	1867.48	1486.93	1214.93	344.26	273.34	223.98
QC-Ref (RBT)	QC	Ref	Fish	5.0253	1787.52	1550.47	1292.33	355.21	307.31	258.86
QC-Ref (RBT)	QC	Ref	Fish	5.8889	2096.27	1726.59	1360.84	356.23	292.67	231.22
QC-Ref (RBT)	QC	Ref	Fish	5.4011	2021.30	1539.47	1217.91	374.15	284.46	225.68
QC-Ref (RBT)	QC	Ref	Fish	5.3811	1800.25	1414.88	1091.18	334.40	262.47	203.35
QC-Ref (RBT)	QC	Ref	Fish	4.8822	1728.87	1396.18	1080.55	353.49	285.48	221.96
QC-Ref (RBT)	QC	Ref	Fish	5.3892	1834.33	1474.04	1148.37	341.40	274.08	214.21
QC-Ref (RBT)	QC	Ref	Fish	5.3813	1863.90	1454.52	1107.71	346.13	269.83	206.17
QC-Ref (RBT)	QC	Ref	Fish	5.1148	2078.47	1625.50	1287.75	406.10	316.80	248.07
QC-Ref (RBT)	QC	Ref	Fish	5.5699	2088.37	1629.62	1269.25	374.70	291.65	228.07
				mean:	1924.31	1525.60	1206.85	361.75	286.23	227.23
				sd:	128.88	95.93	86.35	21.27	15.84	15.52
				count:	12.00	12.00	12.00	12.00	12.00	12.00
				$t_{n-1,0.99}$:	2.72	2.72	2.72	2.72	2.72	2.72
				MDL:	349.77	260.74	234.72	57.80	43.04	42.17
				mean/MDL:	5.50	5.85	5.14	6.26	6.65	5.39
ACD-003	Sample	Sample	Fish	6.0567	6.33	214.48	5.40	0.83	35.01	1.19
ACD-003	Sample	Sample	Fish	5.7885	6.09	211.21	5.10	0.83	36.06	1.19
ACD-003	Sample	Sample	Fish	6.0609	6.62	219.15	6.16	0.88	35.63	1.31
ACD-003	Sample	Sample	Fish	5.9169	6.22	205.71	5.38	0.83	34.34	1.21
ACD-003	Sample	Sample	Fish	5.8821	6.82	215.44	5.59	0.94	36.33	1.26
ACD-003	Sample	Sample	Fish	5.3836	6.14	195.65	4.86	0.90	35.88	1.23
ACD-003	Sample	Sample	Fish	5.4073	6.15	198.26	5.22	0.90	36.21	1.29
				mean:	6.34	208.56	5.39	0.87	35.64	1.24
				sd:	0.28	8.97	0.41	0.04	0.72	0.05
				count:	7.00	7.00	7.00	7.00	7.00	7.00
				$t_{n-1,0.99}$:	3.14	3.14	3.14	3.14	3.14	3.14
				MDL:	0.87	28.18	1.30	0.14	2.27	0.15
				mean/MDL:	7.28	7.40	4.14	6.33	15.69	8.11

EPE-003	Sample	Sample	Fish	5.7848	23.91	232.89	35.68	3.70	39.19	5.91
EPE-003	Sample	Sample	Fish	6.0459	19.81	183.98	30.22	2.86	29.41	4.75
EPE-003	Sample	Sample	Fish	5.5115	25.04	240.22	52.08	4.09	42.47	9.17
EPE-003	Sample	Sample	Fish	4.8571	22.27	208.51	44.00	4.07	41.66	8.75
EPE-003	Sample	Sample	Fish	5.5168	24.32	230.05	47.71	3.96	40.58	8.37
EPE-003	Sample	Sample	Fish	5.1597	22.80	216.09	41.20	3.93	40.69	7.69
EPE-003	Sample	Sample	Fish	5.1818	22.74	223.69	46.15	3.91	41.98	8.61
				mean:	22.99	219.35	42.44	3.79	39.43	7.61
				sd:	1.71	18.85	7.46	0.43	4.55	1.65
				count:	7.00	7.00	7.00	7.00	7.00	7.00
				$t_{n-1;0.99}$:	3.14	3.14	3.14	3.14	3.14	3.14
				MDL:	5.37	59.23	23.43	1.34	14.29	5.20
				mean/MDL:	4.28	3.70	1.81	2.82	2.76	1.46
EPE-003	Sample	Spike	Fish	4.8632	98.16	284.00	130.64	19.67	57.13	26.55
EPE-003	Sample	Spike	Fish	5.6196	101.92	307.72	137.09	17.69	53.66	24.12
EPE-003	Sample	Spike	Fish	4.9634	97.12	290.33	128.80	18.99	57.02	25.54
				mean:	99.07	294.01	132.18	18.78	55.94	25.41
				sd:	2.53	12.28	4.35	1.00	1.97	1.22
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	17.59	85.54	30.31	7.00	13.74	8.49
				mean/MDL:	5.63	3.44	4.36	2.68	4.07	2.99
QC-001	QC	F1-Field Blank	Fish fillet	5.4916	5.33	40.89	4.94	0.75	5.96	1.01
QC-001	QC	F1-Field Blank	Fish fillet	5.3862	5.11	40.13	6.47	0.72	5.93	1.32
QC-003	QC	F1-Process Blank	Fish fillet	5.4979	3.72	34.44	5.40	0.45	4.78	1.09
QC-003	QC	F1-Process Blank	Fish fillet	5.7050	3.24	41.10	6.31	0.35	5.77	1.21
QC-005	QC	F1-Net Blank	Fish fillet	5.4158	5.23	54.48	14.52	0.74	8.55	2.80
QC-005	QC	F1-Net Blank	Fish fillet	5.1829	4.35	47.33	15.96	0.60	7.56	3.20
QC-007	QC	F2-Field Blank	Fish fillet	5.0652	1.38	15.01	2.64	0.06	1.35	0.64
QC-007	QC	F2-Field Blank	Fish fillet	5.7431	1.99	14.02	2.08	0.13	1.02	0.47
QC-009	QC	F2-Process Blank	Fish fillet	5.8689	1.52	19.07	3.05	0.05	1.86	0.62
QC-009	QC	F2-Process Blank	Fish fillet	5.6637	1.60	18.74	2.45	0.05	1.87	0.54
QC-011	QC	F2-Net Blank	Fish fillet	5.6554	1.27	10.44	2.03	0.05	0.40	0.47
QC-011	QC	F2-Net Blank	Fish fillet	5.2323	1.17	12.89	2.69	0.06	0.90	0.63
QC-013	QC	F3-Field Blank	Fish fillet	5.7243	5.90	91.31	9.68	0.81	14.52	1.80
QC-013	QC	F3-Field Blank	Fish fillet	5.7418	5.80	88.44	8.58	0.79	13.98	1.60
QC-015	QC	F3-Process Blank	Fish fillet	5.1803	3.21	86.32	8.34	0.38	15.09	1.34
QC-015	QC	F3-Process Blank	Fish fillet	5.5984	4.16	91.13	7.56	0.52	14.82	1.46
QC-017	QC	F3-Net Blank	Fish fillet	5.2240	3.68	84.98	21.40	0.47	14.70	4.21
QC-017	QC	F3-Net Blank	Fish fillet	5.4293	3.99	85.58	20.83	0.51	14.26	3.95
				mean:	3.48	48.68	7.94	0.42	7.41	1.58
				sd:	1.65	31.23	6.23	0.29	5.71	1.18
				count:	18.00	18.00	18.00	18.00	18.00	18.00
				$t_{n-1;0.99}$:	2.57	2.57	2.57	2.57	2.57	2.57
				MDL:	4.24	80.16	16.00	0.74	14.65	3.04
				mean/MDL:	0.82	0.61	0.50	0.57	0.51	0.52
QC-Fillet (RBT)	QC	Blank	Fish fillet	5.7209	4.01	21.79	1.52	0.48	2.38	0.37
QC-Fillet (RBT)	QC	Blank	Fish fillet	5.4709	2.88	17.85	1.72	0.30	1.77	0.43
QC-Fillet (RBT)	QC	Blank	Fish fillet	5.6273	2.49	16.40	1.49	0.22	1.46	0.37
				mean:	3.12	18.68	1.58	0.33	1.87	0.39
				sd:	0.79	2.79	0.13	0.13	0.47	0.03
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	5.49	19.44	0.89	0.94	3.26	0.22
				mean/MDL:	0.57	0.96	1.76	0.36	0.57	1.80
QC-Fillet (RBT)	QC	Spike	Fish fillet	5.9051	79.50	100.49	87.72	13.25	16.64	14.96
QC-Fillet (RBT)	QC	Spike	Fish fillet	5.9480	78.14	97.57	89.43	12.93	15.03	15.14
QC-Fillet (RBT)	QC	Spike	Fish fillet	5.6847	79.52	100.19	85.40	13.82	16.25	15.19
				mean:	79.05	99.42	87.52	13.33	15.64	15.10
				sd:	0.79	1.61	2.02	0.45	0.61	0.12
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	5.50	11.20	14.07	3.14	4.23	0.83
				mean/MDL:	14.38	8.88	6.22	4.25	3.70	18.24
QC-Muss (BMU)	QC	Blank	Mussel	3.1910	1.85	11.78	3.39	0.12	3.18	1.17
QC-Muss (BMU)	QC	Blank	Mussel	3.4978	1.58	11.71	3.05	0.11	2.88	0.97
QC-Muss (BMU)	QC	Blank	Mussel	3.9458	1.86	16.38	3.94	0.10	3.74	1.08
				mean:	1.76	13.29	3.46	0.11	3.27	1.07
				sd:	0.16	2.67	0.45	0.01	0.43	0.10
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	1.13	18.62	3.12	0.08	3.02	0.69
				mean/MDL:	1.57	0.71	1.11	1.38	1.08	1.55

QC-Muss (BMU)	QC	Spike	Mussel	3.4555	78.22	92.42	87.67	22.26	28.28	25.47
QC-Muss (BMU)	QC	Spike	Mussel	3.4778	77.54	95.45	88.15	21.92	26.98	25.44
QC-Muss (BMU)	QC	Spike	Mussel	4.1521	78.37	98.97	90.27	18.56	23.45	21.82
				mean:	78.04	95.61	88.70	20.91	25.57	24.24
				sd:	0.45	3.28	1.38	2.04	1.87	2.10
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	3.11	22.85	9.61	14.23	13.03	14.62
				mean/MDL:	25.12	4.18	9.23	1.47	1.96	1.66
MUS-003 (sp A)	Sample	Sample	Mussel	2.4000	2.59	39.82	11.49	0.53	15.92	4.93
MUS-003 (sp A)	Sample	Sample	Mussel	2.5854	1.76	31.64	9.29	0.15	11.61	3.72
MUS-003 (sp A)	Sample	Sample	Mussel	2.5718	1.87	32.19	8.45	0.15	11.88	3.42
MUS-003 (sp A)	Sample	Sample	Mussel	2.5124	1.53	30.40	7.81	0.15	11.45	3.24
MUS-003 (sp A)	Sample	Sample	Mussel	2.3498	1.56	30.71	8.11	0.16	12.38	3.60
MUS-003 (sp A)	Sample	Sample	Mussel	2.7777	1.55	41.03	11.31	0.14	14.19	4.19
MUS-003 (sp A)	Sample	Sample	Mussel	1.8788	1.79	40.96	11.19	0.21	20.94	6.13
				mean:	1.81	35.25	9.66	0.21	14.05	4.16
				sd:	0.37	5.06	1.62	0.14	3.44	1.03
				count:	7.00	7.00	7.00	7.00	7.00	7.00
				$t_{n-1;0.99}$:	3.14	3.14	3.14	3.14	3.14	3.14
				MDL:	1.16	15.89	5.10	0.45	10.82	3.24
				mean/MDL:	1.55	2.22	1.89	0.48	1.30	1.29
MUS-005 (sp A)	Sample	Spike	Mussel	3.2521	76.44	125.24	96.62	23.10	38.01	29.81
MUS-005 (sp A)	Sample	Spike	Mussel	3.3001	76.83	126.17	95.30	22.88	37.74	28.98
MUS-005 (sp A)	Sample	Spike	Mussel	3.5170	76.42	129.34	98.05	21.36	36.31	27.97
				mean:	76.57	126.92	96.66	22.45	37.35	28.92
				sd:	0.23	2.15	1.37	0.95	0.91	0.92
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	1.60	14.96	9.55	6.62	6.35	6.41
				mean/MDL:	47.79	8.49	10.13	3.39	5.88	4.51
QC-Shrimp	QC	Blank	Shrimp	5.9198	2.64	2.40	-0.32	0.16	0.44	0.30
QC-Shrimp	QC	Blank	Shrimp	5.8743	1.98	2.11	-0.96	0.11	0.40	0.19
QC-Shrimp	QC	Blank	Shrimp	5.3793	1.91	1.53	-0.85	0.12	0.36	0.23
				mean:	2.18	2.01	-0.71	0.13	0.40	0.24
				sd:	0.40	0.44	0.34	0.03	0.04	0.05
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	2.81	3.08	2.36	0.18	0.28	0.37
				mean/MDL:	0.77	0.65	-0.30	0.69	1.44	0.64
QC-Shrimp	QC	Spike	Shrimp	5.9016	79.35	80.50	87.69	13.15	13.68	15.21
QC-Shrimp	QC	Spike	Shrimp	5.1910	77.58	82.51	85.72	14.62	15.94	16.92
QC-Shrimp	QC	Spike	Shrimp	5.7401	78.77	87.15	87.48	13.42	15.22	15.60
				mean:	78.57	83.39	86.96	13.73	14.95	15.91
				sd:	0.90	3.41	1.08	0.78	1.16	0.89
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	6.27	23.76	7.51	5.41	8.05	6.22
				mean/MDL:	12.53	3.51	11.57	2.54	1.86	2.56
SHR-003	Sample	Sample	Shrimp	6.2279	2.93	167.94	5.41	0.20	27.00	1.20
SHR-003	Sample	Sample	Shrimp	5.4130	3.32	154.87	5.32	0.30	28.65	1.37
SHR-003	Sample	Sample	Shrimp	5.8470	3.20	160.09	5.07	0.25	27.42	1.22
SHR-003	Sample	Sample	Shrimp	5.4482	2.69	151.48	4.63	0.18	27.84	1.23
SHR-003	Sample	Sample	Shrimp	5.7444	2.88	152.68	4.79	0.20	26.62	1.20
SHR-003	Sample	Sample	Shrimp	5.3936	3.10	152.14	5.25	0.26	28.25	1.36
SHR-003	Sample	Sample	Shrimp	4.9072	3.22	127.57	3.38	0.31	26.04	1.11
				mean:	3.05	152.40	4.84	0.24	27.40	1.24
				sd:	0.22	12.41	0.70	0.05	0.92	0.09
				count:	7.00	7.00	7.00	7.00	7.00	7.00
				$t_{n-1;0.99}$:	3.14	3.14	3.14	3.14	3.14	3.14
				MDL:	0.71	39.01	2.21	0.16	2.90	0.29
				mean/MDL:	4.32	3.91	2.19	1.52	9.46	4.30
SHR-003	Sample	Spike	Shrimp	5.8102	81.67	242.06	93.31	13.76	41.70	16.42
SHR-003	Sample	Spike	Shrimp	4.9460	78.45	214.64	89.57	15.51	43.44	18.53
SHR-003	Sample	Spike	Shrimp	5.5728	79.03	234.54	90.29	13.87	42.13	16.58
				mean:	79.71	230.41	91.06	14.38	42.42	17.18
				sd:	1.72	14.16	1.99	0.98	0.91	1.18
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	11.94	98.65	13.83	6.83	6.33	8.20
				mean/MDL:	6.67	2.34	6.58	2.10	6.70	2.10

QC-Ref (SL)	QC	REF	Sediment	6.0534	83.77	131.01	104.43	13.50	20.33	17.34
QC-Ref (SL)	QC	REF	Sediment	6.4399	92.03	133.73	102.32	13.97	19.53	15.97
QC-Ref (SL)	QC	REF	Sediment	6.3608	81.67	130.70	106.75	12.51	19.30	16.87
				mean:	85.82	131.81	104.50	13.33	19.72	16.73
				sd:	5.48	1.67	2.21	0.74	0.54	0.69
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	38.16	11.60	15.42	5.17	3.77	4.84
				mean/MDL:	2.25	11.36	6.78	2.58	5.23	3.46
QC-Sed (SL)	QC	Blank	Sediment	5.8300	2.82	16.03	2.82	0.13	1.38	0.58
QC-Sed (SL)	QC	Blank	Sediment	6.7366	3.04	17.47	3.41	0.14	1.41	0.59
QC-Sed (SL)	QC	Blank	Sediment	5.8875	2.96	17.39	2.96	0.15	1.60	0.59
				mean:	2.94	16.96	3.06	0.14	1.47	0.59
				sd:	0.11	0.81	0.31	0.01	0.12	0.01
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	0.77	5.66	2.16	0.08	0.83	0.06
				mean/MDL:	3.83	3.00	1.42	1.83	1.77	9.15
SED-Comp (IOF)	QC	Composite	Sediment	5.9823	5.70	718.53	135.63	0.61	118.78	22.76
SED-Comp (IOF)	QC	Composite	Sediment	6.7754	6.32	818.91	154.30	0.63	119.69	22.85
SED-Comp (IOF)	QC	Composite	Sediment	6.8425	6.37	818.17	156.60	0.63	118.41	22.97
SED-Comp (IOF)	QC	Composite	Sediment	6.5807	6.03	792.07	150.70	0.60	119.52	23.05
SED-Comp (IOF)	QC	Composite	Sediment	5.9583	5.67	717.31	137.34	0.60	119.05	23.14
SED-Comp (IOF)	QC	Composite	Sediment	6.0338	5.73	719.66	137.60	0.61	117.95	22.89
SED-Comp (IOF)	QC	Composite	Sediment	6.2480	5.94	743.24	139.58	0.62	117.68	22.43
				mean:	5.97	761.13	144.54	0.61	118.73	22.87
				sd:	0.29	47.12	8.97	0.01	0.76	0.23
				count:	7.00	7.00	7.00	7.00	7.00	7.00
				$t_{n-1;0.99}$:	3.14	3.14	3.14	3.14	3.14	3.14
				MDL:	0.91	148.10	28.19	0.03	2.38	0.73
				mean/MDL:	6.52	5.14	5.13	17.77	49.82	31.29
SED-Comp (IOF)	QC	spike	Sediment	5.9815	145.70	848.17	282.73	23.97	140.24	47.28
SED-Comp (IOF)	QC	spike	Sediment	6.0725	148.49	916.95	295.73	24.11	149.69	48.79
SED-Comp (IOF)	QC	spike	Sediment	6.1440	150.30	871.49	289.47	24.13	140.55	47.20
				mean:	148.17	878.87	289.31	24.07	143.49	47.76
				sd:	2.32	34.98	6.50	0.08	5.37	0.89
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	16.14	243.61	45.27	0.59	37.41	6.23
				mean/MDL:	9.18	3.61	6.39	40.72	3.84	7.66
SED-Comp (OOF)	QC	Composite	Sediment	6.4221	2.49	24.85	16.53	0.07	2.63	2.66
SED-Comp (OOF)	QC	Composite	Sediment	6.3793	2.38	22.31	16.19	0.05	2.25	2.62
SED-Comp (OOF)	QC	Composite	Sediment	6.1271	2.29	21.87	15.60	0.04	2.27	2.64
SED-Comp (OOF)	QC	Composite	Sediment	6.1680	2.46	23.34	15.98	0.06	2.50	2.68
SED-Comp (OOF)	QC	Composite	Sediment	6.4340	2.38	23.23	16.26	0.05	2.37	2.61
SED-Comp (OOF)	QC	Composite	Sediment	6.4687	2.50	23.42	16.12	0.07	2.39	2.58
SED-Comp (OOF)	QC	Composite	Sediment	6.1826	2.36	22.25	15.46	0.05	2.31	2.59
				mean:	2.41	23.04	16.02	0.05	2.39	2.63
				sd:	0.08	1.01	0.38	0.01	0.14	0.04
				count:	7.00	7.00	7.00	7.00	7.00	7.00
				$t_{n-1;0.99}$:	3.14	3.14	3.14	3.14	3.14	3.14
				MDL:	0.24	3.16	1.18	0.04	0.42	0.12
				mean/MDL:	9.88	7.29	13.53	1.45	5.62	22.01
SED-Comp (OOF)	QC	spike	Sediment	6.1547	147.29	171.69	168.73	23.59	26.60	27.50
SED-Comp (OOF)	QC	spike	Sediment	5.9829	147.27	169.79	168.21	24.27	27.05	28.21
SED-Comp (OOF)	QC	spike	Sediment	6.0432	148.33	172.38	168.83	24.20	27.21	28.03
				mean:	147.63	171.29	168.59	24.02	26.95	27.91
				sd:	0.61	1.34	0.33	0.37	0.31	0.37
				count:	3.00	3.00	3.00	3.00	3.00	3.00
				$t_{n-1;0.99}$:	6.96	6.96	6.96	6.96	6.96	6.96
				MDL:	4.22	9.34	2.33	2.59	2.18	2.55
				mean/MDL:	34.97	18.35	72.49	9.28	12.34	10.96

				Bkg-Corr cVMS Concn (ng/g ww)								
				D4 (ng/g)			D5 (ng/g)			D6 (ng/g)		
Field/Lab Code	QC Code	Sample Type	Matrix	Mean	MDL	Mean/MDL	Mean	MDL	Mean/MDL	Mean	MDL	Mean/MDL
QC-Fish (RBT)	QC	Blank	Fish	0.52	0.92	0.6	1.32	0.92	1.4	0.42	0.44	1.0
QC-Fish (RBT)	QC	Spike	Fish	14.00	2.66	5.3	15.36	2.90	5.3	15.46	3.43	4.5
ACD-003	Sample	Sample	Fish	0.87	0.14	6.3		2.27	0.0	1.24	0.15	8.1
EPE-003	Sample	Sample	Fish	3.79	1.34	2.8	39.43	14.29	2.8	7.61	5.20	1.5
EPE-003	Sample	Spike	Fish	18.76	7.00	2.7	55.94	13.74	4.1	25.41	8.49	3.0
QC-Ref (RBT)	QC	Ref	Fish		57.80	0.0		43.04	0.0		42.17	0.0
QC-Fillet (RBT)	QC	Blank	Fish fillet	0.33	0.94	0.4		3.26	0.0	0.39	0.22	1.8
QC-017	QC	F3-Net Blank	Fish fillet	0.42	0.74	0.6		14.65	0.0		3.04	0.0
QC-Fillet (RBT)	QC	Spike	Fish fillet	13.33	3.14	4.3	15.64	4.23	3.7		0.83	0.0
			Min MDL:		0.14			0.92			0.15	
			Max MDL:		57.80			43.04			42.17	
			MDL (y-cept):		0.38			0.22			0.43	
			MDL (r-sqr):		0.83			0.90			0.83	
			MDL (n):		8.00			5.00			8.00	
QC-Muss (BMU)	QC	Blank	Mussel	0.11	0.08	1.4	3.27	3.02	1.1	1.07	0.69	1.6
MUS-003 (sp A)	Sample	Sample	Mussel		0.45	0.0	14.05	10.82	1.3	4.18	3.24	1.3
QC-Muss (BMU)	QC	Spike	Mussel	20.91	14.23	1.5		13.03	0.0	24.24	14.62	1.7
MUS-005 (sp A)	Sample	Spike	Mussel	22.45	6.62	3.4		8.35	0.0		6.41	0.0
			Min MDL:		0.08			3.02			0.69	
			Max MDL:		14.23			13.03			14.62	
			MDL (y-cept):		0.33			0.86			0.40	
			MDL (r-sqr):		0.65			1.00			1.00	
			MDL (n):		3.00			2.00			3.00	
QC-Sed (SL)	QC	Blank	Sediment	0.14	0.08	1.83	1.47	0.83	1.77	0.59	0.06	9.15
SED-Comp (OOF)	QC	Composite	Sediment	0.01	0.00	13.53	2.39	0.42	5.62	2.63	0.12	22.01
QC-Ref (SL)	QC	REF	Sediment	13.33	5.17	2.58	19.72	3.77	5.23	16.73	4.84	3.46
SED-Comp (OOF)	QC	spike	Sediment	24.02	2.59	9.28		2.18	0.00	27.91	2.55	10.96
SED-Comp (IOF)	QC	Composite	Sediment	0.61	0.03	17.77		2.38	0.00		0.73	0.00
SED-Comp (IOF)	QC	spike	Sediment		0.59	0.00		37.41	0.00	47.76	6.23	7.66
			Min MDL:		0.00			0.42			0.06	
			Max MDL:		5.17			37.41			6.23	
			MDL (y-cept):		0.41			0.30			0.42	
			MDL (r-sqr):		0.52			0.98			0.74	
			MDL (n):		5.00			3.00			5.00	
QC-Shrimp	QC	Blank	Shrimp	0.13	0.18	0.7	0.40	0.28	1.4	0.24	0.37	0.6
QC-Shrimp	QC	Spike	Shrimp		5.41	0.0		8.05	0.0		8.22	0.0
SHR-003	Sample	Sample	Shrimp	0.24	0.16	1.5	27.40	2.90	9.5	1.24	0.29	4.3
SHR-003	Sample	Spike	Shrimp		6.83	0.0		6.33	0.0		8.20	0.0
			Min MDL:		0.16			0.28			0.29	
			Max MDL:		6.83			8.05			8.20	
			MDL (y-cept):		0.21			0.24			0.39	
			MDL (r-sqr):		1.00			1.00			1.00	
			MDL (n):		2.00			2.00			2.00	

APPENDIX 2: Contributing Scientist Report. Evonik Goldschmidt GmbH

Measurements of food-web related data on cVMS distribution in environmental samples collected in Oslofjord

Study Title:	Analysis of cyclic volatile methylsiloxanes (cVMS) in fat, muscle, and liver tissue of American mink (*Mustela vison*) obtained from Lake Pepin, Minnesota, USA.
HES Study No:	11216-108
Test Substances:	Octamethylcyclotetrasiloxane (D_4) Decamethylcyclopentasiloxane (D_5) Dodecamethylcyclohexasiloxane (D_6)
Authors:	Kent B. Woodburn Jeremy A. Durham
Study Personnel:	Jeremy A. Durham
Sponsor:	Centre Européen des Silicones (CES)
Testing Facility:	Dow Corning Corporation Health & Environmental Sciences (HES) 2200 West Salzburg Road Auburn, MI 48611
HES Group Supervisor:	Debra A. McNett
Study Completion Date:	25 November 2009

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ABSTRACT

This report describes the analytical determination and interpretation of cyclic volatile methylsiloxane (cVMS) residues (i.e., D_4, D_5, and D_6) in terrestrial species, the American mink (*Mustela vison*) harvested from the terrestrial area adjacent to Lake Pepin, Minnesota, USA. The Lake Pepin aquatic ecosystem has been the study of a previous report by Powell et al. (2009). Three male and one female mink were captured by a licensed trapper. Following frozen shipment to Dow Corning, the mink were dissected to remove the liver, perirenal fat, and a portion of quadriceps muscle from the rear leg. The stomach was also removed for content identification to identify dietary preferences. The mink tissues analyzed for cVMS were liver, fat, and muscle. The highest cVMS concentrations were in mink fat and the average lipid-adjusted residues in mink fat for D_4, D_5, and D_6 were <limit of detection, 44, and 5 ng/g-lipid, respectively. The limits of detection (LOD) for tissue samples extracted using tetrahydrofuran (THF) solvent were 0.42, 0.19 and 0.36 ng for D_4, D_5, and D_6, respectively. The method detection limits (MDL) determined for mink liver, fat and muscle were consistent with one another and ranged 1.01-1.48, 1.17-2.23, and 0.26-0.85 ng/g for D_4, D_5 and D_6, respectively. The average cVMS concentrations in mink fat are significantly less than lipid-adjusted cVMS residues in Lake Pepin fish and benthic invertebrate organisms; a number of these species may comprise part of the mink diet on Lake Pepin. These data indicate low level ng/g-lipid cVMS residues in the American mink and suggest that trophic magnification processes are not occurring in this terrestrial species in the Lake Pepin food web for siloxane materials D_4, D_5 and D_6.

SIGNATURES AND APPROVAL

This report consists of 26 pages with 1 figure, 11 tables, and 1 appendix. The undersigned have read and approved this report.

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Date

I. OBJECTIVE

The evaluation of cVMS concentrations and other pertinent data in selected mink tissue will allow an evaluation of bioaccumulation behavior for cVMS materials in a higher trophic level terrestrial species, the American mink, *Mustela vison*, taken from Lake Pepin, Minnesota, USA. This information should allow insight into the food web dynamics of cVMS materials in an aquatic and terrestrial ecosystem that has been previously studied with regard to cVMS behavior (Powell *et al.*, 2009).

II. TEST SYSTEM

The test system for this study was the American mink, consisting of three males and one female collected from the Lake Pepin tributaries from November 5th through November 12th 2008. The mink (*Mustela vison*) is the most abundant and widespread carnivorous mammal in North America, but is often overlooked due to its solitary nature and nocturnal activity (USEPA, 1993). Mink are members of the weasel family which includes skunks, otters, fishers, martens and wolverines. The mink lives in a variety of wetland and riparian habitats including rivers, streams, lakes, ponds and marshes and often feed on aquatic prey such as fish, frogs, and invertebrates, though small mammals and birds are also common prey items. A mink is an aggressive predator and often attacks animals larger than itself. Although the mink lives in a wetland habitat, it is not well adapted for swimming, so it concentrates its search for food to upland areas near the water, along shorelines or in shallow water. An adult male may be 30 inches long and can weigh up to three and a half pounds; a female mink is typically two-thirds that size (USEPA, 1993). Mink are highly sensitive to polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins and dibenzofurans (PCDDs/PCDFs) and predator/prey biomagnification factors (BMFs) for these chemicals in mink fat of 40- to 200-fold have been reported (Hornshaw et al., 1983).

III. REFERENCE ARTICLE INFORMATION

Reference article characterization was done in compliance with the EPA Toxic Substances Control Act (TSCA), Good Laboratory Practice Regulations (40CFR Part 792).

A. Reference Article 1

- Identification: Octamethylcyclotetrasiloxane (D_4)
- CAS Number: 556-67-2
- Lot Number: LL084732 (supplied as Dow Corning™ 244 Fluid)
- Expiration Date: June 17, 2011
- Purity: 99.77 % by GC-FID

B. Reference Article 2

- Identification: Decamethylcyclopentasiloxane (D_5)
- CAS Number: 541-02-6
- Lot Number: 0000341832 (supplied as Dow Corning™ 1693 Fluid)
- Expiration Date: December 31, 2010
- Purity: 99.16 % by GC-FID

C. Reference Article 3

- Identification: Dodecamethylcyclohexasiloxane (D_6)
- CAS Number: 540-97-6
- Lot Number: LL114030(supplied as Dow Corning™ 246 Fluid)
- Expiration Date: June 8, 2009
- Purity: 99.54 % by GC-FID

IV. FIELD SAMPLING

Mink were collected from the tributaries of Lake Pepin, from November 5 to 12, 2008, by a licensed trapper. The mink were captured using a steel spring leghold trap, attached to a cable anchored in deep water. After becoming trapped, the mink tried to escape by entering the water and the weight of the trap pulled them under, causing drowning. All mink were retrieved within 24 hours of capture. The mink were collected near the mouth of small tributary streams to Lake Pepin, generally near bridge crossings (highway and/or railroad). Water temperatures in the streams ranged between 40-45 °F (4-7 °C). The mink were placed in plastic garbage bags while being taken from the field and transferred to freezer bags and stored frozen upon returning from the field until shipment to Dow Corning, Midland, Michigan.

V. SAMPLE PROCESSING AND ANALYSIS

The samples were shipped to Dow Corning in frozen condition from Lake Pepin and received frozen on March 11, 2009. The mink were stored frozen upon receipt at –80±10° C.

Care was taken during the processing to limit cVMS laboratory contamination. Individuals working with samples were not allowed to apply any personal care products known to contain siloxanes on the day the samples were processed. The mink were dissected on June 25, 2009, with the removal of liver, perirenal fat, and a portion of quadriceps muscle from the rear leg. The stomach was also removed for content identification. The stomach was re-frozen and stored frozen and delivered to Michigan State University for content analysis on July 16, 2009.

Mink samples were removed from frozen storage and placed in a refrigerator the evening prior to processing. The thawed mink samples were individually weighed and total length recorded. The mink were then dissected using a scalpel for removal of liver, stomach, fat, and a portion of quadriceps muscle. The dissected samples were individually weighed and then homogenized by cutting into pieces using stainless steel scissors. Aliquots of the homogenate were removed and placed into pre-weighed glass containers for immediate extraction. The stomach was left intact and re-frozen immediately after weighing. The remaining homogenized samples were placed in pre-weighed glass storage jar with Teflon-lined lid for frozen storage at -20°C.

The analyses were based upon the principle of calibrating a gas chromatograph-mass spectrometry with mass selective detection (GC-MS) using solvent standards of tetrahydrofuran (THF) spiked with various concentrations of D_4, D_5, and D_6 and ^{13}C-D_4, ^{13}C-D_5 and ^{13}C-D_6 as internal standards, and then analyzing THF extracts of the homogenates against the standard calibration curves. Extractions were performed by using 2:1 solvent:sample ratios of THF containing the internal standards. After addition of a weighed amount of THF containing internal standards, the samples were vortex mixed for 30 minutes using a bed vortex mixer set on 'high'. The samples were then centrifuged for 5 minutes at a setting of 2000

revolutions per minute. The extract from each sample was transferred to a separate vial. A second extraction was performed using THF without internal standards. The sample was vortex mixed for 30 minutes and centrifuged for 5 minutes. The extract from each sample was combined with the first extract and dried using $MgSO_4$ (~ 250 mg).

The amounts of cVMS materials in each sample were determined from the resulting $1/(\text{peak area})^2$-weighted linear regression calibration functions. The linearity parameters; y – intercepts, slopes, and correlation coefficients, were determined for each of the standard curves. The standard concentration ranges validated were approximately 0.2 to 250 ng/g for D_4, D_5 and D_6 in THF. The minimum acceptance criterion for the linearity of a standard curve was a regression coefficient (R^2) of 0.99.

Peak responses from the GC-MS system were quantitated by automatic electronic integration either by using integration parameters in the software or by drawing a baseline manually using the software utility for the peak. If the baselines were drawn manually, this was indicated on the chromatogram printout. Calibration curves were determined from linear regression analysis of the data using Microsoft Excel Version 9.

A. Stable Isotope Lipid Analysis

Biological samples were analyzed for water content, lipid content and for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) by the Biogeochemistry and Paleoproteomics Laboratory at Michigan State University in East Lansing Michigan. Isotopic signatures were determined on muscle tissue. Water and lipid contents were determined on all three matrices. Small aliquots (about 1 g) of each sample were weighed into individual glass containers and transported by car in a cooler containing blue ice from Dow Corning to Michigan State University. Upon arrival samples were immediately placed into refrigerated storage at about 4°C in the dark until processed for analysis.

Water and Lipid Content: Water and lipid contents were determined on liver, fat and muscle tissue. Water content was determined as weight loss during lyophilization to a constant weight. The remaining lyophilized material was then extracted with chloroform:methanol (87:13) and lipid content determined gravimetrically and expressed on both dry and wet weight basis. The precision (± standard deviation) for this technique, based on replicate analyses of a laboratory standard (rainbow trout, *Oncorhynchus mykiss*), was 0.2 % for water content and 1.25% for lipid content.

Stable Isotope Analysis: Signature patterns of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) have become an effective method for the study of trophic position and food web dynamics (Cabanellas-Reboredo et al., 2009). Isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) of the mink were determined on muscle tissue samples. Samples were lyophilized to a constant weight, extracted with chloroform:methanol (87:13) to remove the lipids, dried in a vacuum oven, and homogenized to a fine powder with a mechanical mill. Samples (about 1.0 mg in tin capsules) were then combusted with O_2 and Cr_2O_2 at about 1030°C in an elemental analyzer (Eurovector), (Matthews and Hayes, 1978). NOx products were reduced with Cu at 650°C. The combustion products N_2, CO_2, and H_2O were separated on a packed column and the $^{15}N/^{14}N$ or $^{13}C/^{12}C$ isotopic ratios determined using an interfaced isotope ratio mass spectrometer (Elementar Americas, Inc). Stable isotope abundances were expressed in per mil notation (δ) as the deviation from standards in parts per thousand (‰) according to the equation:

$$\delta X = \left[\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right] \times 1000$$

where X was ^{15}N or ^{13}C and R was the abundance ratio of the heavy to light isotope (i.e., $^{15}N/^{14}N$ or $^{13}C/^{12}C$) in the sample (R_{sample}) and the standard ($R_{standard}$). The $R_{standard}$ values were based on atmospheric nitrogen gas for ^{15}N and PeeDee Belemnite (PDB) for ^{13}C. The precision (± standard deviation) for this technique, based on replicate analyses of laboratory standard (Atlantic salmon; *Salmo salar*), was ≤ 0.2 ‰ for ^{15}N and ^{13}C.

VI. QUALITY CONTROL

Control rat liver, fat and muscle were used as the control tissue throughout the processing. The control tissues were removed from frozen storage and placed in a refrigerator the evening prior to processing. The control tissues were then processed in the same manner as the mink study samples. These control homogenates were used to evaluate matrix effects during the processing of study samples.

Procedural solvent blanks were completed for every analysis day to determine day-to-day variability that occurs from the instrument, the extraction process, and laboratory contamination.

Extractions of procedural solvent blanks, matrix spikes, matrix controls, study sample replicates, and spike addition to samples were processed the same way as samples for a particular set of analyses. An assessment of accuracy, limit of detection (LOD) and method detection limits (MDLs) was determined. The target analytical concentration for the spikes was ~21 ng D_4, D_5 and D_6. The spikes were completed by spiking a known amount by volume using a gas-tight syringe into the solvent layer prior to the first 30 minute vortex. This method was developed based on techniques developed for the extraction and analysis of cVMS from biological samples (Varaprath *et al.* 1998; and Varaprath *et al.* 2000).

Peak responses from the GC-MS system were quantitated by automatic electronic integration either by using integration parameters in the software or by drawing a baseline manually in the software for the peak. If the baselines were drawn manually, this was indicated on the chromatogram printout in the study file. Calibration curves were determined from linear regression analysis of the data using Microsoft Excel Version 9.

VII. DETERMINATION OF LIMITS OF DETECTION AND METHOD DETECTION LIMITS

Detection limits (DL) were determined as a function of the variance associated with replicate analyses of matrix-free blanks (LOD) and replicate analyses of samples containing a small, but measurable amount of cVMS materials (MDL). The DL (LOD or MDL) at 99% confidence were then defined as:

$$DL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses.

For this study, the LOD was calculated using non-background corrected amounts of D_4, D_5, and D_6 measured in procedural (solvent) blanks that were carried through the entire analytical procedure. The MDL was calculated using non-background corrected amounts and concentrations of D_4, D_5, and D_6 measured in replicate samples.

The measured limit of detection (LOD) and method detection limit (MDL) for D_4, D_5, and D_6 in Lake Pepin mink muscle, fat, and liver tissue are presented in **Table 1**. The LOD for these cyclic siloxanes ranged from 0.15 ng/g-wet weight (ww) (D_5 in liver) to 1.4 ng/g-ww (D_4 in fat). The MDL for D_4 and D_5 are ~1-2 ng/g-ww in all matrices to approximately 0.3 to 1 ng/g-ww for D_6. Supporting information for LOD and MDL is presented in **Appendix A**.

VIII. RESULTS AND DISCUSSION

(A) Mink – Physical/food consumption data

Four mink were captured in the tributaries of Lake Pepin, one female (F) and three males (M); the pertinent data on the collected mink are presented in **Table 2**. The mink varied from approximately 750 g (F) to over 1400 g (M) in weight, with a body length range of 32 cm (F) to 36 cm (M); these findings are in agreement with average adult mink data collected by the U.S. Environmental Protection Agency (US EPA, 1993).

Stomach contents of the four mink are presented in **Table 3**, as analyzed by Michigan State University. Dietary items ranged from aquatic vegetation (all specimens) to fish and crayfish (minks 1 and 2), to avian species (mink 2), to meadow vole (mink 4) and muskrat (mink 3 and 4). The estimated weight contribution to dietary mass at death is presented for each mink in the final column of **Table 3**. These data indicate that dietary composition ranged from predominately aquatic organisms (mink 1) to virtually exclusively terrestrial species (minks 3 and 4). These feeding preferences likely impact the measured mink trophic level, as indicated by stable isotope levels. The stomach contents data show that the mink were not generally feeding only in the aquatic food web of Lake Pepin (i.e., all carbon flow is not through aquatic species), but rather feeding on a variety of terrestrial and aquatic species.

Stable isotope and percent lipid composition data are presented in **Table 4**. The mean $\delta^{13}C$ value was -23.8 and the mean $\delta^{15}N$ value was 11.2. Comparing the carbon isotope data to the respective values from Lake Pepin (Powell *et al.*, 2009), with a $\delta^{13}C$ range from -29.4 to -25.7, the results indicate that the carbon flow to the mink is not the same as the carbon flow in the aquatic compartment of Lake Pepin. If the $\delta^{15}N$ are used to calculate the trophic level of the mink, based on the aquatic food web of the lake (Powell *et al.*, 2009), the mink would occupy a trophic level between that of the Lake Pepin sediment and the benthic invertebrates ($\delta^{15}N$ range of 7.9 to 12.9). As a result, it appears that the prominent terrestrial component of the mink diet (mink 3 and 4) does not allow a trophic level numerical description consistent with the aquatic food web trophic levels of Lake Pepin (Powell *et al.*, 2009). Comparison of a "warm-blooded" or homeothermic species such as mink to the "cold-blooded" or poikilothermic aquatic species that dominated the Lake Pepin aquatic food web complicates the trophic level interpretation, due to metabolic and feeding differences, and seasonal differences of sample collection (Weisbrod *et al.*, 2009).

(B) Mink – cVMS concentrations in liver, fat, and muscle

The measured cVMS residues in Lake Pepin mink muscle, fat, and liver tissues are presented in **Table 5**, both on a wet-weight basis and lipid-adjusted basis. Wet-weight normalized residues ranged from less than the LOD for D_4 in all mink tissues, to ~1 ng/g in muscle and liver and 3-45 ng/g in fat for D_5, to <LOD to ~10 ng/g-ww for D_6. The lipid-adjusted concentrations varied from <LOD for D_4 in all tissues, to 5-92 ng/g-lipid for D_5 in all tissues, to <LOD to14 ng/g-lipid for D_6 in all tissues. Lipid-adjusted concentrations were generally highest in mink fat samples and the mean mink fat cVMS lipid-adjusted residues varied from <LOD for D_4, to 44 ng/g-lipid for D_5, to 5 ng/g-lipid for D_6. These mean mink fat lipid-adjusted cVMS residues were compared to lipid-adjusted concentrations for aquatic organisms from Lake Pepin (Powell *et al.*, 2009), as shown by the residue data presented in **Table 6**. For D_4, Lake Pepin lipid adjusted aquatic organism concentrations ranged from approximately 300 to 900 ng/g-lipid in benthic invertebrates, to ~40 to 350 ng/g-lipid in fish, to <LOD in mink fat (LOD = 1.4 ng/g-ww). For D_5, lipid-adjusted Lake Pepin concentrations ranged from approximately 4000 to 18000 ng/g-lipid in benthic invertebrates, to ~174 to 3000 ng/g-lipid in fish, to a mean value of 44 ng/g-lipid in mink fat. Finally for D_6, the Lake Pepin lipid-adjusted concentrations ranged from approximately 150 to 1300 ng/g-lipid in benthic invertebrates, to 10 to ~170 ng/g-lipid in fish, to a mean value of 5 ng/g-lipid in mink fat.

The potential reasons for the low levels of lipid-normalized cVMS residues in mink muscle, fat, and liver tissue, compared to whole fish residues from Lake Pepin, are numerous. First of all, TMF calculations make the assumption that all species data included are comparable. For example, it is assumed that the chemical assimilation efficiencies and metabolism rates are similar for all the organisms included in the TMF regression analysis (Broman et al., 1992, Rolff et al., 1993); clearly, this may not be the case. Cold- and warm-blooded animals (poikilotherms and homeotherms, respectively) have different energy requirements and biotransformation abilities (Sibly and Calow 1986), and combining these organisms in an trophic magnification evaluation tends to exaggerate TMF values to higher levels compared to using only species within a poikilothermic energy regime (Hop et al., 2002). Secondly, food web and carbon/nitrogen flows may undergo significant seasonal changes, and this may account for the disconnect in carbon flow between Lake Pepin fish/invertebrates and mink (Vezina and Savenkoff, 1999); in Lake Pepin, the benthic invertebrates/fish samples were collected during the summer months, while mink were collected in late fall (November). Lastly, Kelly et al. (2007) have suggested that lipophilic substances (log K_{ow} >5) with low octanol/air partition coefficients (log K_{oa} <6) may not accumulate in terrestrial mammals due to an elevated rate of respiratory elimination from tissues to air. As shown in Text Table 1, the cVMS materials all have log K_{ow} values >5 and log K_{oa} values <6, indicating that respiration or "exhalation" may be a significant loss mechanism for terrestrial mammals, thereby contributing to loss of these materials in terrestrial mammals in a food web system. This exhalation process has been experimentally confirmed as a significant loss process for D5 in rats and humans (Reddy et al., 2008).

Text Table 1. Physico-chemical parameters (~25 °C) for D_4, D_5, and D_6*.

Parameter	D_4	D_5	D_6
Log K_{ow}	6.49	8.03	8.87
Log K_{aw}	2.69	3.13	3.01
Log K_{oa}	3.80	4.90	5.86

*Data from personal communication with Shihe Xu, Dow Corning Corporation.

(C)Quality control

Quality control (QC) samples were prepared and analyzed in conjunction with the samples. The QC samples included solvent blanks, control rat tissue, and spike addition to control rat tissue and field samples. The nominal spike level and the results for quantifying D_4, D_5 and D_6 are presented in **Tables 7-9**. A single spike level concentration was prepared and used to spike triplicate samples. The spike amount into the control tissue or field sample was approximately 21 ng. The method produced acceptable accuracy and precision of within 15% for all quality control samples. An example of the solvent standard accuracy and standard curves obtained from the analysis are presented in **Table 10** and **Figure 1**, respectively. In all cases, the correlation coefficient (R^2) value was greater than 0.99. The GC-MS conditions are listed in **Table 11**.

IX. CONCLUSIONS:

These data collectively indicate low level ng/g-lipid cVMS residues in a top terrestrial species collected from the Lake Pepin area, the American mink (*Mustela vison*). The average cVMS concentrations in mink fat are significantly less than lipid-adjusted cVMS residues in Lake Pepin whole fish and benthic invertebrate organisms; a number of these species comprise part of the mink diet on Lake Pepin. While $\delta^{13}C$ stable isotope data do not clearly link the carbon flow between the aquatic food web and this terrestrial species for Lake Pepin, the low level cVMS residue data demonstrate that trophic magnification processes are not occurring in this key predator species in the Lake Pepin food web with the siloxane materials D_4, D_5, and D_6.

X. REFERENCES

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TABLES

Table 1. LODs and MDLs for cVMS materials in mink tissue.

	D4 (ng)	D5 (ng)	D6 (ng)
THF Extracts LOD:	0.42	0.19	0.36
	LOD (ng/g ww) based on average weight of sample		
Matrix	D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
Muscle (~weight 0.6 grams)	0.66	0.29	0.56
Fat (~weight 0.3 grams)	1.42	0.63	1.21
Liver (~weight 1.2 grams)	0.35	0.15	0.29

	MDL (ng/g ww)		
Matrix	D4 (ng/g)	D5 (ng/g)	D6 (ng/g)
Muscle	1.01	1.17	0.26
Fat	1.11	2.23	0.85
Liver	1.48	1.78	0.44

Table 2. Summary data on mink collected at Lake Pepin, MN

Sample ID	Description	Weight (g-ww)	Total length (cm) (without tail)	Total length (cm)	Liver weight (g-ww)	Liver %Total Weight	Muscle weight (g-ww)	Fat weight (g-ww)	Stomach weight (g-ww)	Stomach %Total Weight
Mink 1	Female 11-7-08, 4:30pm	743.7	32	50	34.9023	4.7	6.3475	1.1306	22.4900	3.0
Mink 2	Male 11-5-08, 10:00am	1294.3	33	54	31.7856	2.5	6.4913	3.7370	20.9658	1.6
Mink 3	Male 11-12-08, 4:00pm	935.3	33	56	53.6117	5.7	5.0078	1.5072	10.6661	1.1
Mink 4	Male 11-12-08 , 4:30pm	1426.0	36	58	44.7157	3.1	17.8434	1.0501	11.1325	0.8

Collection Coordinates

Mink 1 Easting 562,743; Northing 4,918,740

Mink 2 Easting 543,674; Northing 4,936,859

Mink 3 Easting 553,662; Northing 4,928,928

Mink 4 Easting 553,174; Northing 4,928,920

Table 3. Mink stomach contents analysis from Michigan State University (examinations performed by Dr. Matt Zwiernik of the Animal Science Department, under contract to Dow Corning).

			in grams	Estimated wt at consumption in g	%diet
Mink 1	**Stomach**	origional wt	24.335		
		Wt -content	13.218		
		content	11.117	Eaten within hour	
Frequency	**Items**				
1	Aquatic Vegatation		1.423	2	5%
1	Crayfish (Orconectes rusticus)		2.212	7	18%
4	Shinner (Cyprinidea)		6.232	30	77%
		Total wt Ident	9.867	39	
Mink 2	**Stomach**	origional wt	21.935		
		Wt -content	11.095		
		content	10.84	Eaten within hour	
Frequency	**Items**				
1	Aquatic Vegatation		0.73	2	0.6%
1	Crayfish (*Orconectes rusticus*)		1.322	4	1.2%
2	Shinner ?(Cyprinidea)		0.76	20	5.8%
1	Mouse (Peromyscus) White foot or deer		2.234	20	5.8%
1	Coot or Moorhen?		5.232	300	87%
		Total wt Ident	10.278	346	
Mink 3	**Stomach**	origional wt	10.429		
		Wt -content	9.902		
		content	0.527	Had not eaten within hour	
Frequency	**Items**				
1	Aquatic Vegatation		0.132	2	0.2%
1	Muskrat (*Ondatra zibethicus*)		0.342	900	99.8%
		Total wt Ident	0.474	902	
Mink 4	**Stomach**	origional wt	10.742		
		Wt -content	10.73		
		content	0.012	Had not eaten within hour	
Frequency	**Items**				
1	Aquatic Vegatation		0.01	2	0.2%
1	Muskrat (*Ondatra zibethicus*)		Trace	900	95%
1	Medow vole (*Microtus pennsylvanicus*)		Trace	45	5%
		Total wt Ident	0.01	947	

Note: For dietary composition calculations (based on biomass) we assume the following. Daily diet consists of 150g ww /day, for items of between 200 and 500 only 80% of the item is consumed and consumption occurs over 2 days, for dietary items greater than 500 g only 70% of the item is consumed and consumption is over 3 days.

Table 4. Percent lipid and stable isotope analysis of Lake Pepin mink liver, fat, and muscle tissue; work performed at Michigan State University.

Sample ID	% Water	Dry Sample Wt (g)	% Lipid dw	% Lipid ww	Date of lipid extraction	δ15N	δ13C	Date of analysis
m1 liver	73.83	0.2972	24.60	6.44	8/12/2009	*NR*	*NR*	*NR*
m2 liver	70.09	0.3725	21.23	6.35	8/12/2009	*NR*	*NR*	*NR*
m3 liver	76.20	0.2099	22.25	5.30	8/12/2009	*NR*	*NR*	*NR*
m4 liver	72.25	0.4745	16.82	4.67	8/12/2009	*NR*	*NR*	*NR*
m1 fat	36.09	0.1392	80.96	51.74	8/12/2009	*NR*	*NR*	*NR*
m2 fat	32.49	0.1546	76.39	51.57	8/12/2009	*NR*	*NR*	*NR*
m3 fat	33.77	0.2134	85.38	56.55	8/12/2009	*NR*	*NR*	*NR*
m4 fat	39.11	0.1820	79.73	48.55	8/12/2009	*NR*	*NR*	*NR*
m1 muscle	74.94	0.1835	13.62	3.41	8/13/2009	8.87	-21.77	8/19/2009
m2 muscle	78.26	0.1377	7.33	1.59	8/13/2009	11.93	-25.08	8/19/2009
m3 muscle	79.54	0.0808	4.08	0.83	8/13/2009	12.28	-24.43	8/19/2009
m4 muscle	77.01	0.1898	7.90	1.82	8/13/2009	11.74	-24.09	8/19/2009
					Mean =	**11.21**	**-23.84**	

NR = Not run

Table 5. D_4, D_5, and D_6 concentrations in Lake Pepin mink muscle, fat, and liver tissue. The residue levels shown are both the sample wet weight (ww)-adjusted concentrations and the lipid-adjusted concentrations. The mean concentrations of D_5 and D_6 represent average cVMS concentrations in fat tissue.

Sample ID	% Water	%Lipid (dw)	%Lipid (ww)	Average sample weight (g)	Average D4 ng/g - ww			Average D4 ng/g-lipid	Average D5 ng/g - ww			Average D5 ng/g-lipid	Average D6 ng/g - ww			Average D6 ng/g-lipid
Mink -1 (muscle)	74.94	13.62	3.41	0.9175	n = 2	-0.5	a,b	<LOD	n = 2	0.6	b	17.9	n = 2	0.2	a,b	1.8
Mink -2 (muscle)	78.26	7.33	1.59	0.9256	n = 2	-0.4	a,b	<LOD	n = 2	0.6	b	35.4	n = 2	-0.02	a,b	<LOD
Mink -3 (muscle)	79.54	4.08	0.83	0.6347	n = 7	-0.6	a,b	<LOD	n = 6	0.8	b	91.8	n = 6	-0.01	a,b	<LOD
Mink -4 (muscle)	77.01	7.90	1.82	0.8915	n = 2	-0.7	a,b	<LOD	n = 2	0.5	b	29.2	n = 2	0.1	a,b	1.2
Mink -1 (fat)	36 09	80.96	51.74	0.2686	n = 2	-0.8	c,d	<LOD	n = 2	45.5		88.0	n = 2	1.5		1.8
Mink -2 (fat)	32.49	76.39	51.57	0.2953	n = 7	-1.0	c,d	<LOD	n = 7	14.1	d	27.3	n = 7	1.1	c	1.4
Mink -3 (fat)	33.77	85.38	56.55	0.3625	n = 2	-0.8	c,d	<LOD	n = 2	30.1		53.2	n = 2	1.5		1.7
Mink -4 (fat)	39.11	79.73	48.55	0.2989	n = 2	-1.8	c,d	<LOD	n = 2	3.1	d	6.4	n = 2	11.1		14.0
Mink -1 (liver)	73.83	24.60	6.44	0.9506	n = 2	-0.5	e,f	<LOD	n = 2	1.6	f	25.2	n = 2	0.2	e,f	0.7
Mink -2 (liver)	70.09	21.23	6.35	1.2331	n = 2	-0.1	e,f	<LOD	n = 2	0.9	f	14.1	n = 2	-0.04	e,f	<LOD
Mink -3 (liver)	76.20	22.25	5.30	1.2160	n = 6	-0.3	e,f	<LOD	n = 6	0.9	f	16.3	n = 7	0.1	e,f	0.6
Mink -4 (liver)	72.25	16.82	4.67	0.9926	n = 2	-0.2	e,f	<LOD	n = 2	0.3	f	5.7	n = 2	-0.1	e,f	<LOD
Fat tissue only =				**[g]Mean =**				**<LOD**				**43.7**				**4.7**
				Stnd Dev =								**35.2**				**6.2**
				SE =								**17.6**				**3.1**

a: muscle samples are below limit of detection set at 0.66, 0.29, 0.56 ng/g ww for D4, D5 and D6, respectively
b: muscle samples is below method detection limit set at 1.01, 1.17, 0.26 ng/g ww for D4, D5 and D6, respectively

c: fat samples are below limit of detection set at 1.42, 0.63, 1.21 ng/g ww for D4, D5 and D6, respectively
d: fat samples is below method detection limit set at 1.11, 2.23, 0.85 ng/g ww for D4, D5 and D6, respectively

e: liver samples are below limit of detection set at 0.35, 0.15, 0.29 ng/g ww for D4, D5 and D6, respectively
f: liver samples is below method detection limit set at 1.48, 1.78, 0.44 ng/g ww for D4, D5 and D6, respectively

g: Only fat samples with detectable residue levels were used to calculate lipid-adjusted concentration levels and overall mean concentrations.

Sample corrected for instrument background on day of analysis

Table 6. Lipid-adjusted concentration of D_4, D_5, and D_6 in benthic invertebrate species, fish, and mink specimens collected from Lake Pepin, MN USA*

Species	TL (mean)	TL (SE)	%SE	Mean D4 (ng/g-lipid)	D4 (SE)	%SE	Mean D5 (ng/g-lipid)	D5 (SE)	%SE	Mean D6 (ng/g-lipid)	D6 (SE)	%SE
Midge	2.00	0.06	3.2	888	136	15.3	18114	3962	22%	1305	246	19%
Mayfly	2.03	0.12	6.0	309	26	8.3	3895	241	6%	148	20	13%
White sucker	2.64			314			2865			13		
Common carp	2.81	0.05	1.8	38	2	5.2	1050	269	26%	71	30	42%
Gizzard shad (adult)	2.84	0.04	1.4	118	2	1.5	816	111	14%	19	13	68%
Gizzard shad (YOY)	2.95	0.03	0.9	76	18	23.6	402	23	6%	99	64	65%
Silver redhorse	2.96	0.08	2.7	160	32	20.3	927	72	8%	74	28	38%
Bluegill	3.11	0.08	2.7	78	10	13.5	580	76	13%	23	8	36%
River carpsucker	3.26			351			2654			160		
Shorthead redhorse	3.33	0.13	4.0	101	45	44.9	927	72	8%	22	11	49%
Freshwater drum	3.39	0.09	2.7	36	14	39.0	513	230	45%	103	48	47%
Emerald shiner	3.42	0.21	6.2	98	31	31.8	1087	234	21%	166	65	39%
Black crappie	3.43	0.02	0.6	97	14	14.0	531	29	5%	10	0.2	2%
White bass	3.49	0.17	4.9	49	9	18.7	332	45	13%	17	11	66%
Smallmouth bass	3.54	0.02	0.5	91	33	35.8	398	25	6%	36	27	74%
Walleye	3.59	0.13	3.6	64	8	12.4	848	53	6%	25	12	49%
Quillback	3.60	0.06	1.6	140	25	17.6	1283	25	2%	54	18	34%
Largemouth bass	3.83	0.01	0.4	78	17	22.0	175	22	13%	13	2	17%
Mink (residues from fat)				<LOD (LOD ~1.4 ng/g-ww in fat samples)			44	18	40%	5	3.1	65%

*YOY = young of year, TL = trophic level, SE = standard error.

Table 7. Quality Control results for D_4

QC ID	Expected [D4] ng	Recovered [D4] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
		liver			
qc Liver 0-1	0	-0.19			
qc Liver 0-2	0	0.09			
qc Liver 0-3	0	-0.27			
QC Liver S-1	20.7	21.0	1%	-3%	4%
QC Liver S-2	20.7	20.0	-3%		
QC Liver S-3	20.7	19.5	-6%		
Mink 3 Liver s-1	20.7	19.5	-5%	-12%	7%
Mink 3 Liver s-2	20.7	17.7	-14%		
Mink 3 Liver s-3	20.7	17.1	-17%		
		fat			
qc Fat 0-1	0	-0.103			
qc Fat 0-2	0	0.029			
qc Fat 0-3	0	-0.037			
QC Fat S-1	20.7	23.0	12%	6%	10%
QC Fat S-2	20.7	23.2	13%		
QC Fat S-3	20.7	19.4	-6%		
Mink 2 Fat s-1	20.7	21.2	3%	0%	3%
Mink 2 Fat s-2	20.7	20.3	-2%		
Mink 2 Fat s-3	20.7	20.2	-2%		
		muscle			
qc Mus 0-1	0	-0.52			
qc Mus 0-2	0	-0.67			
qc Mus 0-3	0	-0.72			
QC Mus S-1	20.7	20.5	-1%	-3%	2%
QC Mus S-2	20.7	19.8	-4%		
QC Mus S-3	20.7	20.0	-3%		
Mink 4 Mus s-1	20.7	20.5	-1%	-1%	2%
Mink 4 Mus s-2	20.7	20.2	-2%		
Mink 4 Mus s-3	20.7	20.8	1%		

Table 8. Quality Control results for D_5

QC ID	Expected [D5] ng	Recovered [D5] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
		liver			
qc Liver 0-1	0	1.32			
qc Liver 0-2	0	1.30			
qc Liver 0-3	0	1.38			
QC Liver S-1	21.3	22.0	3%	4%	2%
QC Liver S-2	21.3	22.6	6%		
QC Liver S-3	21.3	21.8	3%		
Mink 3 Liver s-1	21.3	19.5	-8%	-11%	4%
Mink 3 Liver s-2	21.3	19.1	-10%		
Mink 3 Liver s-3	21.3	18.1	-15%		
		fat			
qc Fat 0-1	0	6.4			
qc Fat 0-2	0	9.4			
qc Fat 0-3	0	8.1			
QC Fat S-1	21.3	22.7	7%	5%	3%
QC Fat S-2	21.3	21.5	1%		
QC Fat S-3	21.3	22.5	6%		
Mink 2 Fat s-1	21.3	22.1	4%	4%	1%
Mink 2 Fat s-2	21.3	22.2	4%		
Mink 2 Fat s-3	21.3	22.3	5%		
		muscle			
qc Mus 0-1	0	4.93			
qc Mus 0-2	0	3.94			
qc Mus 0-3	0	4.65			
QC Mus S-1	21.3	20.3	-5%	-8%	3%
QC Mus S-2	21.3	19.4	-9%		
QC Mus S-3	21.3	19.0	-11%		
Mink 4 Mus s-1	21.3	22.6	6%	7%	3%
Mink 4 Mus s-2	21.3	23.6	11%		
Mink 4 Mus s-3	21.3	22.2	4%		

Table 9. Quality Control results for D_6

QC ID	Expected [D6] ng	Recovered [D6] ng	%Relative Error (Accuracy)	Average % Relative Error (Accuracy)	%RSD (Precision)
		liver			
qc Liver 0-1	0	-0.07			
qc Liver 0-2	0	0.14			
qc Liver 0-3	0	0.38			
QC Liver S-1	21.3	20.9	-2%	-1%	1%
QC Liver S-2	21.3	21.0	-1%		
QC Liver S-3	21.3	21.4	0%		
Mink 3 Liver s-1	21.3	21.0	-1%	-7%	7%
Mink 3 Liver s-2	21.3	19.7	-7%		
Mink 3 Liver s-3	21.3	18.4	-13%		
		fat			
qc Fat 0-1	0	0.12			
qc Fat 0-2	0	0.18			
qc Fat 0-3	0	0.20			
QC Fat S-1	21.3	22.1	4%	2%	2%
QC Fat S-2	21.3	21.9	3%		
QC Fat S-3	21.3	21.3	0%		
Mink 2 Fat s-1	21.3	22.0	4%	2%	2%
Mink 2 Fat s-2	21.3	21.4	0%		
Mink 2 Fat s-3	21.3	21.4	1%		
		muscle			
qc Mus 0-1	0	0.21			
qc Mus 0-2	0	0.15			
qc Mus 0-3	0	0.14			
QC Mus S-1	21.3	21.0	-1%	-2%	0%
QC Mus S-2	21.3	20.9	-2%		
QC Mus S-3	21.3	20.9	-2%		
Mink 4 Mus s-1	21.3	21.5	1%	1%	0%
Mink 4 Mus s-2	21.3	21.5	1%		
Mink 4 Mus s-3	21.3	21.4	1%		

Table 10. Method Results for Solvent Standards

Example Standard Curve 6-30-2009

Standard ID	Expected $[D_4]$ ng	$[D_4]$ found ng	%Relative Error (Accuracy)
STD 0.4	**3.42**	**3.62**	6.0
STD 0.8	**6.82**	**6.35**	7.0
STD 1.7	**13.9**	**13.6**	2.2
STD 3.5	**28.9**	**28.5**	1.2
STD 7	**58.5**	**59.9**	2.4
STD 15	**124**	**119**	3.7
STD 30	**244**	**246**	0.8
STD 60	**479**	**484**	1.0
STD 125	**989**	**1056**	6.7
STD 250	**2101**	**2086**	0.7
STD 500	**4300**	**4312**	0.3
STD 1000	**9562**	**9614**	0.5

Standard ID	Expected $[D_5]$ ng	$[D_5]$ found ng	%Relative Error (Accuracy)
STD 0.4	**3.56**	**3.60**	1.1
STD 0.8	**7.11**	**7.03**	1.1
STD 1.7	**14.53**	**14.23**	2.1
STD 3.5	**30.1**	**30.43**	1.2
STD 7	**61.0**	**60.4**	1.0
STD 15	**129.1**	**128.7**	0.3
STD 30	**254**	**260**	2.2
STD 60	**499**	**504**	1.0
STD 125	**1031**	**1047**	1.5
STD 250	**2190**	**2202**	0.5
STD 500	**4483**	**4521**	0.8
STD 1000	**9968**	**9645**	3.2

Standard ID	Expected $[D_6]$ ng	$[D_6]$ found ng	%Relative Error (Accuracy)
STD 0.4	**3.87**	**3.75**	3.1
STD 0.8	**7.72**	**7.97**	3.2
STD 1.7	**15.8**	**16.5**	4.4
STD 3.5	**32.6**	**33.1**	1.4
STD 7	**66.2**	**67.5**	2.0
STD 15	**140**	**138**	1.2
STD 30	**276**	**278**	0.9
STD 60	**542**	**534**	1.5
STD 125	**1119**	**1109**	0.9
STD 250	**2377**	**2283**	3.9

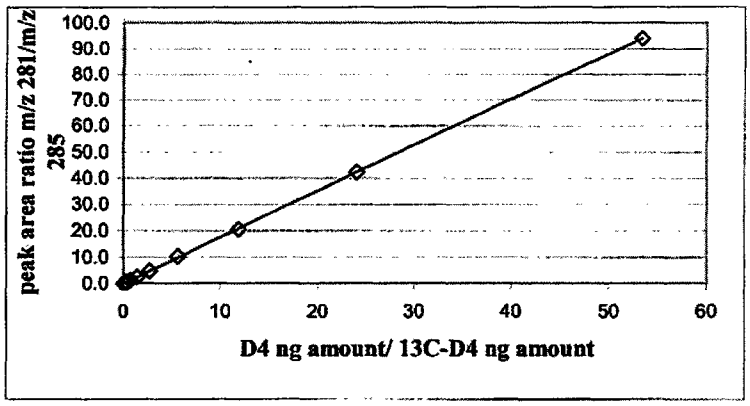
Table 11. GC-MS Conditions

Parameter	Setting
Instrument/Software	**HP6890 Series Gas Chromatograph** **HP5973 Mass Spectrometer** **HP ChemStation version D.03.00**
Inlet conditions	**Pulsed-Split 5:1, Split Flow 7ml/min Total Flow 11.7ml/min, Pulse pressure 20psi, pulse time 1min** **1 μL injection; Merlin Microseal, Temp: 150 °C**
Carrier	**Helium, 1 mL/min constant flow**
Column	**DB-WAXetr, 30m x 0.25mm, 0.25 mm film thickness**
Oven Program	**40 °C (hold 3 min) to 190°C at 25°C/min, to 240°C at 40 °C/ min**
Transfer line	**280 °C**
MSD	**Selective ion monitoring, m/z D_4-281, 13C-D_4-285, D_5-355, 13C-D_5-360, D_6-429, 13C-D_6-435; 100 ms dwell time**

Figures

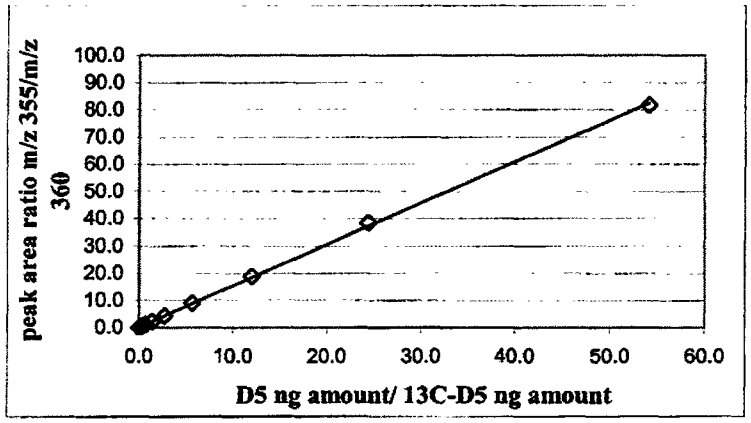
Figure 1. Tetrahydrofuran Standard Curves from analysis for cVMS materials D_4, D_5, and D_6.

D_4 Curve



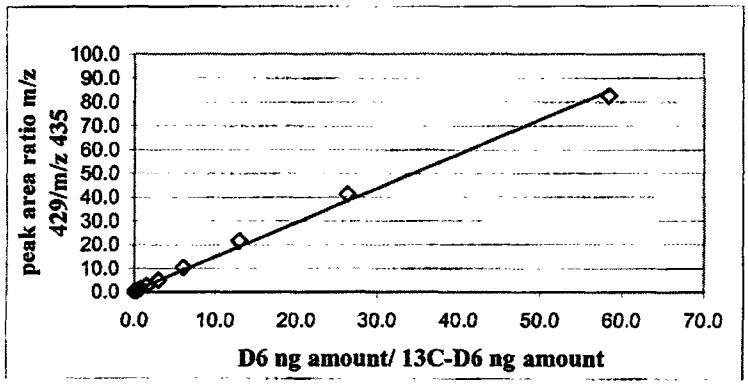
slope = 1.7531 Y - Intercept = 0.0053 R^2 = 0.9984

D_5 Curve



slope = 1.5619 Y - Intercept = 0.0013 R^2 = 0.9986

D_6 Curve



slope = 1.7389 Y - Intercept = 0.0058 R^2 = 0.9991

Note: Peak area ratios are corrected for background amounts as well as contributions from internal standard for D_4 and D_5, peak area ratios are corrected for background amounts for D_6.

Appendix A. Detection limit supplemental information

Procedural/Solvent Blanks

Sample ID	Absolute Amount (ng) D4	D5	D6
pb-1	0.7	*3.14*	0.26
pb-2	0.5	1.04	0.04
pb-3	0.8	1.09	0.05
pb-4	0.8	1.16	0.00
pb-5	0.8	1.07	0.10
pb-6	1.0	1.00	0.19
pb-7	0.8	1.07	-0.08
mean:	**0.8**	**1.07**	**0.08**
sd:	**0.13**	**0.1**	**0.11**
count:	**7**	**6**	**7**
$t_{n-1;0.99}$:	**3.143**	**3.365**	**3.143**
LOD:	**0.42**	**0.19**	**0.36**

Q test rejects PB-1 D5 at 95% confidence

Sample ID	d4 ng/g	d5 ng/g	d6 ng/g
Mus 3a	-0.74	0.27	-0.02
Mus 3b	-0.75	0.64	-0.04
Mus 3c	-0.68	0.69	-0.05
Mus 3d	-0.85	1.22	-0.10
Mus 3e	0.09	*3.41*	*2.59*
Mus 3f	-0.50	1.11	0.12
Mus 3g	-0.76	0.67	0.03
mean:	**-0.6**	**0.8**	**0.0**
sd:	**0.32**	**0.35**	**0.08**
count:	**7**	**6**	**6**
$t_{n-1;0.99}$:	**3.143**	**3.365**	**3.365**
MDL	**1.01**	**1.17**	**0.26**

Q test rejects Mus 3e D5 at 95% confidence

Q test rejects Mus 3e D6 at 95% confidence

Sample ID	d4 ng/g	d5 ng/g	d6 ng/g
Fat 2a	-1.53	*20.65*	1.48
Fat 2b	-0.44	*21.77*	0.98
Fat 2c	-0.87	11.56	0.71
Fat 2d	-1.23	11.79	1.02
Fat 2e	-1.04	11.33	1.30
Fat 2f	-0.69	10.25	1.28
Fat 2g	-0.96	11.18	0.87
mean:	**-1.0**	**11.2**	**1.1**
sd:	**0.35**	**0.59**	**0.27**
count:	**7**	**5**	**7**
$t_{n-1;0.99}$:	**3.143**	**3.747**	**3.143**
MDL	**1.11**	**2.23**	**0.85**

Sample ID Fat 2a and 2b are removed from the MDL calculation due to suspected laboratory contamination for samples 2a and 2b. Those samples were aliquoted at a different time than 2c-2g and are suspected to be contaminated with D5.

Sample ID	d4 ng/g	d5 ng/g	d6 ng/g
Liver 3a	-0.09	1.10	0.26
Liver 3b	-0.12	1.15	0.03
Liver 3c	-0.06	1.21	0.08
Liver 3d	-0.41	1.33	0.39
Liver 3e	-1.12	0.06	0.02
Liver 3f	*3.96*	*7.84*	0.04
Liver 3g	0.07	0.35	0.17
mean:	-0.3	0.9	0.1
sd:	0.44	0.53	0.14
count:	**6**	**6**	**7**
$t_{n-1;0.99}$:	**3.365**	**3.365**	**3.143**
MDL	**1.48**	**1.78**	**0.44**

Q test rejects Liver 3f D4 at 95% confidence

Q test rejects Liver 3f D5 at 95% confidence

Study Title:	Cyclic Methylsiloxane (cVMS) Materials in Surface Sediments and Cores for Lake Ontario
HES Study No:	10724-108
Sponsor Project No:	02/444/S024/07/0043A
Test Substances:	Octamethylcyclotetrasiloxane (D_4) Decamethylcyclopentasiloxane (D_5) Dodecamethylcyclohexadiloxane (D_6)
Authors:	David E. Powell, Ph.D. Gary E. Kozerski, M.S.
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Sponsor:	Centre Européen des Silicones (CES)
Testing Facility:	Dow Corning Corporation Health & Environmental Sciences (HES) 2200 West Salzburg Road Auburn, MI 48611
HES Group Manager:	Roy A. Campbell, B.S.
Study Completion Date:	09 November 2007

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ABSTRACT

Surface sediments and sediment cores were collected from Lake Ontario 17-20 July 2006 and analyzed for the cyclic volatile methylsiloxane (cVMS) materials D_4, D_5, and D_6. Surface sediments consisting of the upper 5-cm of sediment were collected from Toronto Harbor and the Kingston Basin. Sediment cores, which were sectioned into 5-mm to 10-mm thick strata, were collected from the Rochester, Mississauga, and Niagara Basins. The Kingston Basin is a shallow sedimentary basin located at the northeastern end of the lake. The Rochester, Mississauga, and Niagara Basins are deep sub-basins of the main sedimentary basin that covers the rest of the lake. Sediments in Toronto Harbor and the four sedimentary basins are known to be contaminated with a variety of toxic organic materials that enter the lake through direct discharges of treated wastewater, flow from the upper Great Lakes (Erie, Huron, and Michigan) and the Niagara River, and atmospheric deposition. Because of the significant potential for samples to become contaminated with cVMS materials, a rigorous quality control (QC) program was incorporated into all phases of the project and great care was taken to limit contamination during collection, storage, processing, and analysis. Nonetheless, results from the QC program indicated that background contamination was significant for some samples and could be attributed to exposure to air, sample processing, and the solvents used for extractions.

Surface sediments from Toronto Harbor contained the greatest wet weight (ww) and dry weight (dw) concentrations of the cVMS materials, which were 130 ng/g ww (287 ng/g dw) for D_4, 358 ng/g ww (790 ng/g dw) for D_5, and 89.6 ng/g ww (198 ng/g dw) for D_6. In contrast, concentrations of the cVMS materials in surface sediments and sediment cores from the four sedimentary basins were less than the analytical method limits of detection, which were 1.7 ng/g ww (5.8 ng/g dw) for D_4, 3.6 ng/g ww (11.9 ng/g dw) for D_5, and 1.8 ng/g ww (6.1 ng/g dw) for D_6. Moreover, the masses of D_4, D_5, and D_6 measured in the solvent extracts from these sediment samples were not significantly different from the masses measured in the reagent blanks and field blanks, indicating that the cVMS materials originated from the extraction solvents and/or processing procedures, and not from the sediment samples themselves. These results suggest that transport and/or deposition of cVMS materials to the sedimentary basins of Lake Ontario were very limited. The results also suggest that flow from the upper Great Lakes, atmospheric deposition, and direct discharge of wastewater were not likely to be significant sources of cVMS materials to the sediment deposition basins of lake. Nonetheless, the extent of transport and deposition of cVMS materials to the sediment basins of Lake Ontario can not be quantitatively evaluated without improving the analytical method and implementing procedures to further minimize sources of background contamination.

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SIGNATURES AND APPROVAL

This report consists of 71 pages with 8 figures, 25 tables, and no appendices. The undersigned have read and approved this report.

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INTRODUCTION

Cyclic volatile methylsiloxane materials (cVMS; specifically D_4, D_5, and D_6) are widely used in industrial and consumer applications and the wastewater stream represents a major post-use disposal route. Generally, cVMS materials are volatile, have very low water solubility, have intermediate values for K_{OA} (octanol/air partition coefficient), and have very high values for K_{OW} (octanol/water partition coefficient) and K_{AW} (air/water partition coefficient). Because of these partitioning properties (Table 1), cVMS materials occupy a somewhat unique chemical space and are expected to partition primarily to air during use and after disposal to wastewater. Multimedia modeling using a level I model (EQC model, Mackay et al. 1996), which provides a general indication of the likely media into which a chemical will partition, indicates that about 50-92% of the total emission of cVMS materials will partition to air (Powell 2007). Cyclic VMS materials that remain in the wastewater (about 8-50% of the total emission, Table 1) are efficiently removed during the wastewater treatment process, with an estimated 60-78% of the mass removed by adsorption to bio-solids (i.e., sludge), 18-40% removed by volatilization to air, and < 1-4% remaining in the effluent (Table 1).

The key properties known to influence the fate of cVMS materials in aquatic environments are hydrolytic degradation, volatility, very low water solubility, and a very strong tendency to adsorb to organic carbon and the surfaces of suspended solids. Because of their hydrophobic nature, cVMS materials that remain in the wastewater effluent stream (i.e. material which are not volatilized or removed to sludge) are expected to be associated with the dissolved, colloidal (i.e. associated with humic or fulvic acids) and particulate phases. However, our understanding of the fate and bioavailability of cVMS materials in aquatic environments (water, sediment and biota) is largely based on a combination of laboratory experiments and environmental fate modeling. Little data is currently available on the behavior of cVMS materials in the environment (reviewed by Brooke and Crookes 2006a; 2006b; 2006c) or measured levels of in different environmental compartments (Kaj et al. 2004; Kaj et al. 2005; Knudsen et al. 2007; Schlabach et al. 2007). The results of standard laboratory tests suggest that some cVMS materials may meet regulatory screening criteria for "P", "B" and "T" properties (persistent, bioaccumulative, toxic) in Europe (Brooke and Crookes 2006a; 2006b; 2006c) and North America (Government of Canada, 2007a; 2007b; 2007c). However, since the physiochemical behavior of these chemicals is somewhat unusual (particularly with respect to their volatility and very low water solubility), it is important that monitoring data be generated to confirm whether or not cVMS materials are present in the environment, and if so, at what levels.

Cyclic VMS materials may be removed from the water column by various processes, including volatilization, pH-dependent hydrolytic degradation, and deposition to the sediment bed. Re-suspension of sediments to which cVMS materials are sorbed, and subsequent partitioning into the water column, may result in additional hydrolytic degradation and volatile loss. Hence, persistence, spatial distribution, and bioavailability of cVMS materials in aquatic systems may be strongly influenced by water chemistry (i.e., pH), hydrologic flow, and system geomorphology. When released to receiving waters, cVMS materials are expected to re-distribute according to the prevailing concentrations of particulate and dissolved organic matter, which may impact the overall persistence and

bioavailability in aquatic systems. A highly sorbed fraction of cVMS may result in a reduction of volatile loss but also a reduction in bioavailability and hence, lower potential for accumulation in aquatic organisms. Cyclic VMS materials that remain associated with the particulate phase will either deposit to the bed sediment in depositional areas of the receiving water system or (in the case of very fine size fractions) be advected further afield (e.g. from near shore point of emission to offshore deposition basins).

In order to better understand the fate of cVMS materials in the environment, the Silicone Manufacturer Associations in Europe (Centre Européen des Silicones; CES) and North America (Silicones Environmental Health and Safety Council; SEHSC) have initiated environmental monitoring across study areas in Europe and North America. This monitoring program is anticipated to provide additional information and insight on: temporal trends; spatial distribution at the local, regional, and remote levels; sources of aquatic exposure; bioavailability; and the potential for bioaccumulation and biomagnification in the natural environment. The industry associations are working closely with competent regulatory authorities, academia, and industry in Europe and North America to identify potential study areas, develop scientifically robust experimental designs, and provide guidance on sample collection and data interpretation. As part of this effort, the industry associations were invited by Environment Canada to participate on a research cruise on Lake Ontario aboard the Canadian Coast Guard Ship (CCGS) *Limnos*. The overall objective of this collaborative study was to measure concentrations of cVMS materials, specifically, D_4, D_5, and D_6 in surface sediments and sediment cores collected from Lake Ontario.

MATERIALS AND METHODS

A. *Study Area*

The study area, Lake Ontario (Fig. 1a), has been described in detail elsewhere (Thomas et al. 1972; USEPA and Government of Canada 1995; LOLMP 1998, 2006; Beletsky et al. 1999; Forsythe and Marvin 2005; Marvin et al. 2003, 2004). Lake Ontario is the last of the chain of Laurentian Great Lakes that straddle the Canada/United States border. Its shoreline is bordered by the Province of Ontario on the Canadian side and New York State on the U.S. side. Since Lake Ontario is the downstream Great Lake, it is impacted by human activities occurring throughout the Lake Superior, Michigan, Huron, and Erie basins. More than 8.2 million people live in the Lake Ontario basin, concentrated in the northwest part of the Canadian shoreline, which is highly urbanized and industrialized and includes Metropolitan Toronto and the industrial center of Hamilton. The U.S. side of the lake is not as heavily populated, although there are concentrated areas of urbanization at Rochester, Syracuse, and Oswego. Outside of these areas, agriculture and forests dominate the land uses within the basin.

Lake Ontario, the 14th largest lake in the world, is smallest of the Great Lakes in terms of surface area (18,960 km^2), but is second in water depth only to Lake Superior. It is relatively deep, with an average depth of 86 meters and a maximum depth of 244 meters. Volume of the lake is estimated at 1640 km^3. Approximately

80% of the water flowing into Lake Ontario comes from Lake Erie through the Niagara River. The remaining flow comes from Lake Ontario basin tributaries (14%) and precipitation (7%). About 93 percent of the water in Lake Ontario flows out to the St. Lawrence River; the remaining 7 percent leaves through evaporation. The average hydraulic residence time of the lake is estimated to be about eight years. There are two main sedimentary basins within Lake Ontario: 1) the Kingston Basin, which is a shallow sedimentary basin located at the northeastern end of the Lake; and 2) a deeper main basin that covers the rest of the lake (Fig. 1a). Within the main basin there are three deep sub-basins: the Rochester, Mississauga, and Niagara Basins. These basins are bordered by a shallow inshore zone that extends along the perimeter of the main basin. The present sedimentology of Lake Ontario is generally characterized by continued deposition of fine clayey sediments in deep-water areas, as described in detail elsewhere (Thomas et al. 1972).

B. Sample Collection

Sediments were collected from Toronto Harbor and the four major sediment deposition basins in the lake—the Niagara Basin, Mississauga Basin, Rochester Basin, and Kingston Basin (Fig. 1b). Sediments in Toronto Harbor and the four sedimentary basins are known to be contaminated with a variety of persistent and hydrophobic organic materials that enter the lake through direct discharges of treated wastewater, flow from the upper Great Lakes through the Niagara River, and atmospheric deposition.

Surface sediments and sediment cores were collected 17-20 July 2006 (Fig. 1b; Table 2) during a research cruise aboard the Canadian research vessel *CCGS LIMNOS*. Surface sediments consisting of the upper 5-cm of sediment were collected from Toronto Harbor (station 725) and the Kingston Basin (station 81) using a stainless steel Ponar dredge. Surface sediment samples were removed from the Ponar on deck, placed into a pre-cleaned HDPE plastic bucket, homogenized with a stainless steel spoon, transferred to pre-cleaned glass jars with Teflon-lined lids and stored at about 4°C in the dark for the duration of the cruise. During homogenization large particulate materials (e.g., shells, sticks, stones, etc.) were removed from the samples by hand and discarded. After the ship had returned to port at Burlington, Ontario, the refrigerated samples were transferred to coolers and stored under frozen blue ice for transport to Dow Corning Corporation in Midland, Michigan. At Dow Corning, samples were transferred from the coolers to refrigerated storage at about 4°C in the dark until processed for extraction and analysis.

Sediment cores were collected from the Rochester Basin (station 64), Mississauga Basin (station 40), and Niagara Basin (station 13) using a box core. The box core was sub-cored on deck using three pre-cleaned 10 cm i.d. polycarbonate tubes. Two of the three subcores were immediately extruded and sectioned on deck using a hydraulic extruder in a glove box under positive flow of nitrogen gas. The third subcore, which was retained as a backup, was discarded after successful sectioning of the other two subcores. A duplicate box core and set of replicate subcores were also collected at station 64, and were extruded and sectioned on deck outside of the glove

box. To minimize smearing and contamination, the outer 1-cm of sediment in contact with the sides of the core tube was trimed and discarded during extrusion and sectioning. Subcores from stations 13 and 64 were sectioned into 5 mm thick strata from 0-6 cm and 10 mm thick strata from 6-12 cm. Subcores from station 40 were sectioned into 10 mm thick strata from 0-18 cm. Extruded strata from the replicate subcores were combined and placed into pre-cleaned glass jars with Teflon-lined lids and stored at 4°C in the dark for the duration of the cruise. After the ship returned to port at Burlington, Ontario, the refrigerated samples were transferred to coolers and stored under frozen blue ice for transport to Dow Corning Corporation in Midland, Michigan. At Dow Corning, samples were transferred from the coolers to refrigerated storage at about 4°C in the dark until processed for extraction and analysis.

C. *Reagents*

Hexanes (Optima grade) and acetonitrile (HPLC grade) were obtained from Fisher Scientific and used without further purification for extraction of cVMS materials from sediments. Anhydrous magnesium sulfate, also from Fisher Scientific, was used for removing incidental water from sediment extracts. Isotopically enriched ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6, used as internal standards for the GC-MS determination of cVMS materials in sediment extracts, were synthesized and characterized at Dow Corning Corporation (Midland, MI).

D. *Sample Preparation and Extraction*

1. Processing and Storage

Field-collected sediment samples and QC samples were stored in their original containers under refrigeration at about 4 °C in the dark until just prior to processing for analysis. Wet sediment samples were homogenized by stirring with a stainless steel spatula or mixing spoon, and sub-samples collected for sediment characterization and determination of cVMS concentrations. For sediment core samples from stations 13 and 64 (5 mm strata), there was sufficient space to homogenize each sample in the glass storage jar. Samples of surface sediments and the larger core samples from stations 64 and 40 (10 mm strata) were transferred to a stainless steel mixing bowl for homogenization. Any sediment remaining after removing the sub-sample was returned to the original storage container.

2. Sample Characterization

Sediment composition and characterization were determined by the Limnological Research Center at the University of Minnesota in Minneapolis. Small aliquots (about 10 g) of each sediment sample were placed into individual plastic specimen cups and shipped under ice from Dow Corning to the University of Minnesota by next day air on 07 September 2006. Samples were received in good condition at the University of Minnesota on 08 September 2006, and placed into refrigerated storage at about 4°C in the dark until processed for analysis. The upper ten strata from each of the three

sediment cores (stations 13, 40, and 64) and the surface sediment samples from Toronto Harbor (station 725) and Kingston Basin (station 81) were analyzed by *carbon coulometry* and *loss-on-ignition*. The remainders of the samples were not analyzed because cVMS materials were not detected in these samples.

3. Cyclic Volatile Methylsiloxane Materials (cVMS)

Field samples were processed for extraction of cVMS materials in two batches, grouped by collection station, 08-10 August 2006 (about 3 weeks post-collection). Samples from stations 13 and 40, and their associated QC samples, were processed in the first batch. The remaining field and QC samples from stations 64, 81, and 725 constituted the second batch. GC-MS analyses of the resulting solvent extracts were performed 09-14 August 2006.

For extraction of cVMS materials from sediment, a 6-g sub-sample of wet sediment was weighed into a single-use borosilicate glass vial (28 x 108 mm, ca. 40 mL capacity), followed by addition of 6 mL of acetonitrile. After brief manual agitation, 12 mL of hexanes was added to the vial. The hexanes solvent contained known concentrations of isotopically labeled $^{13}C\text{-}D_4$, $^{13}C\text{-}D_5$, and $^{13}C\text{-}D_6$ to serve as internal standard surrogates. The vial with sediment was re-weighed after each solvent addition so that accurate internal standard amounts could be determined. Capped vials were placed on a vortex mixer for 30 min, followed by brief centrifugation to facilitate separation of the phases. The upper hexane layer was removed to a round-bottom glass tube (20 x 150 mm) containing anhydrous magnesium sulfate (ca. 0.25 g) for drying the extract. A second portion of hexanes without the internal standards was added to the extraction vial. The extraction process was repeated and the hexanes were combined in the glass tube. The extract volume in each tube was reduced in volume to approximately 1-2 mL under a stream of high purity nitrogen in a 25 °C bath. A portion of the resulting concentrated extract was transferred to a crimp-cap vial for GC-MS analysis.

E. Sample Analysis

1. Loss-on-Ignition (LOI) Analyses

Loss-on-ignition (LOI) analyses were conducted by the Limnological Research Center at the University of Minnesota in Minneapolis. A small quantity (about 3 cm^3) of sediment from each sample was used to determine sediment composition by LOI analysis according to the recommendations of Heiri et al. (2001). The entire sediment sample was vigorously stirred until homogenized, then subsampled with a spatula into a pre-weighed ceramic crucible and weighed again. Samples were oven-dried at 100°C overnight, cooled completely, and weighed to determine water content. Samples were then heated in a muffle furnace at 550°C for four hours, cooled completely, and weighed to determine organic matter content. Samples were finally heated at 1000°C for two hours, cooled, and weighed to determine $CaCO_3$

content. The sample mass remaining after the 1000°C burn was considered the "inorganic" content, i.e., silicate minerals, oxides, and silicate algal (diatom) remains.

2. Carbon Coulometry Analyses

Coulometry analyses were conducted by the Limnological Research Center at the University of Minnesota in Minneapolis. Organic carbon and carbonate mineral content were determined on freeze-dried and ground samples by coulometric titration (Engleman et al. 1985), using a UIC model 5011 CO_2 coulometer. Results were obtained as total carbon (%TC) and total inorganic carbon (%TIC); with total organic carbon (%TOC) calculated by difference. Percent calcite was calculated by dividing %TIC by 0.12, the mole fraction of C in $CaCO_3$. Given the local geology and water chemistry of Lake Ontario, calcite was assumed to be the only carbonate mineral present. Identification of other carbonate phases in the lake sediments would lead to small corrections in this calculation.

3. cVMS Analyses

GC-MS analyses of the sediment extracts were performed on an Agilent 6890 gas chromatograph interfaced to an Agilent 5973 mass selective detector with an electron impact (EI) ionization source, operated in selected ion monitoring (SIM) mode. The GC was configured with a conventional inlet (150 °C) for making splitless injections (0.5 min purge time); lower inlet temperatures were useful for minimizing the magnitude of instrument-related background, with only modest reduction in sensitivity. Analytes were separated on a HP-5 capillary GC column (5% phenylmethyl silicone, 30 m x 0.25 mm x 0.25 μm df) with helium carrier gas (1 mL/min). Following a 3 min post-injection hold at 50 °C, the column oven temperature was increased to 190 °C over 5.6 min, followed immediately by a second ramp to 250 °C over 1.5 min. Typical retention times were 6.5, 7.6, and 8.7 min, respectively, for D_4, D_5, and D_6. The target ions used for quantitative analysis were: $D_4/^{13}C\text{-}D_4$, *m/z* 281 and 285; $D_5/^{13}C\text{-}D_5$, *m/z* 355 and 360; $D_6/^{13}C\text{-}D_6$, *m/z* 429 and 435. These ions are formed by loss of a single $-CH_3$ group from the parent molecule and have the highest abundance in the EI spectra, excluding the common $[Si(CH_3)_3]^+$ ion at *m/z* 73. Peak area ratios obtained from the resulting single ion chromatograms were used to calibrate response ratio against amount ratio for each compound using standards prepared in hexanes, and covering an approximate concentration range of 3.6 to 2700 ng/mL. The amounts of cVMS materials in each extract were determined from the resulting $1/(\text{peak area})^2$-weighted linear regression calibration functions, from which concentrations in the original sediment sample were calculated based on solids content.

F. *Quality Control*

Cyclic VMS materials are widely used in consumer products and may be present in personal care products, commercial products, and lubricants. Given the significant potential for sample contamination during collection, processing, storage, and analysis for cVMS materials in environmental matrices, a rigorous quality control (QC) program was developed and implemented in the field and laboratory.

1. Bias and Precision

Equipment in direct contact with sediment was decontaminated before collecting any samples by washing with dishwashing detergent followed by consecutive rinses with deionized water, acetone, and hexane. Sediments in direct contact with equipment that could not be decontaminated before use (i.e., box core, ponar, etc.) were not retained. To minimize potential contamination from air, sediment cores were immediately extruded and sectioned on deck using a hydraulic extruder in a glove box under positive flow of nitrogen gas. The potential for contamination from air was evaluated by analyzing strata from a duplicate set of sediment cores (station 64) that were extruded and sectioned on deck outside of the glove box. To minimize smearing and contamination, the outer 1-cm of sediment in contact with the sides of the core tubes were trimmed and discarded during extrusion and sectioning. Core tubes were used only once. Stainless steel instruments were rinsed with water during sectioning of the cores to prevent cross-contamination between strata.

To evaluate bias and precision, and to verify that samples were not contaminated by sample collection, handling, shipment, storage, and processing procedures, the following field and laboratory QC samples were collected and analyzed:

a) Reagent Blank

Extraction solvents dispensed directly into an empty extraction vial; used to detect contamination of solvents and containers, as well as contamination from analytical operations; 6 per analytical batch. Results used for blank-correction of sample data and calculation of instrument detection limits.

b) Field Blank

Sample container filled with reference sediment containing very low or non-detectable concentrations of cVMS materials; taken into the field and processed concurrently with field samples; 4 per sampling site. Results used for detecting contamination incurred during field operations, or sample storage and transport, and for calculation of detection limits.

c) **Field Blank Control**

Same as field blank, but never removed from the laboratory; 2 per sampling site. Results used for comparison to field blanks to identify contamination originating from outside the laboratory, and for calculation of detection limits.

d) **Reference Sample**

Sample container filled with reference sediment to which known amounts of cVMS materials were subsequently added; taken into the field and processed concurrently with field samples; 4 per sampling site. A single concentration of 60 ng/g ww (200 ng/g dw) was used for this study. Results used for determining loss of cVMS materials from sediment during field operations, or sample storage and transport, and for calculation of detection limits.

e) **Reference Sample Control**

Same as reference sample, but never removed from the laboratory; extracted concurrently with collection of field samples; 2 per sampling site. Results used for comparison to reference samples, primarily to detect problems related to analyte losses (e.g. storage stability), and for calculation of detection limits.

f) **Field Spike**

Duplicate sub-samples of field-collected sediment to which known amounts of cVMS materials were added directly to the solvent layer at commencement of solvent extraction procedure; 3 per sampling site. A single spike level of 250 ng, equal to a dry weight concentration of 250 ng/g for a sample size of 1 g dw, was used for this study. Results used for assessment of analytical recoveries and variability.

g) **Field Split**

Duplicate sub-samples of field-collected sediment processed for analysis as individual samples for the purpose of assessing analytical variability; 3 per sampling site.

h) **Laboratory Blank**

Extraction vial filled with a sub-sample of reference sediment known to contain very low or non-detectable concentrations of cVMS materials that remained in the lab during collection of field samples; 2 per analytical batch. Blanks were analyzed in parallel with field samples and used for assessment of daily analytical method performance.

i) Laboratory Spike

Extraction vial filled with a sub-sample of reference sediment, never leaving the lab, to which known amounts of cVMS materials were added directly to solvent layer upon commencing solvent extraction procedure; 2 per level per analytical batch. Spike levels of 25, 250, and 2500 ng were used for this study. Spikes were analyzed in parallel with field samples and used for assessment of daily analytical method performance.

j) Reference Sediment

Reference sediment used for the field blanks, field blank controls, reference samples, and reference sample controls was collected from Sanford Lake, a reservoir created by impoundment of the Tittabawasee River at Sanford, Michigan. Surface sediment (upper 5-10 cm) having a sandy-silt texture was collected on 06 June 2007. Characteristics of the surface sediment collected from Sanford Lake and used as QC samples for this study are shown below:

Classification	Silty Clay
Texture (%, dry wt)	
• Sand	13
• Silt	39
• Clay	48
Solids content (%, wet wt)	29.9
Water content (%, wet wt)	70.1
Total organic carbon (%, dry wt)[1]	3.52
LOI (organic matter content; %)	12.7
Bulk Density (gws cm^{-3})[2]	1.1

[1] Determined by Walkley Black titration method.

[2] Calculated from loss on ignition, and water content assuming a particle density of 2.6 g cm^{-3}. (Håkanson and Jansson 1983)

2. Limits of Detection

For field monitoring, a measurement that is less than a specified detection level (DL) may be: 1) reported as "below detection", 2) reported as zero, 3) reported as less than (<) the value of the DL, 4) reported as some value between zero and the DL, for example one-half the DL, or 5) reported as the actual value (positive or negative), whether or not it is below the DL. The last option, the reporting of the actual value, is the recommended procedure; otherwise the data is considered to be "censored". Hence, actual measured values are reported for this study, even if the values were less than the DL or were negative. The values of the various DL's are provided as a reference with a definition of how the DL's were determined.

Because of inadequate definitions in use and confusion of terms, detection levels are controversial. For example, the instrumental detection level is frequently used for the method detection level and *vice versa*. For the purpose of this study, the various detection levels as defined by APHA (1999) were used since they were frequently identified in the field monitoring literature. Although the terminology may differ from that provided in more definitive sources (ASTM 2003; IUPAC 1995, 2002) the definitions are analogous.

Methods for determining detection levels are available in various publications (Analytical Methods Committee 1987; Taylor 1987; Kateman and Buydens 1993; IUPAC 1995; Berger et al. 1996; ASTM 1997; Smith 1997; Eurachem 1998; APHA 1999; IUPAC 2002). Of the different detection levels that are defined, the instrument detection level (IDL), the lower limit of detection (LLD), and the method detection level (MDL) are the most valuable for field monitoring. Occasionally the IDL may be used as a guide for determining the MDL. The IDL, LLD, and MDL are very similar in concept to the signal-to-noise ratio. The IDL is based on the ability to distinguish between signal and noise of the instrument and is generally determined by repetitive analysis of matrix-free blanks. The LLD is a measure of a methods ability to detect an analyte in a sample matrix, and is generally determined by repetitive analysis of a sample with very low or non-detectable concentrations of the analyte. The MDL is a measure of a methods ability to quantify an analyte in a sample matrix and is generally determined by repetitive analysis of a sample spiked with a known level of analyte. The LDL will be greater than the IDL because of additional background noise resulting form the sample matrix and variability introduced through processing the sample for analysis. Similarly, the MDL will be greater than the LDL because of the higher concentration of analyte in the sample. The relationship among these limits of detection should be approximately (APHA 1999): IDL:LLD:MDL = 1:2:4. The minimum level of target analyte in a sample that can be detected and accurately quantified is generally defined as some multiple of the MDL, typically 5 to 20 times the MDL.

The IDL, LLD, and MDL were determined as a function of the variance associated with replicate analyses of matrix-free blanks (IDL), replicate analyses of a sample with very low or non-detectable concentrations of the cVMS materials (LLD), or replicate analyses of a sample containing a small, but measurable amount of cVMS materials (MDL). The IDL, LLD, and MDL at 99% confidence were then defined as:

$$DL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses. For this study, the IDL was

calculated using non-background corrected amounts of D_4, D_5, and D_6 measured in reagent blanks that were carried through the entire analytical procedure. The LLD was calculated using non-background corrected amounts and concentrations of D_4, D_5, and D_6 measured in the field blanks. Similarly, the MDL was calculated using non-background corrected amounts and concentrations of D_4, D_5, and D_6 measured in the reference samples. Concentration-based limits of detection for individual samples were calculated by dividing the mass-based limits of detection for the pooled samples by the mass of sample (wet weight or dry weight) that was analyzed. However, limits of detection based on dry weight concentrations, especially the LLD, were not considered appropriate measures of analytical performance because of artificial bias resulting from variation in water content between sediment samples and the absence of cVMS materials in these samples (see section A.1.d under Results and Discussion).

3. Background Correction

Measured amounts of cVMS materials in the samples were corrected for background levels of cVMS using results from the reagent blanks. Results for the reagent blanks (Table 3) represented background levels of cVMS materials associated with extraction solvents or lab ware, as well as contamination incurred during handling or treatment (e.g. volume reduction) of the extracts. Comparison of analytical results for all reagent blanks (n=18) indicated no significant differences (ANOVA; $p > 0.05$) for D_4 or D_6 between the two analytical batches of samples. In contrast, levels of D_5 in reagent blanks analyzed with the second analytical batch of samples (n=6; from stations 64, 81, and 725) were significantly greater (ANOVA; $p < 0.01$) than levels of D_5 in reagent blanks analyzed with the first analytical batch of samples (n=12; from stations 13 and 40). The greater amounts of D_5 in reagent blanks analyzed with the second analytical batch of samples were related to contamination originating from the compressed nitrogen cylinder used during the solvent evaporation step. Consequently, background levels of cVMS materials were estimated as the average amounts of D_4 and D_6 in reagent blanks pooled from both analytical batches (n=18) and the average amount of D_5 in reagent blanks pooled from the first analytical batch (n=12). The resulting estimates and associated uncertainties (mean ± 1s) for each material were 12.3 ± 2.9, 29.3 ± 6.3, and 17.1 ± 4.2 ng for D_4, D_5, and D_6, respectively (Table 3). These average values were used to background-correct the raw data for all remaining QC samples and field samples.

G. *Data Analysis*

Statistical analyses were performed using the Data Analysis Tool Package, as provided with Microsoft Excel 2003 (ver 11.0). A Type I error (α) of 0.05 was used to judge the significance of all statistical tests. A two-sample t-test assuming equal variances was used to test for differences in the amounts of cVMS materials measured in sediment cores collected at station 64 that were sectioned and processed in the glove box from those in replicate cores sectioned and processed outside of the

glove box. One-way analysis of variance (ANOVA) was performed to test for differences in mean amounts and concentrations (wet weight basis) of cVMS materials measured in reagent blanks, field blanks, and reference samples associated with each sample collection station or analytical batch of samples. If the omnibus *F* value indicated significant differences between the mean values, a Tukey-Kramer multiple comparisons test was used to compare individual means (Sheskin 2000) and to compute the critical difference between means (CD_{TK}). Critical difference was the minimum required difference in order for two means to differ significantly from one another at a pre-specified level of significance (i.e., $\alpha = 0.05$).

RESULTS AND DISCUSSION

A. *Quality Control*

1. Limits of Detection

Mass-based limits of detection were calculated using non-background corrected amounts of D_4, D_5, and D_6 measured across pooled reagent blanks (IDL), pooled field blanks (LLD), and pooled reference samples (MDL). Concentration-based limits of detection were calculated using non-background corrected concentrations (wet weight and dry weight) of D_4, D_5, and D_6 measured across pooled field blanks (LLD) and pooled reference samples (MDL). Concentration-based limits of detection for individual samples were calculated by dividing the mass-based limits of detection for the pooled samples by the mass of sample (wet weight and dry weight) that was analyzed. However, limits of detection based on dry weight concentrations, especially the LLD, were not considered appropriate measures of analytical performance because of artificial bias resulting from variation in water content between sediment samples and the absence of cVMS materials in these samples (see section A.1.d under Results and Discussion).

a) Instrument Detection Limit (IDL)

Results for the reagent blanks (Table 3) represented background levels of cVMS materials associated with extraction solvents or labware, as well as contamination incurred during handling or treatment (e.g. volume reduction) of the extracts. Comparison of analytical results for all reagent blanks (n=18) indicated no significant differences (ANOVA; $p > 0.05$) for D_4 ($CD_{TK} = 5.1$ ng) or D_6 ($CD_{TK} = 5.8$ ng) between the two analytical batches of samples. In contrast, levels of D_5 in reagent blanks analyzed with the second analytical batch of samples (n=6; from stations 64, 81, and 725) were significantly greater (ANOVA; $p < 0.01$; $CD_{TK} = 24$ ng) than levels of D_5 in reagent blanks analyzed with the first analytical batch of samples (n=12; from stations 13 and 40). The greater amounts of D_5 in reagent blanks analyzed with the second analytical batch of samples were related to contamination originating from the compressed nitrogen cylinder used

during the solvent evaporation step. Consequently, the uncertainty associated with background levels of cVMS materials were estimated as the standard deviation (s_0) of the average amounts of D_4 and D_6 in reagent blanks pooled from both analytical batches (n=18) and standard deviation (s_0) of the average amount of D_5 in reagent blanks pooled from the first analytical batch (n=12). The resulting estimates of the IDL were 7.3 ng for D_4, 17.1 ng for D_5, and 10.7 ng for D_6 (Table 3). These estimated IDL values represent the minimum amounts of D_4, D_5, and D_6 that could be detected in a matrix-free sample with 99% confidence.

b) Lower Limit of Detection (LLD)

The LLD was estimated based on the uncertainty associated with non-background corrected amounts of D_4, D_5, and D_6 measured in the field blanks and field blank controls. Amounts of D_4, D_5, and D_6 measured in the field blanks and field blank controls (Table 4) represented background levels associated with extraction solvents and labware, contamination incurred during collection, processing, and treatment (e.g. volume reduction) of the extracts, and the sediment matrix itself. The field blanks and field blank controls were prepared from a large, homogenous batch of reference sediment that was known to contain very low or non-detectable amount of cVMS materials. It was anticipated that results from all the field blanks and field blank controls would be pooled and the LLD calculated on basis of the pooled results. However, as previously discussed for the reagent blanks and determination of IDL, the field blanks and field blank controls associated with the analyses of samples from station 64 appeared to have been contaminated with D_5 (Table 4), relative to the field blank and field blank controls from stations 13 and 40 (ANOVA; $p < 0.01$; $CD_{TK} = 20$ ng). Consequently, LLDs for the cVMS materials were estimated using the standard deviation (s_0) of the average amounts of D_4 and D_6 in all the pooled field blanks and field blank controls (n=24) and the standard deviation (s_0) of the average amount of D_5 in field blanks and field blank controls pooled from the station 13 and station 40 samples (n=16). The resulting estimates of the LLD were 10.8 ng for D_4, 23.6 ng for D_5, and 10.7 ng for D_6 (Table 4). These estimated LLD values represent the minimum amounts of D_4, D_5, and D_6 that could be detected in a processed sediment sample with 99% confidence.

c) Method Detection Limit (MDL)

The method detection limit (MDL) was estimated based on the uncertainty associated with non-background corrected amounts of D_4, D_5, and D_6 measured in the reference samples (Table 5). Reference samples were prepared by adding known amounts of cVMS materials to a large, homogenous batch of reference sediment that was known to

contain very low or non-detectable amount of cVMS. A single concentration of 60 ng/g ww (200 ng/g dw) was used for this study.

It was anticipated that results from all the reference samples would be pooled and the MDL calculated on the basis of the pooled results. However, as previously discussed for the determination of IDL and LLD, reference samples associated with samples from station 64 appeared to have been contaminated with D_5 (Table 5), relative to the other reference samples (ANOVA; $p < 0.01$; $CD_{TK} = 33$ ng). Consequently, MDLs for the cVMS materials were estimated using the standard deviation (s_0) of the average amounts of D_4 and D_6 in all the pooled reference samples (n=24) and the standard deviation (s_0) of the average amount of D_5 in reference samples pooled from the station 13 and station 40 samples (n=16). The resulting estimates of the MDL were 54.1 ng for D_4, 70.2 ng for D_5, and 75.4 ng for D_6 (Table 5).

d) Concentration-Based Limits of Detection

Concentration-based limits of detection for individual samples were calculated by dividing the mass-based limits of detection for the pooled samples by the mass (wet weight or dry weight) of sample that was analyzed. However, low-level concentrations (and detection limits) were biased when expressed on the basis of dry weight. This bias resulted from 1) the background cVMS originating in the extraction solvents and/or from processing procedures, 2) using wet sediments for the analysis, and 3) natural variability of water content (or solids content) of the sediment samples (Tables 9-12).

The QC results showed that masses of D_4, D_5, and D_6 measured in the in the reagent blanks, field blanks were not significantly different (Tables 3-4). Similarly, masses of D_4, D_5, and D_6 measured in solvent extracts from sediment samples (except samples from Toronto Harbor) were not significantly different from the masses measured in the reagent blanks and field blanks (data not shown). This indicated that most (if not all) of the cVMS materials in extracts from the sediments originated from the extraction solvents and not from the sediment samples themselves. Because a constant target weight of wet sediment (about 6 g) was used for the analyses, the amount of sediment solids extracted (i.e., the dry mass) was inversely related to the water content of the samples. Consequently, the mass of cVMS in the sample extracts was essentially constant across all strata whereas the mass of solids in the strata varied with water content of the sample. The result of this artifact was that dry weight concentrations (i.e., ng/g dw) had the appearance of being greater in the surface sediments, relative to deeper sediments, because of the greater water content of the surface sediment. In contrast, concentrations of cVMS expressed on the basis of wet weight, which is how the samples were dispensed for

processing and analysis, were not significantly different (ANOVA; $p > 0.05$). Therefore, for this study, dry weight concentration-based limits of detection for individual samples were not considered to be appropriate measures of analytical performance.

e) Comparison to Other Studies

The limits of detection estimated for analysis of sediments from Lake Ontario should represent the minimum amounts of cVMS that could be detected in a matrix-free sample (IDL), the minimum amounts of cVMS that could be detected in a processed sediment sample (LLD), and the minimum amounts of cVMS that could be quantified in a processed sediment sample (MDL). The relationship among these limits of detection should be approximately (APHA 1999): IDL:LLD:MDL = 1:2:4. However, the MDL values are likely to have been overestimated because concentrations of cVMS in the reference samples used to estimate the MDL were generally greater than five times the MDL. Hence, it was decided that the actual limit of detection was between the LLD and the MDL, and that the LLD better represented the amount of cVMS in the original sediment sample required to give a response that was statistically distinguishable from the reagent blanks and matrix background.

As shown in the summary below, the limits of detection for analysis of sediments from Lake Ontario (this study) were similar to limits of detection reported for analysis of sediments from the Nordic environment (Kaj et al. 2005). However, in contrast to the Lake Ontario limits of detection, the Nordic limits of detection were calculated based on replicate analyses of matrix-free water blanks rather than replicate analyses of reagent blanks and sediment samples. The Nordic limits of detection do not incorporate uncertainty resulting from the sample matrix and sample processing. Consequently, the Nordic limits of detection were likely underestimated (Analytical Methods Committee 1987), and reported detection and occurrence of cVMS materials in sediment may have been over estimated.

	Lake Ontario (ng)		Nordic Samples (ng)	
cVMS	IDL[1]	LLD[2]	LoD[3]	LoQ[4]
D_4	7.3	10.8	3.9	19.5
D_5	17.1	23.6	1.9	9.5
D_6	10.7	10.7	1.5	7.5

[1] IDL: instrument detection limit (replicate analyses of reagent blanks)
[2] LLD: lower limit of detection (replicate analyses of sediment)
[3] LoD: limit of detection (replicate analyses of water blanks)
[4] LoQ: limit of quantification (calculated as 5 times the LoD)

2. Bias and Precision

Tabular summaries of the analytical results for the three sets of QC samples associated with this study are provided in Tables 6 through 8.

The results for the reagent blanks represented background levels of cVMS associated with extraction solvents or labware, as well as contamination incurred during handling or treatment (e.g. volume reduction) of the extracts. In comparing the results for the two sets of six reagent blanks associated with analysis of the first batch of samples from sites 13 and 40, very good agreement was observed. For the second analytical batch that included all remaining field samples (sites 64, 81, and 725), the six reagent blanks gave results that fell into two distinct groups. This was particularly evident for D_5 where the average blank value varied by 50 ng between the sets. This observation was apparently related to how the sample extracts were grouped for the solvent evaporation step. Since the evaporator could only accommodate 50 samples at a time, the extracts were divided into two sets, which were processed using different cylinders of compressed nitrogen. Subsequent work has shown that blank levels can increase dramatically when first using a new cylinder, irrespective of whether it came from the same fill lot as the previous cylinder. Blank levels then decrease with continued use of the initially problematic cylinder. This appeared to be the case with the second batch of QC and field samples. Fortunately, the field sample extracts were processed with the set of reagent blanks which showed the lower background levels. However the QC samples from this latter set were likely impacted, as suggested by the greater variability observed in some of these samples.

Generally, the mean amounts of D_4, D_5, and D_6 measured in the reagent blanks (Table 3) were less than or equal to the mean amounts measured in the field blanks (Table 4), with the exception of samples associated with station 64, as previously discussed. These results demonstrated that the extraction solvents and the solvent evaporation step represented the greatest sources of contaminant cVMS during this study. The results also demonstrated that samples were not compromised by collection, processing, and storage procedures in the field.

In general, highly repeatable and quantitative results were observed for the laboratory spike samples at all levels, when adjusted for the laboratory blanks. Including the results from both sample analysis campaigns, spike recoveries ranged from 78 to 121% for all analytes at the lower 25 ng level. The two lowest recoveries (78.2, 79.7%), observed for D_5 in the batch associated with the elevated reagent blanks, were related to a large discrepancy between the two laboratory blank samples which were used to correct for any native cVMS detected in the reference sediment; this was not observed for D_4 or D_6. The three highest individual recoveries, ranging from 111-121%, were all associated with D_6 at the 25 ng level. For the two greater spike levels, the

range of recoveries was narrower, 99.0 to 107% across all compounds. These results demonstrated acceptable performance of the analytical method in providing quantitive results over a range of 25 to 2500 ng in the sample extracts, equal to the same range of dry weight concentration for a typical 1 g dw sub-sample.

As shown in the QC results tables (Tables 6-8), good agreement was observed among the three sets of field blanks (each n=4). For D_4, D_5, and D_6, respectively, the range of average field blank concentration was 1.3 to 3.9, -0.4 to 7.9, and -0.3 to 2.7 ng/g dw. These results were generally consistent with previous observations for sediments obtained from the same location. Typical standard deviations were on the order of ±1 to 2 ng/g dw; the only exception involved the D_5 results from the final QC set, which showed a much greater concentration range, -10.6 to 11.5 ng/g dw. This was probably related to the increased variability observed for D_5 in the corresponding reagent blanks, as discussed above. The majority of the reported concentrations for the field blank controls were not statistically different from the field blanks; 10 of the 18 values were within ±2 standard deviations of the reported average for the field blanks. Two of the remaining 8 concentrations for the controls were actually greater than +2 standard deviations of the average field blank concentration. For the remaining 6 cases where the observed concentrations for the field blank controls were less than -2 standard deviations, the discrepancy was less than 5 ng/g dw; in 5 of these cases, the discrepancy was 1 ng/g dw or less. These results indicated that there was no evidence for significant contamination of field samples during collection, processing, and storage aboard ship, or transport of the samples to the lab.

For the two sets of reference samples associated with sites 13 and 64 and analyzed during the first analysis set, average recoveries ranged from 91.7 to 102% across all cVMS materials. Standard deviations were between ±1 and 3% (n=4). Similar results were obtained for the reference sample controls, the analyses of which were initiated in the lab on the days that the field samples were collected. For the third set of reference samples associated with the field samples from the other collection sites, lower and more variable average recoveries were observed for all materials. A similar trend was observed for the reference sample controls. Inspection of the results for the individual samples revealed that certain samples showed uniformly lower recoveries across the analytes. Even duplicate analysis of one of the two reference sample controls showed greater than expected variation, suggesting that the problem was likely due to analytical error rather than actual analyte losses. Together, the above observations supported the conclusion that insofar as the reference sediments are representative of those collected from Lake Ontario, no significant extent of analyte loss or transformation was observed during the time between sample collection and analysis.

The field spikes, which were performed by adding a known amount of cVMS to a sediment-solvent mixture at the time of extraction, served mainly to verify the absence of matrix effects associated with analysis of the field samples. Duplicate sub-samples of three sediments selected from the upper, middle, and lower one-third of the strata from each of the three core sites were spiked. Very good results were observed for all cVMS materials across the three QC sets, with average recoveries ranging from 97.4 to 103%, and overall standard deviations of ±0.8 to 6.5%. For the 9 sets of duplicate sample spikes the absolute difference between the duplicates ranged from 0.4 to 14.2%; excluding the D_5 results from the third QC sample set, the range was only 0.4 to 3.1%. These results demonstrated the absence of interferences or other matrix-dependent effects associated with analysis of the field sediments, as well as good analytical precision at the chosen spike level.

Field splits were intended to provide another metric of analytical variability. An additional sub-sample was analyzed from each of three sediment strata selected from different locations (upper, mid, and lower) in the core. For each split sample, the absolute differences in apparent cVMS dry weight concentrations were calculated. The average concentration difference and associated standard deviation (n=3) were calculated for each analyte (Tables 6-8). Unfortunately, since the sample concentrations were found to be at or below the limit of detection, the field splits gave no information regarding repeatability at quantitative levels.

Non-background corrected amounts of cVMS materials in sediment cores collected at station 64 were generally greater in cores sectioned and processed outside of the glove box relative to amounts in cores sectioned and processed inside the glove box (Fig. 2). The differences were statistically significant for D_6 ($p = 0.01$), marginally significant for D_5 ($p = 0.11$), and not significant for D_4 ($p = 0.25$). These results suggest that sediment samples may be contaminated with cVMS materials if exposed to air or processed outside of a controlled environment.

B. Sediment Characteristics and Core Chronology

1. Sediment Characteristics

Sediment core profiles for total organic carbon (TOC), water content, bulk density and $CaCO_3$ content were similar across the three lake basins (stations 13, 40, and 64) where cores were collected (Tables 9-12). Generally, TOC and water content were greatest in the surface strata and decreased with increasing depth in the sediment column. Bulk density, which is a function of water content and solids content, showed a slight increase with increasing depth in the sediment column that was indicative of sediment diagenesis and compaction processes.

Comparison of the surface sediments across the lake (Table 13) indicated that TOC and water content were greater in the deep basin sediments (stations 13, 40, and 64) and that bulk density was greater in the shallow water sediments (stations 725 and 81). Differences in bulk density and TOC between the deep basin sediments and the shallow water sediments presumably reflect focusing of fine-grained solids (i.e., silts and clays), which contained elevated amounts of TOC from the shallow near-shore areas to the deeper off-shore areas. Total organic carbon contents in the upper 5-cm of surface sediment ranged from about 2.1-2.4 % (dry weight) in Toronto Harbor (station 725) and Kingston Basin (station 81) to about 4.4-5.1 % in the deep basins (Table 13). Total organic carbon contents in the range of 4-5% are typical of surface sediments from the deep basins of Lake Ontario (Thomas et al. 1972; Kemp et al. 1974; Eisenreich et al. 1989; Wong et al. 1995). Surface accumulation rates for organic carbon range from 1.4 mg cm^{-2} yr^{-1} in the Niagara Basin to 3.1 mg cm^{-2} yr^{-1} in the Rochester Basin (Wong et al. 1995).

2. Core Chronology

Sediment cores from this study were not chronologically dated or analyzed for ^{210}Pb. Results from other studies (Table 14) indicated that the mass-based sedimentation rate was about 0.03 g cm^{-2} y^{-1} in the Niagara Basin (Pearson et al. 1997; Wong et al. 1995), about 0.03-0.06 g cm^{-2} y^{-1} in the Mississauga Basin (Pearson et al. 1997; Song et al. 2005; Peck et al. 2006; Yang 2006), and about 0.04-0.07 g cm^{-2} y^{-1} in the Rochester Basin (Pearson et al. 1997; Song et al. 2005). These mass rates of sedimentation are equivalent to linear rates of sedimentation of about 0.2-0.4 cm y^{-1} (Oliver et al, 1989; Wong et al. 1995; Marvin et al. 2002b; Yang 2006). Consequently, the sediment core profiles represent about 30-60 years of sediment deposition for the Niagara and Rochester Basins and about 45-90 years of sediment deposition for the Mississauga Basin. The estimated time resolutions for the cores were 1.3-2.5 years/stratum for the Niagara and Rochester Basins and 2.5-5.0 years/stratum for the Mississauga Basin.

3. Focusing Factors

Focusing is the process by which fine sediment particles and associated materials are suspended by currents and episodic storm events and redistributed laterally within a lake basin, with particles typically being transported from shallower near-shore regions to deeper, more quiescent regions (Robbins et al. 1978; Bell and Eadie 1983; Wong et al. 1995). The focusing factor describes the enhanced or reduced sedimentation at a particular location relative to the lake wide average. A focusing factor greater than 1 indicates a location with greater than average sedimentation. Reported focusing factors for the deposition basins in Lake Ontario (Table 14) are about 1.1 in the Niagara Basin (Pearson et al. 1997; Wong et al. 1995), about 1.2-1.7 in the Mississauga Basin (Peck et al. 2006; Pearson et al. 1997; Song et al. 2005; Wong et al. 1995), and about 1.2-2.0 in the Rochester Basin (Pearson et al. 1997; Song et al. 2005; Wong et al. 1995). Sedimentation rates and

focusing factors are generally higher in the eastern portion of Lake Ontario because of the counterclockwise circulation pattern in the lake (Kemp and Harper 1976; Wong et al. 1995) and subsequent trapping of particles in the eastern basin (Pickett and Bermick 1977; Pickett and Dossett 1979; Wong et al. 1995).

C. *Cyclic Methylsiloxane (cVMS) Materials*

Concentrations of D_4, D_5, and D_6 measured in the sediment cores and surface sediments are summarized in Tables 15-19 (wet weight concentrations), Tables 20-24 (dry weight concentrations), Figs. 3-5 (sediment core profiles) and Figs. 6-8 (surface sediments). Cyclic volatile methylsiloxane materials were greater than the LLD only in the surface sediment sample collected from Toronto Harbor (station 725; Tables 19 and 24; Figs. 6-8). Concentrations of the cVMS materials in the Toronto Harbor sample were 130 ng/g ww (286 ng/g dw) for D_4, 358 ng/g ww (790 ng/g dw) for D_5, and 89.6 ng/g ww (198 ng/g dw) for D_6. In contrast, concentrations of the cVMS materials in the surface sediments (Tables 19 and 24; Figs 6-8) and sediment cores (Tables 15-18, 20-23; Figs 3-5) from the four sedimentary basins were less than the sample LLDs and less than or equal to the pooled LLDs, which were 1.7 ng/g ww (5.8 ng/g dw) for D_4, 3.6 ng/g ww (11.9 ng/g dw) for D_5, and 1.8 ng/g ww (6.1 ng/g dw) for D_6. Generally, mean concentrations of D_4, D_5, and D_6 in surface sediments from the four sedimentary basins (i.e., the upper 4 to 8 cm of sediment, depending on location) were not significantly different (ANOVA; $p > 0.05$). Moreover, mean concentrations of D_4, D_5, and D_6 measured in solvent extracts of surface sediments from the four sedimentary basins were less than or equal to mean concentrations measured in field blanks and reagent blanks. These results indicate that cVMS materials measured in the sediment samples originated from the extraction solvents and that detectable levels of D_4, D_5, and D_6 were not present in sediments from the four sedimentary basins.

Our results for cVMS materials in surface sediments from Lake Ontario were comparable to results reported for surface sediments from the Nordic environment (Kaj et al. 2005) collected from locations defined as background (n=9), urban (n=10), and point source (n=5). The cVMS materials for the Nordic environment were not detected (detection limits: 3-65 ng/g dw for D_4, 2-30 ng/g dw for D_5, 1-25 ng/g dw for D_6) in surface sediments collected from the background locations. For surface sediments from the urban and point source locations (n=15), D_4 was measured in 1 sample (84 ng/g dw), D_5 was measured in 12 samples (mean 0.21 ng/g dw; range 2-2000 ng/g dw), and D_6 was measured in 6 samples (mean 36 ng/g dw; range 1-170 ng/g dw). Except for D4, concentrations of cVMS materials measured in Toronto Harbor sediments (this study) were also comparable to concentrations measured in sediments from the Inner Oslofijord near the Bekkelaget sewage treatment plant (Schlabach et al. 2007). Concentrations of cVMS in surface sediments from the the Inner Oslofijord were below detection (4-38 ng/g dw) for D_4, ranged from 93-920 ng/g dw for D_5, and from <17-100 ng/g dw for D_6. Based on these results, it was concluded (Kaj et al. 2005; Schlabach et al. 2007) that cVMS materials in sediments from the Nordic Environment were not widespread and were only found in sediments

from urban areas and areas in close proximity to sewage treatment plants. The results from this study for Lake Ontario further support this conclusion.

Sediments in Toronto Harbor and the sedimentary basins in Lake Ontario are known to be contaminated with a variety of persistent hydrophobic compounds (for example, PCBs, DDT, pesticides, etc) that enter the lake through direct discharges of treated wastewater, flow from the upper Great Lakes through the Niagara River, and atmospheric deposition. Numerous studies (for example: Eisenreich et al. 1989; Muir et al. 2001; Marvin et al. 2002a, 2002b, 2003a; Forsythe and Marvin 2005; Song et al. 2005; LOLMP 2006; Peck et al. 2006) have shown that persistent hydrophobic compounds accumulate in the bottom sediments of Lake Ontario such that historic use and disposal patterns are preserved in sediment core profiles. The profiles of hydrophobic compounds in a sediment core reflect input rates to a water body if sorption to particles and deposition to sediments is a major loss process for removal from the water column. If a hydrophobic compound is not sufficiently persistent in the water column (i.e., is removed by degradation or other processes such as volatilization), sedimentation will not be a significant removal mechanism, the compound will not accumulate in the sediment column, and a sediment profile will not be observed. Consequently, results from this study, which show non-detection of cVMS materials in the sediment deposition basins of Lake Ontario, suggest that transport and/or deposition of cVMS materials to the sedimentary basins of Lake Ontario were very limited. The results also suggest that flow from the upper Great Lakes, atmospheric deposition, and direct discharge of wastewater were not likely to be significant sources of cVMS materials to the sediment deposition basins of lake. However, the extent of transport and deposition of cVMS materials to the sediment basins of Lake Ontario, while apparently low, can not be quantitatively evaluated without improving the analytical method and implementing procedures to further minimize sources of background contamination.

The highest concentrations of persistent hydrophobic compounds in Lake Ontario sediments are associated with fine-grained depositional sediment typically observed within the major lake basins. Concentrations and spatial distributions in the surface sediments are similar across the basins (Marvin et al. 2002b, 2003a, 2004) because of the predominant circulation pattern in Lake Ontario, which resembles a counterclockwise gyre (Pickett and Bermick 1977). As a result of this circulation pattern, hydrophobic contaminants associated with suspended particulate material in the water column are uniformly distributed on a lake-wide basis. Studies have shown that contaminants such as Mirex (Pickett and Dossett 1979) and fluorinated organic compounds that enter Lake Ontario from the Niagara River (Jaffe and Hites 1985, 1986), which enters the lake on the western shore, are carried to the eastern basins of the lake and ubiquitously deposited in sediments of the major deposition basins. Similarly, high concentrations of short-chain chlorinated paraffins measured in the Niagara Basin of the lake (Marvin et al. 2003b) were similar to or greater than concentrations measured in some harbors and embayments, including Toronto Harbor (Muir et al 2001). These studies demonstrate that the water column dynamics in Lake Ontario are sufficient to distribute fine-grained organic rich particles throughout the

lake within a relatively short time period (Wong et al. 1995), such that hydrophobic compounds adsorbed to the particulates are deposited to the bed sediments in proportion to the amount of sediment focusing.

Removal of a chemical substance from the water column by sedimentation is largely determined by the partitioning properties of the substance and by the organic carbon content of the sorbing matrix, which is generally associated with fine-grained suspended solids, such as silts and clays. Hydrophobic materials readily adsorb to the organic-rich fraction of silts and clays (Håkanson and Jansson 1983; Stumm and Morgon 1996; Schwarzenbach et al. 2002), which may be transported long distances to more quiescent areas where they deposit to the bed sediments in proportion to the amount of sediment focusing. The residence time of a contaminant in a water column is strongly dependent on the amount of organic particulate matter in the water column and the affinity of the contaminant for the suspended particulate material (Eadie and Robbins 1987). Affinity of a contaminant for particulate material is typically defined by a particle-water distribution coefficient (K_d; in mL g^{-1}), as:

$$K_d = \frac{C_P}{C_W} \approx K_{OC} \times f_{OC}$$

where C_P is the concentration (mg g^{-1}) in the particulate phase, C_W is the concentration (mg mL^{-1}) in the dissolved phase, K_{OC} is the organic carbon to water partition coefficient (mL g^{-1}), and f_{OC} is the fraction of organic carbon in the particulate phase (g g^{-1}). The fraction of contaminant associated with the suspended particulate phase (f_P) is then:

$$f_P = \frac{K_d(TSM)}{1 + K_d(TSM)}$$

where TSM is the concentration (g mL^{-1}) of total suspended material in the water column. Under ideal conditions, the apparent residence time of a perfectly persistent (i.e., does not degrade) contaminant in the water column of a lake (T_A), with respect to particle settling, is related to the value of f_P by:

$$T_A = \frac{T_L}{f_P}$$

where T_L is the mean lifetime of a particle settling through the water column of the lake and is equal to the average depth of the lake divided by the characteristic settling rate for the particle (approximately 1 m d^{-1}). Based on these simple relationships, it is apparent that at sufficiently large values of K_d and/or TSM, the fraction of contaminant associated with the particulate phase (f_P) can approach 1 (or 100% sorbed) and the apparent residence time in the water column is equal to the mean lifetime of the particles in the water column. In contrast, if values of K_d and/or TSM are small the fraction of contaminant associated with the particulate phase (f_P) is low

and the apparent residence time in the water column becomes greater than the mean lifetime. Mean particle settling times are always much shorter than hydraulic residence times in a lake. For example, the mean particle setting time for Lake Ontario is about 0.24 years compared to a hydraulic residence time of about 6 years. Consequently, the significance of sedimentation as a removal mechanism for a persistent hydrophobic compound increases as the K_d or the amount of suspended particulates increases. As the apparent residence time of the particle associated contaminant increases and approaches the hydraulic residence time of the lake, sedimentation becomes less significant as a removal mechanism. Generally, if the apparent residence time of a particle associated contaminant is >10% of the hydraulic residence time of the lake (i.e., > 1 year for Lake Ontario), sedimentation is not considered to be a major removal mechanism (Eadie and Robbins 1987).

Because of the very hydrophobic nature of cVMS materials, as shown by the high values for log K_{OW} and log K_{OC} (Table 1), cVMS materials in wastewater effluent will be primarily associated with the suspended solids component. When released to receiving water suspended solids, and particle-associated cVMS materials, may deposit to the bed sediments or may be transported out of the area by prevailing currents. Particles that deposit will result in sediments having elevated concentrations of cVMS materials, as was observed for sediment from Toronto Harbor. Particle-associated cVMS materials that do not deposit (or bottom sediments that are re-suspended) will be transported out of the area and re-distribute according to the prevailing concentrations of suspended solids and particulate organic matter. For Lake Ontario, advective transport of suspended solids from near-shore areas to off-shore areas would result in particle-associated cVMS materials partitioning from the solids phase to the dissolved phase.

For example, in the near-shore harbors and embayments of Lake Ontario (for example, Hamilton Harbor) total suspended materials and organic matter content are about 10 mg L^{-1} and 12%, respectively (Ling et al. 1993). In the off-shore areas of the major lake basins total suspended materials and organic matter content are about 1.1 mg L^{-1} and 20%, respectively (Eadie and Robbins 1987; Ling et al. 1993; Mudroch et al. 1994). Using these values, the estimated fraction of cVMS materials associated with the particulate phase (f_P) in near-shore areas (i.e., Toronto Harbor) was about of 2% for D_4, 19% for D_5, and 71% for D_6 (Table 25). Similarly, the apparent residence time of particle-associated cVMS in the water column (T_A) in near-shore areas was about 13 yr for D_4, 1.2 yr for D_5, and 0.3 yr for D_6. Comparison of the apparent residence times for particle-associated cVMS to the hydraulic residence time of 6 yr, suggests that sedimentation in near-shore areas may be a significant removal process for D_5, D_6, and possibly D_4. In contrast to the near-shore areas, the fraction of cVMS associated with the particulate phase (f_P) in off-shore areas (i.e., the deposition basins) was on the order of 0.3% for D_4, 4.2% for D_5, and 31% for D_6 (Table 25). The apparent residence time of particle-associated cVMS in the water column (T_A) in the off-shore areas was about 67 yr for D_4, 5.6 yr for D_5, and 0.8 yr for D_6. Comparison of the apparent residence times for particle associated

cVMS to the hydraulic residence time of 6 yr, suggests that sedimentation in off-shore areas may not be a significant removal process for D_4 and D_5.

While these calculations represent only gross approximations, they do provide an explanation for why cVMS materials were detected in the Toronto Harbor sediments but not in sediments of the deposition basins. Cyclic VMS materials in wastewater effluent, which is believed to be the major source of cVMS to Lake Ontario, will be associated with the dissolved, colloidal (i.e. associated with humic or fulvic acids) and particulate phases. Once the effluent is discharged to receiving water, cVMS materials will re-distribute according to the prevailing concentrations of particulate and dissolved organic matter. Cyclic VMS materials may be removed from the water column by various processes, including volatilization, pH-dependent hydrolytic degradation, and deposition to the sediment bed. The high fraction of adsorbed cVMS expected in the particulate phase of near-shore waters where total suspended solids and fraction of organic carbon are relatively high, would result in reduced volatile loss and degradation but increased deposition to the sediment bed. Consequently, it is not unexpected that elevated concentrations of cVMS materials were measured in surface sediments from Toronto Harbor. However, in the open lake where total suspended solids are relatively low, the cVMS materials should exist primarily in the dissolved phase. Consequently, in the open lake environment cVMS is more likely to volatilize from the water column or undergo hydrolytic degradation. Because cVMS was not quantifiably detected in sediments of the deposition basins, the lifetime for volatilization and degradation in the dissolved phase of the water column must be significantly less than the lifetime for sedimentation of the particle phase from the water column. In contrast to cVMS materials, the residence times of particle-bound persistent contaminants in Lake Ontario (for example, PCBs, DDT, pesticides) are less than 1 yr, which is relatively short compared to the hydraulic residence time of 6 yr (Jaffe and Hites 1985, 1986; Eadie and Robbins 1987; Wong et al. 1995). Consequently, these hydrophobic and persistent contaminants, which do not volatilize or degrade in the water column, deposit to the bottom sediments. As previously discussed, particle-reactive compounds in Lake Ontario are mixed and distributed evenly throughout the lake, and deposited to the bed sediments in proportion to the amount of sediment focusing. Hence, the greatest concentrations of particle-reactive compounds should be observed in areas such as the deep basins were sediment focusing factors were the greatest.

Surface sediments in the Lake Ontario are in contact with oxygenated water and often undergo surface mixing by benthic organisms, as well as by fish and near-bottom currents. Mixing depths (Table 14) ranged from 1.8 cm in the Mississauga Basin to 4.7 cm in the Rochester Basin (Pearson et al. 1997; Wong et. al. 1989), although mixing appears to be insufficient to homogenize the sediment bed over the time scale for deposition of persistent hydrophobic contaminants (Wong et al. 1995). Nonetheless, once deposited to the bed sediments, burial may be slowed by sediment re-suspension and bioturbation (Warren et al 2003; Bachteram et al 2005; Lick 2006; Mulligan and Yong 2006). Particulate-bound hydrophobic substances in the mixed zone of the sediment column, including cVMS materials, may be brought to the

surface and directly re-suspended into the water column by bioturbation, or may partition into porewater or bind to colloidal organic matter and migrate from the sediments through diffusion or bioirrigation. Once re-suspended, cVMS adsorbed to the particulate phase may desorb and enter the water column where hydrolytic degradation may occur.

Re-suspension of cVMS adsorbed to near-shore sediment and subsequent partitioning into the water column may result in additional hydrolytic degradation and volatile loss. Hence, the spatial distributions of cVMS materials in sediments of Lake Ontario appear to be determined by water chemistry (i.e., pH), hydrologic flow, and system geomorphology to the extent that persistence in sediment is confined to the local area of cVMS release. Moreover, differences in the amounts of total suspended solids may serve as a protective barrier that prevents significant amounts of cVMS from being transported from the near-shore sediments to the deep basin sediments. However, other factors may be partially responsible for the non-detection of cVMS materials in the deep basin sediments.

CONCLUSIONS

Particle-contaminant interactions and subsequent behavior of the particulate matter are known to control the long-term concentrations of many persistent hydrophobic contaminants in Lake Ontario. Even in deep systems such as found in the Great Lakes, particle settling times from the water column are typically less than 1 yr. After reaching the bottom, contaminant-laden particles are redistributed by episodic cycles of resuspension and redeposition, resulting in focusing, which is the spatially inhomogeneous distribution of contaminants in sediments. Bioturbation, coupled with focusing, provides source material to the re-suspendable pool. The combination of these processes coupled with degradation, mediates both the concentration and the long-term behavior of contaminants.

Results from this study indicated that transport and/or deposition of cVMS materials to the sedimentary basins of Lake Ontario were very limited. The results also indicated that flow from the upper Great Lakes, atmospheric deposition, and direct discharges of wastewater were not likely to be significant sources of cVMS materials to the sediment deposition basins of lake. It is suggested that transport and deposition of cVMS materials was not significant in Lake Ontario because re-suspension of cVMS adsorbed to sediment and subsequent partitioning into the water column may have resulted in additional hydrolytic degradation and volatile loss. Hence, the spatial distribution and bioavailability of cVMS materials in aquatic systems such as Lake Ontario may be determined by water chemistry (i.e., pH), hydrologic flow, and system geomorphology to the extent that persistence in sediment appears to be confined to the local area of cVMS release. Moreover, changes in water chemistry or the amounts of total suspended solids may serve as a protective barrier that prevents significant amounts of cVMS from being transported from the local environment.

The extent of transport and deposition of cVMS materials to the sediment basins of Lake Ontario, while apparently low, could not be quantitatively evaluated because of significant sources of background contamination. Although great care was taken to limit contamination

during collection, storage, processing, and analysis, results from the QC program demonstrated that background contamination was significant for some samples and could be attributed to exposure to air, sample processing, and the solvents used for extractions. While the methods used for this study appear to be appropriate for near-field sites (e.g., Toronto Harbor) it is apparent that the methods must be improved to reduce background contamination before monitoring can be used to evaluate transport of cVMS materials to remote regions. For example, it is recommended that consideration be given to implementing clean-room technology and use of ultra-pure solvents and reagents.

ACKNOWLEDGMENTS

We thank the captain and the crew of the *CCGS Limnos* for their help and assistance with sample collection. We are especially grateful for the technical guidance and assistance provided by Camilla Teixeira (National Water Research Institute, Environment Canada). Derek Muir (National Water Research Institute, Environment Canada) arranged ship time for this work and provided comments on an earlier draft of the report. Technical oversight during characterization of the sediment samples was provided by Amy Myrbo (National Lacustrine Core Repositiory, Limnological Research Center, University of Minnesota).

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Table 1. Physical and chemical properties of cyclic volatile methylsiloxane materials.

Property	D_4		D_5		D_6	
$T_{melting}$ (°K)	291	(1)	235	(1)	270	(1)
$T_{boiling}$ (°K)	448	(1)	484	(1)	518	(1)
P_V (Pa)	132	(1)	33.2	(1)	4.57	(1)
S_{water} (ng mL^{-1})	56	(2)	17	(2)	5.1	(2)
log $K_{air/water}$	2.69	(3)	3.13	(3)	3.30	(4)
log $K_{octanol/water}$	6.49	(5)	8.03	(6)	9.06	(4)
log $K_{octanol/air}$	4.34	(7)	5.06	(7)	5.76	(7)
log $K_{SOC/water}$	4.24		5.25		6.25	
Multimedia Partitioning[a]						
• Air (%)	91.8		87.4		49.3	
• Water (%)	8.2		12.6		50.7	
Removal in Wastewater Treatment[b]						
• Air (%)	39.8		34.0		17.6	
• Sludge (%)	59.9		64.8		78.5	
• Effluent (%)	0.3		1.2		3.9	

[a] Multimedia partitioning was estimated using the EQC level I model (Mackay et al. 1996), which provides a general indication of the likely media into which a chemical will partition,

[b] Removal in wastewater treatment was estimated using the multimedia model STPWIN provided in EPI Suite® (ver. 3.12) as obtained from the U.S. EPA (2007). The STPWIN program is a version of the Toronto Model (Clark et al., 1995).

(1) AIChE DIPPR(2007)
(2) Varaprath et al(1996)
(3) Xu and Kropscott (2007)
(4) Xu et al (2007)
(5) Kozerski and Shawl (2007)
(6) Kozerski et al (2007)
(7) Xu and Kropscott (2006)

Table 2. Sample stations and types of samples collected from Lake Ontario 17-20 July 2006.

Location	Station	Date	Latitude	Longitude	Water Depth (m)	Sample Type	Sediment Depth (cm)	Stratum Thickness (cm)
Toronto Harbor	725	17 July	N 43° 38' 16"	W 79° 21' 45"	10.7	Surface sediment	5	5.0
Kingston Basin	81	19 July	N 44° 01' 00"	W 76° 40' 18"	34.9	Surface sediment	5	5.0
Niagara Basin	13	17 July	N 43° 25' 00"	W 79° 24' 00"	105.6	Sediment core	12	0.5–1.0[a]
Mississauga Basin	40	18 July	N 43° 35' 24"	W 78° 00' 42"	183.4	Sediment core	18	1.0
Rochester Basin	64	19 July	N 43° 31' 30"	W 76° 55' 36"	229.6	Sediment core	12	0.5–1.0[a]

[a] Subcores from stations 13 and 64 were sectioned into 0.5 cm strata from 0-6 cm and 1.0 cm strata from 6-12 cm.

Table 3. Summary of uncorrected amounts of cVMS measured in reagent blanks. Mean values were used to estimate background levels of cVMS in QC samples and field samples. Uncertainties associated with the mean values (i.e., standard deviation, s_0) were used to estimate the instrument detection limit (IDL) for each material.

cVMS Material	n	Amount (ng)[a] mean	std dev (s_0)
D_4 Results			
• Station 13	6	12.4	1.7
• Station 40	6	13.2	2.5
• Station 64	6	11.4	4.1
Overall mean:		12.3	
Overall std dev (s_0):		2.9	
n:		18	
$t_{0.99,\,n-1}$:		2.567	
IDL[b]:		7.3	
D_5 Results			
• Station 13	6	33.0	6.2
• Station 40	6	25.6	4.0
• Station 64	(6)	(69.2)	(35.2)
Overall mean:		29.3	
Overall std dev (s_0):		6.3	
n:		12	
$t_{0.99,\,n-1}$:		2.718	
IDL[b]:		17.1	
D_6 Results			
• Station 13	6	18.5	4.7
• Station 40	6	15.9	2.0
• Station 64	6	17.0	5.3
Overall mean:		17.1	
Overall std dev (s_0):		4.2	
n:		18	
$t_{0.99,\,n-1}$:		2.567	
IDL[b]:		10.7	

[a] Values in () were not included in calculation of overall mean values or overall standard deviations, based on comparisons showing that omitted values were significantly greater (ANOVA; $p < 0.01$) than other values in the data set.

[b] The IDL instrument detection limit (IDL) was a function of the variance associated with replicate analyses of matrix-free blanks. The IDL at 99% confidence was defined as:

$$IDL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses.

Table 4. Summary of uncorrected amounts and concentrations of cVMS materials measured in field blanks. Uncertainties associated with the overall mean values (i.e., overall standard deviation, s_0) were used to estimate the lower limit of detection (LLD) for each material.

cVMS Material	n	Amount (ng)[a] mean	Amount (ng)[a] std dev (s_0)	Concentration (ng g^{-1} ww)[a] mean	Concentration (ng g^{-1} ww)[a] std dev (s_0)
D_4 Results					
• Station 13	8	17.7	3.7	2.8	0.7
• Station 40	8	13.1	2.7	2.0	0.4
• Station 64	8	19.9	3.6	3.2	0.4
Overall mean:		16.9		2.7	
Overall std dev (s_0):		4.3		0.7	
n:		24		24	
$t_{0.99,\,n-1}$:		2.500		2.500	
LLD[b]:		10.8		1.7	
D_5 Results					
• Station 13	8	42.5	4.7	6.7	0.6
• Station 40	8	29.8	8.0	4.6	1.1
• Station 64	(8)	(97.5)	(16.0)	(15.7)	(2.3)
Overall mean:		36.1		5.6	
Overall std dev (s_0):		9.1		1.4	
n:		16		16	
$t_{0.99,\,n-1}$:		2.602		2.602	
LLD[b]:		23.6		3.6	
D_6 Results					
• Station 13	8	24.4	3.1	3.9	0.7
• Station 40	8	16.7	3.4	2.6	0.4
• Station 64	8	21.8	2.0	3.5	0.4
Overall mean:		21.0		3.3	
Overall std dev (s_0):		4.3		0.7	
n:		24		24	
$t_{0.99,\,n-1}$:		2.500		2.500	
LLD[b]:		10.7		1.8	

[a] Values in () were not included in calculation of the overall mean values or overall standard deviations, based on comparisons showing that omitted values were significantly greater (ANOVA; $p < 0.01$) than other values in the data set.

[b] The lower limit of detection (LLD) was a function of the variance associated with replicate analyses of sediment that was known to contain very low or non-detectable amounts of cVMS. The LLD at 99% confidence was defined as:

$$LLD = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses.

Table 5. Summary of uncorrected amounts and concentrations of cVMS materials measured in reference samples. Uncertainties associated with the overall mean values (i.e., overall standard deviation, s_0) were used to estimate the method detection limit (MDL) for each material.

cVMS Material	n	Amount (ng)[a]		Concentration (ng g^{-1} ww)[a]	
		mean	std dev (s_0)	mean	std dev (s_0)
D_4 Results					
• Station 13	8	321.9	26.4	51.5	1.6
• Station 40	8	321.8	20.7	51.3	1.1
• Station 64	8	312.8	18.7	48.8	3.8
Overall mean:		318.8		50.5	
Overall std dev (s_0):		21.6		2.7	
n:		24		24	
$t_{0.99, n-1}$:		2.500		2.500	
MDL[b]:		54.1		6.6	
D_5 Results					
• Station 13	8	368.6	28.1	59.0	1.1
• Station 40	8	354.3	25.5	56.4	1.4
• Station 64	(8)	(403.8)	(24.7)	(63.2)	(6.7)
Overall mean:		361.5		57.7	
Overall std dev (s_0):		27.0		1.8	
n:		16		16	
$t_{0.99, n-1}$:		2.602		2.602	
MDL[b]:		70.2		4.7	
D_6 Results					
• Station 13	8	348.7	29.8	55.8	0.7
• Station 40	8	341.4	22.3	54.4	1.0
• Station 64	8	312.7	27.8	49.0	6.6
Overall mean:		334.3		53.1	
Overall std dev (s_0):		30.2		4.8	
n:		24		24	
$t_{0.99, n-1}$:		2.500		2.500	
MDL[b]:		75.4		11.9	

[a] Values in () were not included in calculation of the overall mean values or overall standard deviations, based on comparisons showing that omitted values were significantly greater (ANOVA; $p < 0.01$) than other values in the data set.

[b] The method detection limit (MDL) was a function of the variance associated with replicate analyses of sediment that was known to contain detectable amounts of cVMS. The MDL at 99% confidence was defined as:

$$MDL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses.

Table 6. Results summary for quality control (QC) samples from sediment core LO-13, collected from the Niagara Basin (station 13) of Lake Ontario on 17 July 2007.

QC Type/Units	Statistic	D_4	D_5	D_6
Reagent Blank, ng (n=6)	Avg±SD Range	12.5 ± 1.7 9.3-14.1	33.0 ± 6.2 27.5-44.7	18.5 ± 4.7 13.6-27.4
Field Blank, ng/g dw (n=4)	Avg±SD Range	2.6 ± 1.2 1.0-3.7	7.9 ± 2.1 5.0-9.5	2.7 ± 1.1 1.2-3.5
FB Control, ng/g dw (n=2)	Range	1.3-3.7	3.4-8.2	4.0-7.6
Reference Sample, %Recovery (n=4)	Avg±SD Range	91.7 ± 2.7 88.8-95.2	99.1 ± 1.8 96.9-101	102 ± 1 100-103
RS Control, %Recovery (n=2)	Range	93.3-94.8	98.6-99.1	97.9-98.6
Field Spike x 2, %Recovery (n=6)	Avg±SD Range	101 ± 1 100-103	102 ± 1 101-104	102 ± 2 99.2-104
Field Split, $\lvert\Delta$ ng/g dw$\rvert$ (n=3)	Avg±SD Range	6.6 ± 3.0 3.9-9.8	12.8 ± 5.3 7.4-18.1	11.6 ± 4.9 8.6-17.3
Lab Blank, ng (n=2)	Range	2.9-4.6	1.3-2.1	8.4-8.9
Lab Spike x 2, %Recovery (n=6)	Avg±SD Range 25 ng 250 ng 2500 ng	96.1 ± 4.8 86.6-99.2 95.7-98.7 98.1-98.4	94.7 ± 5.6 84.2-92.9 95.8-98.6 97.9-98.6	103 ± 9 96.8-121 99.3-102 99.0-99.0

Table 7. Results summary for quality control (QC) samples from sediment core LO-40, collected from the Missasauga Basin (station 40) of Lake Ontario on 18 July 2007.

QC Type/Units	Statistic	D_4	D_5	D_6
Reagent Blank, ng (n=6)	Avg±SD Range	13.2 ± 2.5 9.3-16.2	25.6 ± 4.0 21.4-32.6	15.9 ± 2.0 13.9-19.2
Field Blank, ng/g dw (n=4)	Avg±SD Range	1.3 ± 0.7 0.7-2.3	3.9 ± 1.4 2.2-5.1	0.8 ± 1.2 -0.2-2.1
FB Control, ng/g dw (n=2)	Range	-1.1- -1.1	-3.7- -3.7	-2.6- -0.3
Reference Sample, %Recovery (n=4)	Avg±SD Range	94.5 ± 1.5 92.6-95.7	97.7 ± 1.8 95.1-99.1	99.5 ± 1.9 96.8-101
RS Control, %Recovery (n=2)	Range	91.3-95.1	93.1-94.7	96.8-99.5
Field Spike x 2, %Recovery (n=6)	Avg±SD Range	102 ± 1 101-104	102 ± 1 101-103	101 ± 1 99.9-103
Field Split, $\lvert \Delta$ ng/g dw$\rvert$ (n=3)	Avg±SD Range	3.0 ± 1.8 1.0-4.5	6.0 ± 2.1 3.6-7.4	5.6 ± 2.2 3.3-7.7
Lab Blank, ng (n=2)	Range	2.9-4.6	1.3-2.1	8.4-8.9
Lab Spike x 2, %Recovery (n=6)	Avg±SD Range 25 ng 250 ng 2500 ng	96.1 ± 4.8 86.6-99.2 95.7-98.7 98.1-98.4	94.7 ± 5.6 84.2-92.9 95.8-98.6 97.9-98.6	103 ± 9 96.8-121 99.3-102 99.0-99.0

Table 8. Results summary for quality control (QC) samples from sediment cores LO-64GB (extruded and sectioned in a glove box) and LO-64A (extruded and sectioned outside the glove box), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

QC Type/Units	Statistic	D_4	D_5	D_6
Reagent Blank[1], ng (n=3)	Avg±SD	8.0 ± 2.0	40.2 ± 7.6	12.5 ± 1.6
	Range	6.0-10.0	32.3-47.4	10.8-14.0
Reagent Blank[2], ng (n=3)	Avg±SD	14.7 ± 1.9	98.1 ± 22.9	21.4 ± 3.1
	Range	13.0-16.7	72.4-116	17.8-23.3
Field Blank, ng/g dw (n=4)	Avg±SD	3.9 ± 1.9	-0.4 ± 11.5	-0.3 ± 0.6
	Range	2.4-6.5	-10.6-15.6	-1.1-0.4
FB Control, ng/g dw (n=2)	Range	1.6-1.6	-3.4-2.4	-0.1-1.6
Reference Sample, %Recovery (n=4)	Avg±SD	83.3 ± 6.8	81.4 ± 8.5	77.6 ± 9.9
	Range	76.0-91.1	71.9-91.3	68.5-91.5
RS Control, %Recovery (n=2)	Range	89.8-93.7	86.6-100	90.5-98.6
Field Spike x 2, %Recovery (n=6)	Avg±SD	103 ± 3	97.4 ± 6.5	98.2 ± 1.7
	Range	101-107	89.2-105	96.1-101
Field Split, |Δ ng/g dw| (n=3)	Avg±SD	1.0 ± 0.6		5.4 ± 3.2
	Range	0.5-1.7		1.9-8.2
Lab Blank, ng (n=2)	Range	1.1-4.4	0.7-3.8	-0.3-0.4
Lab Spike x 2, %Recovery (n=6)	Avg±SD	98.6 ± 3.9	94.1 ± 12.0	107 ± 5
	Range			
	25 ng	92.1-95.9	78.2-79.7	111-115
	250 ng	99.7-102	99.2-106	104-107
	2500 ng	100-102	99.8-102	101-102

Table 9. Results summary for characterization analyses of sediment strata from sediment core LO-13, collected from the Niagara Basin (station 13) of Lake Ontario on 17 July 2007.

Sample Station	Stratum Interval (mm) top	base	Carbon Coulometry Analyses[a] TC (% dw)	TIC (% dw)	TOC (% dw)	$CaCO_3$ (% dw)	Density (g cm^{-3} wet)	Loss-on-Ignition Analyses[b] Water (% ww)	Solids (% ww)	Organic (% dw)	$CaCO_3$ (% dw)	Inorganic (% dw)
LO-13	0	5	5.9	0.6	5.2	5.2	1.085	86.5	13.5	10.6	10.1	79.3
LO-13	5	10	5.9	1.0	4.9	8.4	1.106	83.5	16.5	10.5	12.8	76.7
LO-13	10	15	6.0	1.1	5.0	9.0	1.105	83.7	16.3	10.3	13.2	76.5
LO-13	15	20	6.1	1.4	4.8	11.5	1.112	82.7	17.3	9.9	15.3	74.8
LO-13	20	25	6.1	1.4	4.6	12.1	1.116	82.3	17.7	9.8	15.9	74.3
LO-13	25	30	6.2	1.5	4.7	12.8	1.119	81.9	18.1	9.5	17.5	73.1
LO-13	30	35	5.9	1.5	4.4	12.4	1.115	82.5	17.5	9.2	16.7	74.1
LO-13	35	40	5.6	1.3	4.3	10.7	1.120	81.7	18.3	9.1	14.9	76.0
LO-13	40	45	4.9	0.8	4.1	6.8	1.126	81.0	19.0	8.8	11.8	79.4
LO-13	45	50	4.4	0.5	3.9	4.4	1.134	80.0	20.0	8.4	10.0	81.6
LO-13	50	55										
LO-13	55	60										
LO-13	60	70										
LO-13	70	80										
LO-13	80	90										
LO-13	90	100										
LO-13	100	110										
LO-13	110	120										

[a] For the carbon coulometry analyses: TC = total carbon content; TIC = total inorganic carbon content; TOC = total organic carbon content.

[b] For loss-on-ignition analyses: Water = water content; Solids = solids content; Organic = organic matter content; Inorganic = inorganic matter content.

Table 10. Results summary for characterization analyses of sediment strata from sediment core LO-40, collected from the Missasauga Basin (station 40) of Lake Ontario on 18 July 2007.

Sample Station	Stratum Interval (mm) top	base	Carbon Coulometry Analyses[a] TC (% dw)	TIC (% dw)	TOC (% dw)	$CaCO_3$ (% dw)	Loss-on-Ignition Analyses[b] Density (g cm^{-3} wet)	Water (% ww)	Solids (% ww)	Organic (% dw)	$CaCO_3$ (% dw)	Inorganic (% dw)
LO-40	0	10	6.0	0.2	5.8	1.4	1.072	88.4	11.6	10.9	8.4	80.7
LO-40	10	20	6.0	0.5	5.5	4.0	1.084	86.6	13.4	11.6	9.0	79.4
LO-40	20	30	6.3	1.3	5.0	11.1	1.102	84.1	15.9	10.7	15.3	74.0
LO-40	30	40	6.6	2.2	4.4	18.6	1.117	82.1	17.9	9.5	22.8	67.6
LO-40	40	50	6.5	2.4	4.1	19.8	1.127	80.9	19.1	9.3	23.6	67.1
LO-40	50	60	6.3	2.0	4.3	16.9	1.118	82.0	18.0	9.4	21.8	68.8
LO-40	60	70	5.9	1.7	4.2	13.9	1.117	82.2	17.8	9.5	19.0	71.4
LO-40	70	80	5.4	1.3	4.1	11.0	1.121	81.7	18.3	9.3	16.5	74.2
LO-40	80	90	4.8	1.0	3.8	8.4	1.125	81.1	18.9	8.8	14.1	77.1
LO-40	90	100	4.4	0.8	3.6	6.5	1.131	80.3	19.7	8.8	12.3	78.9
LO-40	100	110										
LO-40	110	120										
LO-40	120	130										
LO-40	130	140										
LO-40	140	150										
LO-40	150	160										
LO-40	160	170										
LO-40	170	180										

[a] For the carbon coulometry analyses: TC = total carbon content; TIC = total inorganic carbon content; TOC = total organic carbon content.

[b] For loss-on-ignition analyses: Water = water content; Solids = solids content; Organic = organic matter content; Inorganic = inorganic matter content.

Table 11. Results summary for characterization analyses of sediment strata from sediment core LO-64GB (extruded and sectioned in a glove box), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

Sample Station	Stratum Interval (mm) top	base	Carbon Coulometry Analyses[a] TC (% dw)	TIC (% dw)	TOC (% dw)	$CaCO_3$ (% dw)	Loss-on-Ignition Analyses[b] Density (g cm^{-3} wet)	Water (% ww)	Solids (% ww)	Organic (% dw)	$CaCO_3$ (% dw)	Inorganic (% dw)
LO-64G	0	5	5.9	0.9	4.9	7.9	1.076	87.9	12.1	10.5	14.0	75.6
LO-64G	5	10	5.7	1.0	4.7	8.3	1.100	84.3	15.7	10.3	14.2	75.5
LO-64G	10	15	5.7	1.4	4.3	11.7	1.109	83.2	16.8	9.7	17.1	73.2
LO-64G	15	20	5.8	1.5	4.3	12.4	1.117	82.1	17.9	9.8	17.5	72.7
LO-64G	20	25	6.0	1.5	4.5	12.3	1.113	82.6	17.4	10.3	18.2	71.5
LO-64G	25	30	5.8	1.4	4.4	11.7	1.113	82.6	17.4	10.5	16.5	72.9
LO-64G	30	35	5.6	1.2	4.3	10.3	1.108	83.2	16.8	10.7	15.3	74.0
LO-64G	35	40	5.4	1.1	4.3	9.5	1.106	83.5	16.5	10.4	14.5	75.1
LO-64G	40	45	5.2	1.0	4.2	8.3	1.104	83.9	16.1	10.3	13.8	75.9
LO-64G	45	50	4.8	0.9	3.9	7.1	1.112	82.7	17.3	9.7	12.7	77.6
LO-64G	50	55										
LO-64G	55	60										
LO-64G	60	70										
LO-64G	70	80										
LO-64G	80	90										
LO-64G	90	100										
LO-64G	100	110										
LO-64G	110	120										

[a] For the carbon coulometry analyses: TC = total carbon content; TIC = total inorganic carbon content; TOC = total organic carbon content.

[b] For loss-on-ignition analyses: Water = water content; Solids = solids content; Organic = organic matter content; Inorganic = inorganic matter content.

Table 12. Results summary for characterization analyses of sediment strata from sediment core LO-64A (extruded and sectioned in air), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

Sample Station	Startum Interval (mm)		Carbon Coulometry Analyses[a]				Loss-on-Ignition Analyses[b]					
	top	base	TC (% dw)	TIC (% dw)	TOC (% dw)	$CaCO_3$ (% dw)	Density (g cm^{-3} wet)	Water (% ww)	Solids (% ww)	Organic (% dw)	$CaCO_3$ (% dw)	Inorganic (% dw)
LO-64A	0	5	5.8	0.9	4.9	7.7	1.082	86.9	13.1	12.1	11.4	76.5
LO-64A	5	10	5.7	1.1	4.7	8.8	1.107	83.4	16.6	11.4	12.7	75.8
LO-64A	10	15	5.7	1.3	4.5	10.5	1.126	80.8	19.2	11.1	14.2	74.7
LO-64A	15	20	5.9	1.5	4.4	12.6	1.113	82.6	17.4	10.7	16.3	73.0
LO-64A	20	25	6.0	1.6	4.4	13.4	1.116	82.2	17.8	10.7	16.9	72.5
LO-64A	25	30	5.7	1.5	4.2	12.4	1.118	81.8	18.2	10.8	15.7	73.5
LO-64A	30	35	5.7	1.3	4.3	11.2	1.109	83.1	16.9	10.9	14.4	74.7
LO-64A	35	40	5.4	1.2	4.3	9.7	1.133	79.7	20.3	11.0	13.6	75.4
LO-64A	40	45	5.3	1.0	4.3	8.5	1.113	82.5	17.5	10.9	12.6	76.5
LO-64A	45	50	4.8	0.9	4.0	7.1	1.135	79.7	20.3	10.3	11.9	77.8
LO-64A	50	55										
LO-64A	55	60										
LO-64A	60	70										
LO-64A	70	80										
LO-64A	80	90										
LO-64A	90	100										
LO-64A	100	110										
LO-64A	110	120										

[a] For the carbon coulometry analyses: TC = total carbon content; TIC = total inorganic carbon content; TOC = total organic carbon content.

[b] For loss-on-ignition analyses: Water = water content; Solids = solids content; Organic = organic matter content; Inorganic = inorganic matter content.

Table 13. Results summary for characterization analyses of surface sediments (upper 5 cm) collected from Toronto Habor (station 725), the Niagara Basin (station 13), the Missasauga Basin (station 40), the Rochester Basin (station 64), and the Kingston Basin (station 81) of Lake Ontario on 17-20 July 2007.

Sample Station	Startum Interval (mm)		Carbon Coulometry Analyses[a]					Loss-on-Ignition Analyses[b]				
	top	base	TC (% dw)	TIC (% dw)	TOC (% dw)	$CaCO_3$ (% dw)	Density (g cm^{-3} wet)	Water (% ww)	Solids (% ww)	Organic (% dw)	$CaCO_3$ (% dw)	Inorganic (% dw)
LO-725	0	50	4.2	2.1	2.1	17.6	1.374	54.7	45.3	5.3	22.0	72.7
LO-13	0	50	5.7	1.1	4.6	9.5	1.114	82.6	17.4	9.6	13.8	76.6
LO-40	0	50	6.2	1.1	5.1	9.4	1.100	84.4	15.6	10.4	15.8	73.8
LO-64GB	0	50	5.6	1.2	4.4	10.1	1.106	83.6	16.4	10.2	15.4	74.4
LO-64A	0	50	5.6	1.2	4.4	10.0	1.115	82.3	17.7	11.0	14.0	75.0
LO-81	0	50	2.7	0.4	2.4	3.2	1.222	69.4	30.6	6.9	4.5	88.6

[a] For the carbon coulometry analyses: TC = total carbon content; TIC = total inorganic carbon content; TOC = total organic carbon content.

[b] For loss-on-ignition analyses: Water = water content; Solids = solids content; Organic = organic matter content; Inorganic = inorganic matter content.

Table 14. Reported rates of sedimentation and focusing factors for the Niagara, Mississauga, and Rochester Basins in Lake Ontario.

Location	Rate of Sedimentation ($g\ cm^{-2}\ yr^{-1}$)	Rate of Sedimentation ($cm\ yr^{-1}$)	Focusing Factor	Mixed Depth (cm)	Reference
Niagara Basin					
• N 43° 22' W 79° 21'	0.030	0.20	1.07	2.3	Pearson et al., 1997
• N 43° 22' W 79° 21'	0.030	0.18	1.07	2.3	Wong et al., 1995
• N 43° 23' W 79° 24'		0.40			Oliver et al., 1989
Mississauga Basin					
• N 43° 35' W 78° 12'		0.35			Marvin et al., 2003
• N 43° 35' W 78° 48'	0.027	0.20	1.72		Peck et al., 2006
• N 43° 35' W 78° 00'	0.064	0.40	1.71	1.8	Pearson et al., 1997
• N 43° 35' W 78° 00'	0.037	0.20	1.15		Song et al., 2005
• N 43° 35' W 78° 01'	0.064	0.43	1.71	1.8	Wong et al., 1995
• N 43° 35' W 78° 01'	0.048	0.30			Yong et al., 2006
• N 43° 36' W 78° 14'		0.30			Oliver et al., 1989
• N 43° 35' W 78° 00'	0.039		1.19		Li et al., 2006
Rochester Basin					
• N 43° 32' W 76° 54'	0.067	0.40	2.04	4.7	Pearson et al., 1997
• N 43° 32' W 76° 54'	0.039	0.30	1.19		Song et al., 2005
• N 43° 32' W 76° 54'	0.068	0.34	2.04	4.7	Wong et al., 1995
• N 43° 32' W 76° 55'		0.30			Oliver et al., 1989
• N 43° 32' W 76° 54'	0.037		1.15		Li et al., 2006

Table 15. Results summary for background corrected, wet weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-13, collected from the Niagara Basin (station 13) of Lake Ontario on 17 July 2007.

Sample Station	Stratum Interval (mm) top	base	Water (%)	TOC (%)	Analyzed Sample Mass (g wet wt)	Background Corrected cVMS Concentrations (ng g^{-1} wet weight) D_4 Measured	D_4 LLD[a]	D_5 Measured	D_5 LLD[a]	D_6 Measured	D_6 LLD[a]
LO-13	0	5	86.5	5.2	5.9361	0.1	1.8	2.8	4.0	1.0	1.8
LO-13	5	10	83.5	4.9	6.6418	-0.4	1.6	1.8	3.6	0.8	1.6
LO-13	10	15	83.7	5.0	6.4284	0.8	1.7	3.8	3.7	2.0	1.7
LO-13	15	20	82.7	4.8	6.1197	0.3	1.8	2.5	3.9	1.6	1.7
LO-13	20	25	82.3	4.6	6.0625	0.5	1.8	3.0	3.9	1.8	1.8
LO-13	25	30	81.9	4.7	5.6784	0.4	1.9	2.5	4.2	1.6	1.9
LO-13	30	35	82.5	4.4	5.6017	0.8	1.9	3.1	4.2	2.0	1.9
LO-13	35	40	81.7	4.3	6.1743	0.2	1.7	1.6	3.8	0.9	1.7
LO-13	40	45	81.0	4.1	5.5572	0.0	1.9	1.1	4.2	0.0	1.9
LO-13	45	50	80.0	3.9	6.1606	-0.2	1.8	0.7	3.8	-0.4	1.7
LO-13	50	55			6.5551	0.0	1.6	1.5	3.6	-0.8	1.6
LO-13	55	60			6.2785	0.3	1.7	2.0	3.8	-0.4	1.7
LO-13	60	70			6.6830	0.0	1.6	1.3	3.5	-0.2	1.6
LO-13	70	80			6.0039	0.5	1.8	2.5	3.9	0.5	1.8
LO-13	80	90			5.9856	0.4	1.8	2.4	3.9	0.5	1.8
LO-13	90	100			6.3497	0.8	1.7	2.8	3.7	0.9	1.7
LO-13	100	110			6.6872	0.7	1.6	2.7	3.5	1.0	1.6
LO-13	110	120			6.1281	-0.2	1.8	0.6	3.9	-0.3	1.7

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g wet weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (1.7 ng g^{-1} wet weight)
- D_5: 23.6 ng (3.6 ng g^{-1} wet weight)
- D_6: 10.7 ng (1.8 ng g^{-1} wet weight)

Table 16. Results summary for background corrected, wet weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-40, collected from the Missasauga Basin (station 40) of Lake Ontario on 18 July 2007.

Sample Station	Stratum Interval (mm) top	Stratum Interval (mm) base	Water (%)	TOC (%)	Analyzed Sample Mass (g wet wt)	Background Corrected cVMS Concentrations (ng g^{-1} wet weight) D_4 Measured	D_4 LLD[a]	D_5 Measured	D_5 LLD[a]	D_6 Measured	D_6 LLD[a]
LO-40	0	10	88.4	5.8	5.7521	-0.2	1.9	0.3	4.1	0.2	1.9
LO-40	10	20	86.6	5.5	6.5245	-0.1	1.7	0.7	3.6	0.9	1.6
LO-40	20	30	84.1	5.0	6.8756	0.0	1.6	0.8	3.4	1.1	1.6
LO-40	30	40	82.1	4.4	6.9476	0.1	1.6	0.8	3.4	1.1	1.5
LO-40	40	50	80.9	4.1	6.7873	0.0	1.6	0.5	3.5	0.6	1.6
LO-40	50	60	82.0	4.3	5.9768	-0.2	1.8	0.3	3.9	0.3	1.8
LO-40	60	70	82.2	4.2	6.2421	-0.1	1.7	0.3	3.8	0.2	1.7
LO-40	70	80	81.7	4.1	6.7754	-0.5	1.6	-0.4	3.5	-0.4	1.6
LO-40	80	90	81.1	3.8	6.7545	-0.6	1.6	-0.5	3.5	-0.8	1.6
LO-40	90	100	80.3	3.6	6.5074	-0.8	1.7	-0.5	3.6	-1.0	1.6
LO-40	100	110			7.0296	0.2	1.5	0.8	3.4	-0.9	1.5
LO-40	110	120			6.8995	0.2	1.6	1.7	3.4	-0.6	1.6
LO-40	120	130			6.4874	0.1	1.7	0.6	3.6	-0.6	1.6
LO-40	130	140			6.9734	0.1	1.5	0.6	3.4	-0.4	1.5
LO-40	140	150			7.0159	-0.3	1.5	0.0	3.4	-0.5	1.5
LO-40	150	160			6.1936	0.1	1.7	0.8	3.8	-0.2	1.7
LO-40	160	170			6.7049	0.3	1.6	1.2	3.5	0.4	1.6
LO-40	170	180			6.3619	-0.5	1.7	-0.3	3.7	-0.6	1.7

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g wet weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (1.7 ng g^{-1} wet weight)
- D_5: 23.6 ng (3.6 ng g^{-1} wet weight)
- D_6: 10.7 ng (1.8 ng g^{-1} wet weight)

Table 17. Results summary for background corrected, wet weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-64G (extruded and sectioned in a glove box), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

Sample Station	Stratum Interval (mm)		Water (%)	TOC (%)	Analyzed Sample Mass (g wet wt)	Background Corrected cVMS Concentrations (ng g^{-1} wet weight)					
						D_4		D_5		D_6	
	top	base				Measured	LLD[a]	Measured	LLD[a]	Measured	LLD[a]
LO-64G	0	5	87.9	4.9	5.7582	-0.7	1.9	2.6	4.1	-0.6	1.9
LO-64G	5	10	84.3	4.7	5.9562	-0.6	1.8	3.2	4.0	-0.1	1.8
LO-64G	10	15	83.2	4.3	7.0834	-0.6	1.5	2.5	3.3	0.3	1.5
LO-64G	15	20	82.1	4.3	7.2730	-0.6	1.5	1.7	3.2	0.0	1.5
LO-64G	20	25	82.6	4.5	6.1373	-0.7	1.8	2.9	3.8	0.4	1.7
LO-64G	25	30	82.6	4.4	7.0085	-0.8	1.5	1.3	3.4	0.1	1.5
LO-64G	30	35	83.2	4.3	6.4214	-0.7	1.7	2.6	3.7	0.6	1.7
LO-64G	35	40	83.5	4.3	6.7851	-0.8	1.6	1.8	3.5	-0.4	1.6
LO-64G	40	45	83.9	4.2	6.0761	-0.4	1.8	4.2	3.9	-1.4	1.8
LO-64G	45	50	82.7	3.9	5.9404	-0.6	1.8	3.2	4.0	-1.4	1.8
LO-64G	50	55			7.0797	-0.7	1.5	2.1	3.3	-1.0	1.5
LO-64G	55	60			6.4092	-0.7	1.7	3.1	3.7	-0.5	1.7
LO-64G	60	70			6.3148	-0.7	1.7	3.7	3.7	-0.1	1.7
LO-64G	70	80			7.1581	-0.5	1.5	3.5	3.3	0.2	1.5
LO-64G	80	90			6.3261	-0.7	1.7	3.3	3.7	-0.2	1.7
LO-64G	90	100			6.4832	-0.9	1.7	1.9	3.6	-0.9	1.7
LO-64G	100	110			6.2612	-0.6	1.7	3.6	3.8	-1.7	1.7
LO-64G	110	120			6.1231	-0.8	1.8	2.6	3.9	-1.8	1.7

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g wet weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (1.7 ng g^{-1} wet weight)
- D_5: 23.6 ng (3.6 ng g^{-1} wet weight)
- D_6: 10.7 ng (1.8 ng g^{-1} wet weight)

Table 18. Results summary for background corrected, wet weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-64A (extruded and sectioned in air), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

Sample Station	Stratum Interval (mm)		Water (%)	TOC (%)	Analyzed Sample Mass (g wet wt)	Background Corrected cVMS Concentrations (ng g^{-1} wet weight)					
						D_4		D_5		D_6	
	top	base				Measured	LLD[a]	Measured	LLD[a]	Measured	LLD[a]
LO-64A	0	5	86.9	4.9	6.1867	-0.4	1.7	5.0	3.8	0.6	1.7
LO-64A	5	10	83.4	4.7	6.3880	-0.5	1.7	4.7	3.7	0.9	1.7
LO-64A	10	15	80.8	4.5	5.8085	-0.4	1.9	5.7	4.1	1.2	1.8
LO-64A	15	20	82.6	4.4	6.5193	-0.4	1.7	4.5	3.6	1.1	1.6
LO-64A	20	25	82.2	4.4	6.6854	-0.3	1.6	4.6	3.5	1.6	1.6
LO-64A	25	30	81.8	4.2	6.0784	-0.6	1.8	3.6	3.9	0.1	1.8
LO-64A	30	35	83.1	4.3	6.3482	-0.7	1.7	2.8	3.7	-1.3	1.7
LO-64A	35	40	79.7	4.3	6.1879	-0.7	1.7	3.2	3.8	-0.8	1.7
LO-64A	40	45	82.5	4.3	5.6702	-0.8	1.9	3.3	4.2	-0.7	1.9
LO-64A	45	50	79.7	4.0	6.7713	-0.6	1.6	2.9	3.5	0.1	1.6
LO-64A	50	55			6.5541	-0.8	1.6	2.5	3.6	-0.2	1.6
LO-64A	55	60			7.2362	-0.6	1.5	2.8	3.3	0.8	1.5
LO-64A	60	70			6.3401	-0.8	1.7	2.0	3.7	0.3	1.7
LO-64A	70	80			7.2090	-0.8	1.5	1.7	3.3	-0.6	1.5
LO-64A	80	90			6.0701	-0.6	1.8	3.6	3.9	0.8	1.8
LO-64A	90	100			6.4747	-0.5	1.7	3.2	3.6	0.9	1.7
LO-64A	100	110			6.9255	-0.8	1.6	1.5	3.4	-0.5	1.5
LO-64A	110	120			6.3365	-1.0	1.7	0.5	3.7	-1.3	1.7

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g wet weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (1.7 ng g^{-1} wet weight)
- D_5: 23.6 ng (3.6 ng g^{-1} wet weight)
- D_6: 10.7 ng (1.8 ng g^{-1} wet weight)

Table 19. Results summary for background corrected, wet weight concentrations of D_4, D_5, and D_6 measured in surface sediments (upper 5 cm) collected from Toronto Harbor (station 725), the Niagara Basin (station 13), the Missasauga Basin (station 40), the Rochester Basin (station 64), and the Kingston Basin (station 81) of Lake Ontario on 17-20 July 2007.

Sample Station	Stratum Interval (mm)		Water (%)	TOC (%)	Analyzed Sample Mass (g wet wt)	Background Corrected cVMS Concentrations (ng g^{-1} wet weight)					
						D_4		D_5		D_6	
	top	base				Measured	LLD[a]	Measured	LLD[a]	Measured	LLD[a]
LO-725	0	50	54.7	2.1	6.7906	129.7	1.6	357.7	3.5	89.6	1.6
LO-13	0	50	82.6	4.6	6.0361	0.3	1.8	2.3	3.9	1.1	1.8
LO-40	0	50	84.4	5.1	6.5774	-0.1	1.6	0.6	3.6	0.8	1.6
LO-64G	0	50	83.6	4.4	6.4440	-0.6	1.7	2.6	3.7	-0.3	1.7
LO-64A	0	50	82.3	4.4	6.2644	-0.5	1.7	4.0	3.8	0.3	1.7
LO-81	0	50	69.4	2.4	6.6075	-0.8	1.6	2.4	3.6	1.1	1.6

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g wet weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (1.7 ng g^{-1} wet weight)
- D_5: 23.6 ng (3.6 ng g^{-1} wet weight)
- D6: 10.7 ng (1.8 ng g^{-1} wet weight)

Table 20. Results summary for background corrected, dry weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-13, collected from the Niagara Basin (station 13) of Lake Ontario on 17 July 2007.

Sample Station	Stratum Interval (mm) top	Stratum Interval (mm) base	Water (%)	TOC (%)	Analyzed Sample Mass (g dry wt)	Background Corrected cVMS Concentrations (ng g^{-1} dry weight) D_4 Measured	D_4 LLD[a]	D_5 Measured	D_5 LLD[a]	D_6 Measured	D_6 LLD[a]
LO-13	0	5	86.5	5.2	0.8010	0.5	13.5	21.1	29.5	7.1	13.4
LO-13	5	10	83.5	4.9	1.0949	-2.6	9.9	10.8	21.6	5.0	9.8
LO-13	10	15	83.7	5.0	1.0469	5.1	10.3	23.6	22.5	12.5	10.2
LO-13	15	20	82.7	4.8	1.0557	1.6	10.2	14.7	22.4	9.0	10.1
LO-13	20	25	82.3	4.6	1.0710	3.1	10.1	17.0	22.0	10.1	10.0
LO-13	25	30	81.9	4.7	1.0302	2.3	10.5	13.8	22.9	8.8	10.4
LO-13	30	35	82.5	4.4	0.9799	4.6	11.0	17.9	24.1	11.3	10.9
LO-13	35	40	81.7	4.3	1.1272	1.0	9.6	8.6	20.9	5.1	9.5
LO-13	40	45	81.0	4.1	1.0575	0.0	10.2	5.7	22.3	0.1	10.1
LO-13	45	50	80.0	3.9	1.2345	-0.9	8.7	3.7	19.1	-2.2	8.7
LO-13	50	55									
LO-13	55	60									
LO-13	60	70									
LO-13	70	80									
LO-13	80	90									
LO-13	90	100									
LO-13	100	110									
LO-13	110	120									

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g dry weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (5.8 ng g^{-1} dry weight)
- D_5: 23.6 ng (11.9 ng g^{-1} dry weight)
- D_6: 10.7 ng (6.1 ng g^{-1} dry weight)

Table 21. Results summary for background corrected, dry weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-40, collected from the Missasauga Basin (station 40) of Lake Ontario on 18 July 2007.

Sample Station	Stratum Interval (mm) top	base	Water (%)	TOC (%)	Analyzed Sample Mass (g dry wt)	Background Corrected cVMS Concentrations (ng g^{-1} dry weight) D_4 Measured	D_4 LLD[a]	D_5 Measured	D_5 LLD[a]	D_6 Measured	D_6 LLD[a]
LO-40	0	10	88.4	5.8	0.6666	-1.8	16.2	2.9	35.4	1.5	16.1
LO-40	10	20	86.6	5.5	0.8718	-0.6	12.4	5.0	27.1	6.6	12.3
LO-40	20	30	84.1	5.0	1.0912	-0.3	9.9	4.8	21.6	7.1	9.8
LO-40	30	40	82.1	4.4	1.2424	0.3	8.7	4.6	19.0	6.2	8.6
LO-40	40	50	80.9	4.1	1.2964	-0.1	8.3	2.8	18.2	3.0	8.3
LO-40	50	60	82.0	4.3	1.0765	-0.8	10.0	1.6	21.9	1.9	9.9
LO-40	60	70	82.2	4.2	1.1132	-0.8	9.7	1.8	21.2	1.1	9.6
LO-40	70	80	81.7	4.1	1.2427	-2.8	8.7	-2.1	19.0	-2.0	8.6
LO-40	80	90	81.1	3.8	1.2778	-3.3	8.5	-2.9	18.5	-4.0	8.4
LO-40	90	100	80.3	3.6	1.2822	-3.9	8.4	-2.3	18.4	-5.2	8.3
LO-40	100	110									
LO-40	110	120									
LO-40	120	130									
LO-40	130	140									
LO-40	140	150									
LO-40	150	160									
LO-40	160	170									
LO-40	170	180									

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g dry weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (5.8 ng g^{-1} dry weight)
- D5: 23.6 ng (11.9 ng g^{-1} dry weight)
- D_6: 10.7 ng (6.1 ng g^{-1} dry weight)

Table 22. Results summary for background corrected, dry weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-64G (extruded and sectioned in a glove box), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

Sample Station	Stratum Interval (mm)		Water (%)	TOC (%)	Analyzed Sample Mass (g dry wt)	Background Corrected cVMS Concentrations (ng g^{-1} dry weight)					
						D_4		D_5		D_6	
	top	base				Measured	LLD[a]	Measured	LLD[a]	Measured	LLD[a]
LO-64G	0	5	87.9	4.9	0.6972	-5.6	15.5	21.7	33.9	-5.1	15.3
LO-64G	5	10	84.3	4.7	0.9340	-3.7	11.6	20.6	25.3	-0.5	11.5
LO-64G	10	15	83.2	4.3	1.1890	-3.3	9.1	14.8	19.8	1.6	9.0
LO-64G	15	20	82.1	4.3	1.3025	-3.6	8.3	9.8	18.1	0.0	8.2
LO-64G	20	25	82.6	4.5	1.0686	-3.7	10.1	16.8	22.1	2.1	10.0
LO-64G	25	30	82.6	4.4	1.2228	-4.4	8.8	7.2	19.3	0.5	8.8
LO-64G	30	35	83.2	4.3	1.0776	-3.9	10.0	15.2	21.9	3.3	9.9
LO-64G	35	40	83.5	4.3	1.1179	-4.9	9.7	10.8	21.1	-2.3	9.6
LO-64G	40	45	83.9	4.2	0.9790	-2.3	11.0	26.1	24.1	-8.5	10.9
LO-64G	45	50	82.7	3.9	1.0264	-3.4	10.5	18.6	23.0	-7.9	10.4
LO-64G	50	55									
LO-64G	55	60									
LO-64G	60	70									
LO-64G	70	80									
LO-64G	80	90									
LO-64G	90	100									
LO-64G	100	110									
LO-64G	110	120									

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g dry weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (5.8 ng g^{-1} dry weight)
- D_5: 23.6 ng (11.9 ng g^{-1} dry weight)
- D_6: 10.7 ng (6.1 ng g^{-1} dry weight)

Table 23. Results summary for background corrected, dry weight concentrations of D_4, D_5, and D_6 measured in sediment strata from sediment core LO-64A (extruded and sectioned in air), collected from the Rochester Basin (station 64) of Lake Ontario on 19 July 2007.

Sample Station	Stratum Interval (mm)		Water (%)	TOC (%)	Analyzed Sample Mass (g dry wt)	Background Corrected cVMS Concentrations (ng g^{-1} dry weight)					
						D_4		D_5		D_6	
	top	base				Measured	LLD[a]	Measured	LLD[a]	Measured	LLD[a]
LO-64A	0	5	86.9	4.9	0.7490	-2.9	14.4	41.4	31.5	4.9	14.3
LO-64A	5	10	83.4	4.7	1.0017	-3.0	10.8	29.8	23.6	5.8	10.7
LO-64A	10	15	80.8	4.5	0.9750	-2.7	11.1	34.1	24.2	7.2	11.0
LO-64A	15	20	82.6	4.4	1.1675	-2.3	9.3	24.9	20.2	6.0	9.2
LO-64A	20	25	82.2	4.4	1.1640	-1.9	9.3	26.3	20.3	9.0	9.2
LO-64A	25	30	81.8	4.2	1.0606	-3.6	10.2	20.7	22.3	0.5	10.1
LO-64A	30	35	83.1	4.3	1.0653	-4.1	10.1	16.7	22.2	-7.6	10.0
LO-64A	35	40	79.7	4.3	1.0195	-4.3	10.6	19.2	23.1	-4.6	10.5
LO-64A	40	45	82.5	4.3	0.9136	-4.9	11.8	20.4	25.8	-4.3	11.7
LO-64A	45	50	79.7	4.0	1.1700	-3.7	9.2	16.8	20.2	0.5	9.1
LO-64A	50	55									
LO-64A	55	60									
LO-64A	60	70									
LO-64A	70	80									
LO-64A	80	90									
LO-64A	90	100									
LO-64A	100	110									
LO-64A	110	120									

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g dry weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (5.8 ng g^{-1} dry weight)
- D_5: 23.6 ng (11.9 ng g^{-1} dry weight)
- D_6: 10.7 ng (6.1 ng g^{-1} dry weight)

Table 24. Results summary for background corrected, dry weight concentrations of D_4, D_5, and D_6 measured in surface sediments (upper 5 cm) collected from Toronto Harbor (station 725), the Niagara Basin (station 13), the Missasauga Basin (station 40), the Rochester Basin (station 64), and the Kingston Basin (station 81) of Lake Ontario on 17-20 July 2007.

Sample Station	Stratum Interval (mm) top	Stratum Interval (mm) base	Water (%)	TOC (%)	Analyzed Sample Mass (g dry wt)	Background Corrected cVMS Concentrations (ng g^{-1} dry weight) D_4 Measured	D_4 LLD[a]	D_5 Measured	D_5 LLD[a]	D_6 Measured	D_6 LLD[a]
LO-725	0	50	54.7	2.1	3.0744	286.5	3.5	790.1	7.7	197.9	3.5
LO-13	0	50	82.6	4.6	1.0499	1.5	10.4	13.7	22.7	6.7	10.3
LO-40	0	50	84.4	5.1	1.0337	-0.5	11.1	4.0	24.3	4.8	11.0
LO-64G	0	50	83.6	4.4	1.0615	-3.9	10.5	16.2	22.9	-1.7	10.4
LO-64A	0	50	82.3	4.4	1.0286	-3.3	10.7	25.0	23.3	1.8	10.6
LO-81	0	50	69.4	2.4	2.0215	-2.5	5.3	7.9	11.7	3.6	5.3

[a] LLD is the lower limit of detection for the sample, which was calculated by dividing the pooled, mass-based LLD (in ng) by the mass of sample (in g dry weight) that was analyzed. The pooled, mass-based LLD was based on analyses of the pooled field blanks, which were replicate aliquots of a sediment sample known to have very low or non-detectable concentrations of cVMS materials. For this study, the pooled mass-based LLD values and the pooled concentration-based LLD values were (Table 4):

- D_4: 10.8 ng (5.8 ng g^{-1} dry weight)
- D_5: 23.6 ng (11.9 ng g^{-1} dry weight)
- D_6: 10.7 ng (6.1 ng g^{-1} dry weight)

Table 25. The estimated fraction associated with suspended particulate phase (f_P) and the apparent residence time (T_A) of cVMS materials in near-shore and off-shore waters of Lake Ontario.

cVMS Material	Hydraulic Residence Time (yr)	Mean Particle Lifetime (T_L) (yr)	Log K_{OC} (mL g^{-1})	Near-Shore Waters TSM = 10 mg L^{-1} f_{OC} = 0.12 g g^{-1}		Off-Shore Waters TSM = 1.1 mg L^{-1} f_{OC} = 0.20 g g^{-1}	
				f_P (%)	T_A (yr)	f_P (%)	T_A (yr)
D_4	6.0	0.24	4.2	1.9	13	0.35	67
D_5	6.0	0.24	5.3	19	1.2	4.2	5.6
D_6	6.0	0.24	6.3	71	0.33	31	0.77

- T_L is the mean lifetime of a particle settling through the water column of the lake and is equal to the average depth of the lake (86 m for Lake Ontario) divided by the characteristic settling rate for the particle (approximately 1 m d^{-1}).
- K_d (in mL g^{-1}) is the particle-water distribution coefficient of the cVMS material, which describes the affinity of the material for a particle suspended in the water column, and is defined as:

$$K_d = \frac{C_P}{C_W} \approx K_{OC} \times f_{OC}$$

where: C_P is the concentration in the particulate phase (in mg g^{-1})
C_W is the concentration in the dissolved phase (in mg mL^{-1})
K_{OC} is the organic carbon-water distribution coefficient (in mL g^{-1})
f_{OC} is the fraction of organic carbon in the particulate phase (in g g^{-1})

- f_P is the fraction of cVMS material associated with the suspended particulate phase, which is defined as:

$$f_P = \frac{K_d(TSM)}{1 + K_d(TSM)}$$

where: TSM is the concentration of total suspended material in the water column (in g mL^{-1})

- T_A is the apparent residence time (under ideal conditions) of the cVMS material in the water column, with respect to particle settling, as defined by:

$$T_A = \frac{T_L}{f_P}$$

- Values for TSM and f_{OC} were obtained from Ling et al. (1993).

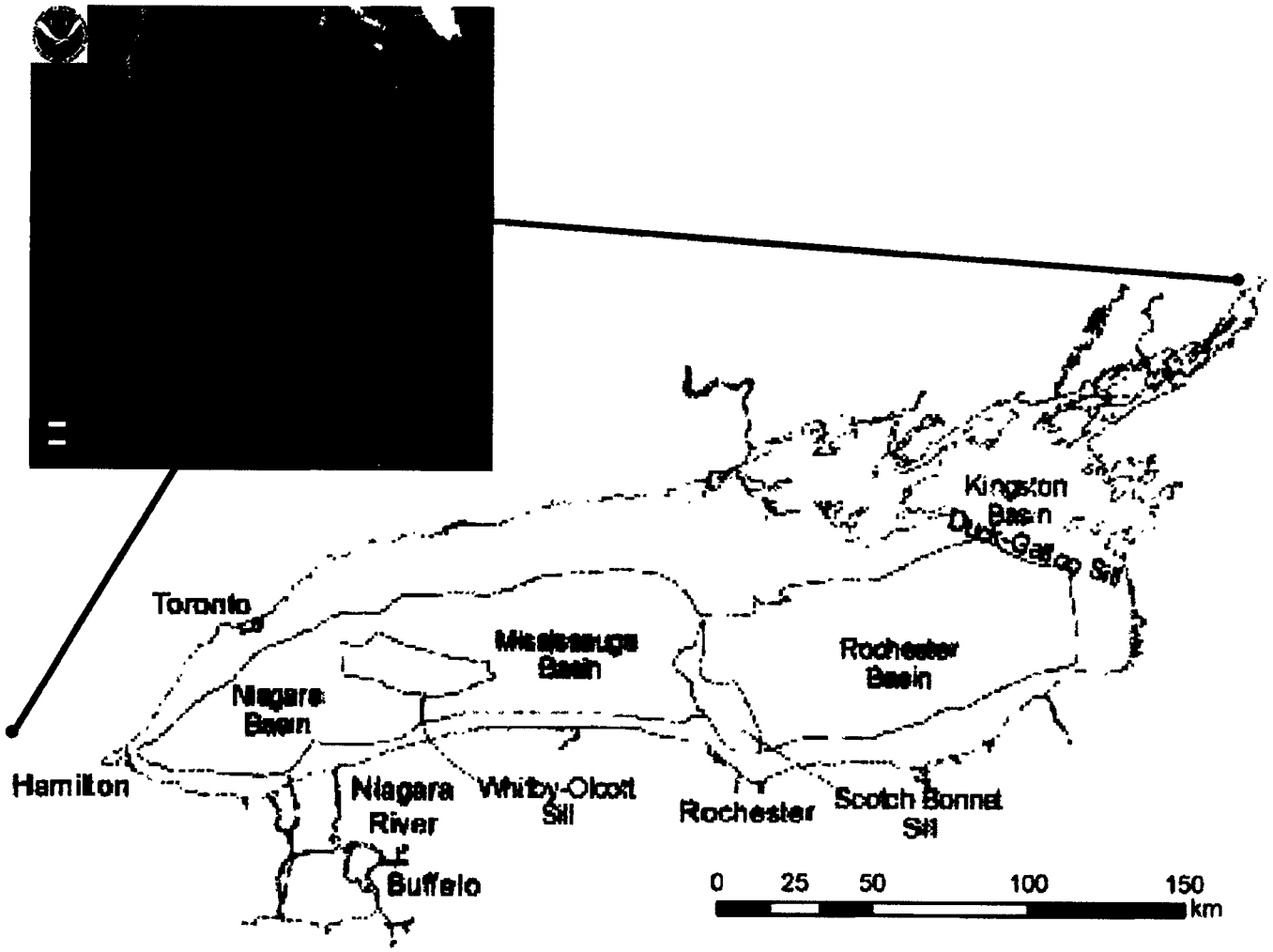

Figure 1a. Map of Lake Ontario, showing location of the lake in North America and locations of the sediment deposition basins in the lake.

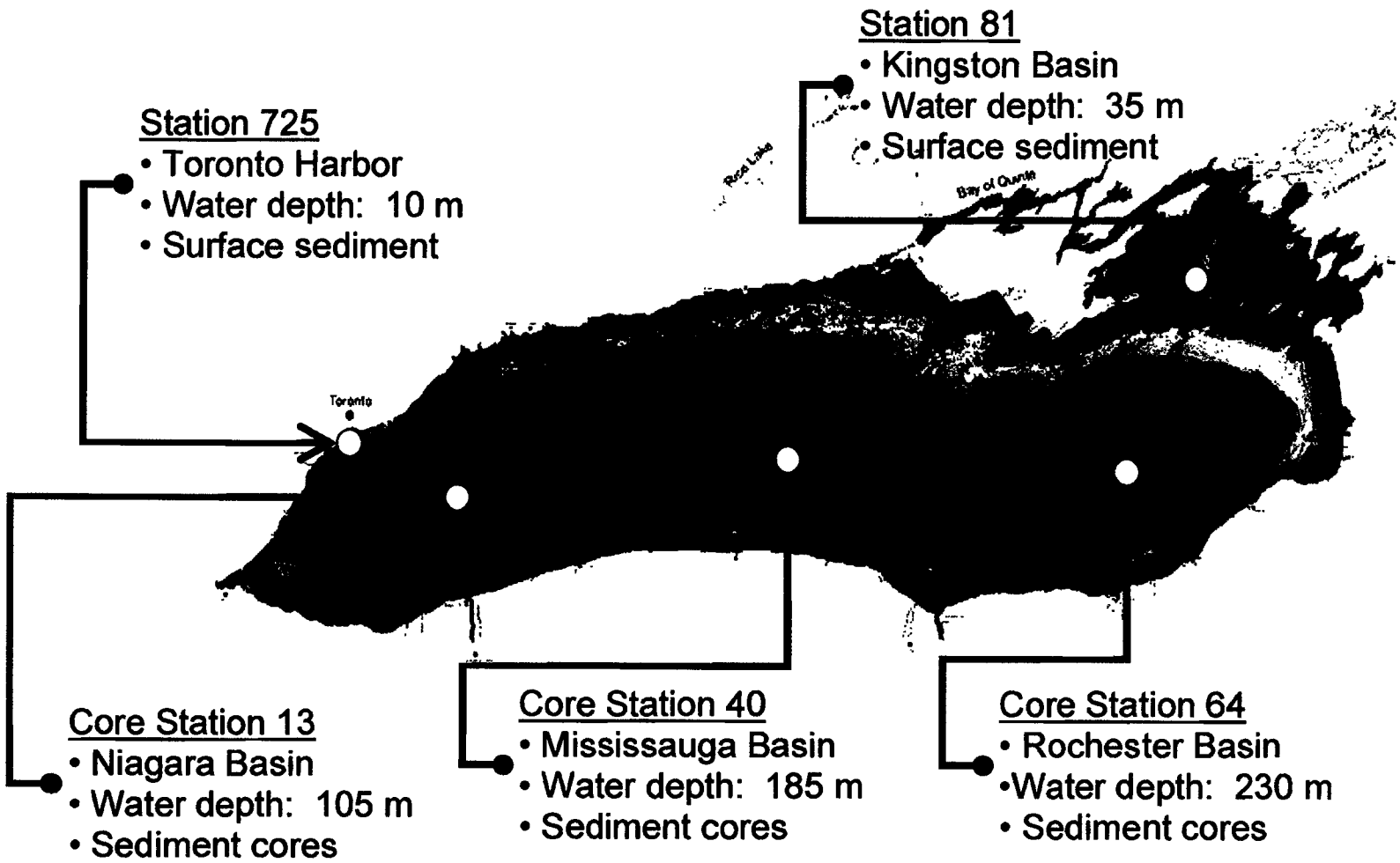

Figure 1b. Locations of sample collection stations.

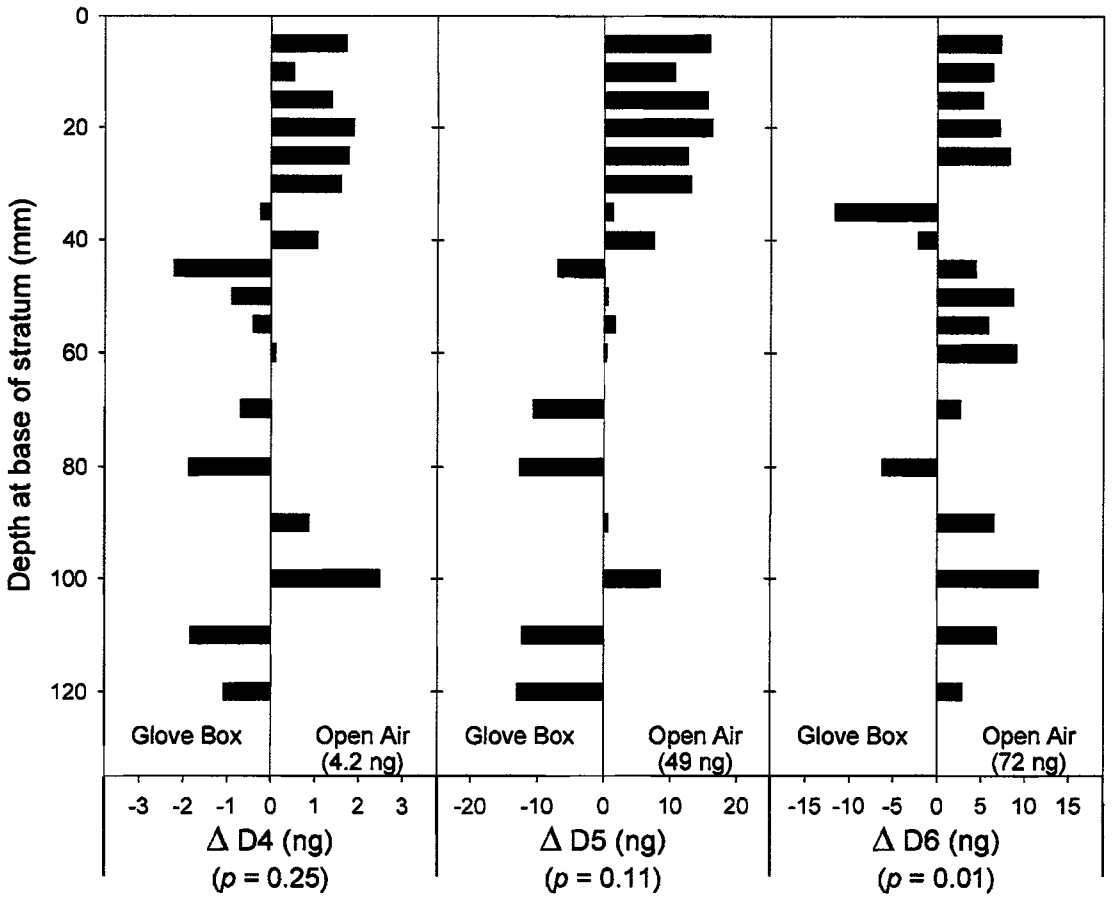

Figure 2. Comparison of non-background corrected amounts of cVMS materials measured in replicate sediment cores collected from Lake Ontario at core site 64. One set of the replicate cores were processed (i.e., extruded and sectioned) in a glove box under positive flow of nitrogen gas and a separate set were processed on deck in the open air. The delta value (Δ) was obtained by subtracting the amounts of cVMS measured in individual strata from the glove box cores from the amounts measured in the open air cores. The *p* values are the levels of significance for differences in the amounts of cVMS materials between the replicate cores, based on a two-sample t-test assuming equal variances.

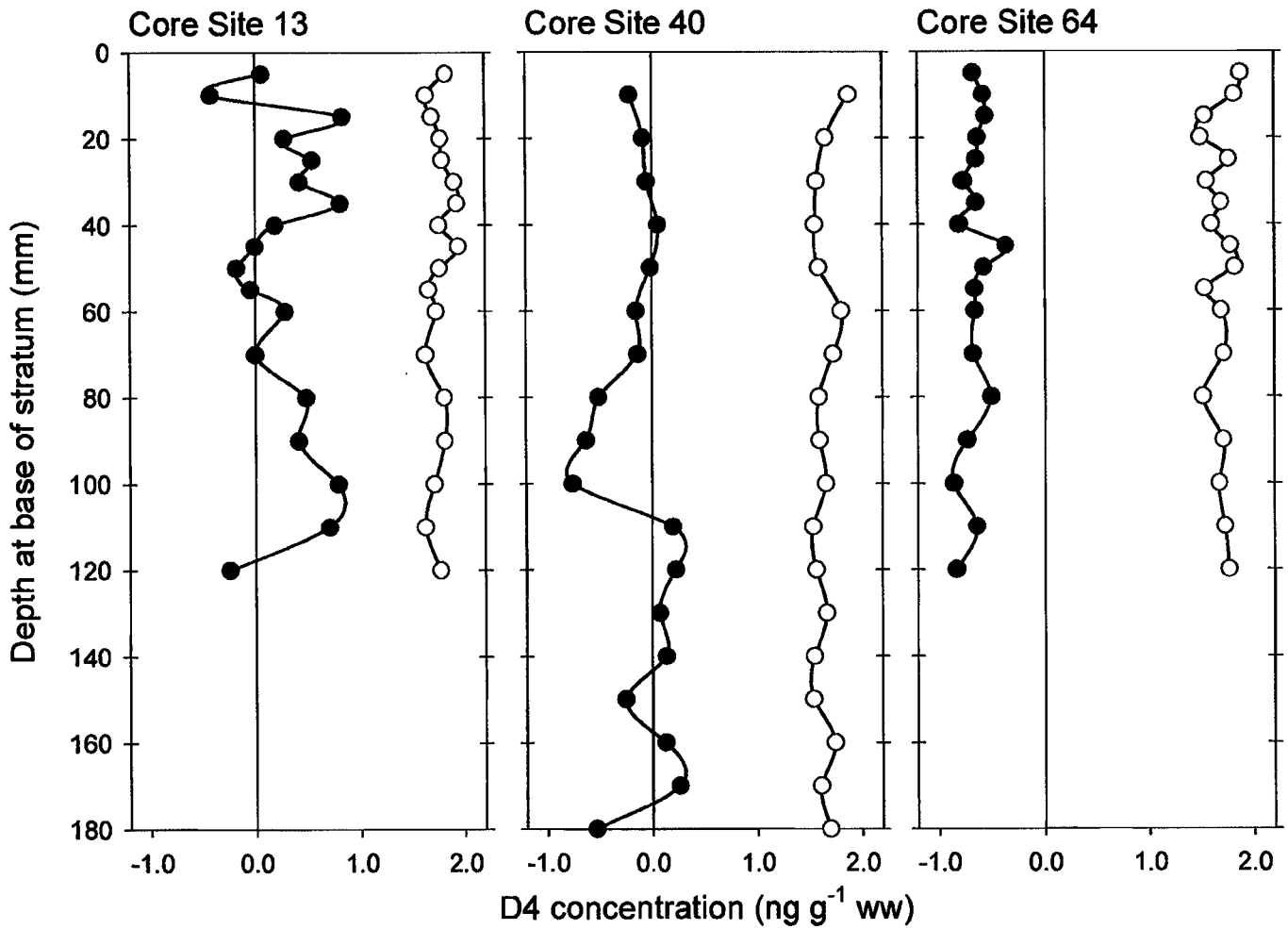

Figure 3. Background corrected concentrations (closed circles) and lower limits of detection (open circles) for D_4 measured in sediment cores collected form Lake Ontario 17-20 July 2006.

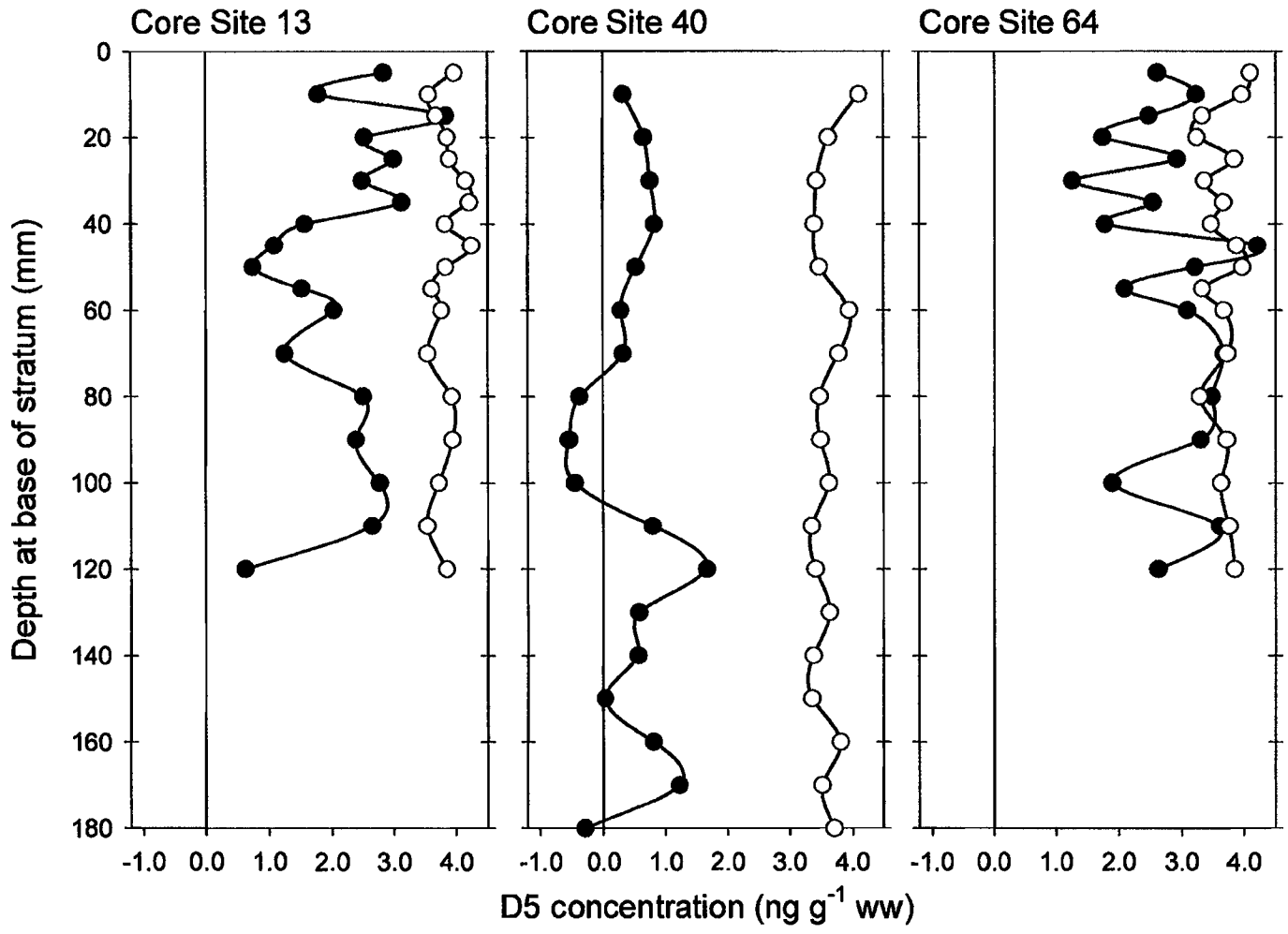

Figure 4. Background corrected concentrations (closed circles) and lower limits of detection (open circles) for D_5 measured in sediment cores collected form Lake Ontario 17-20 July 2006.

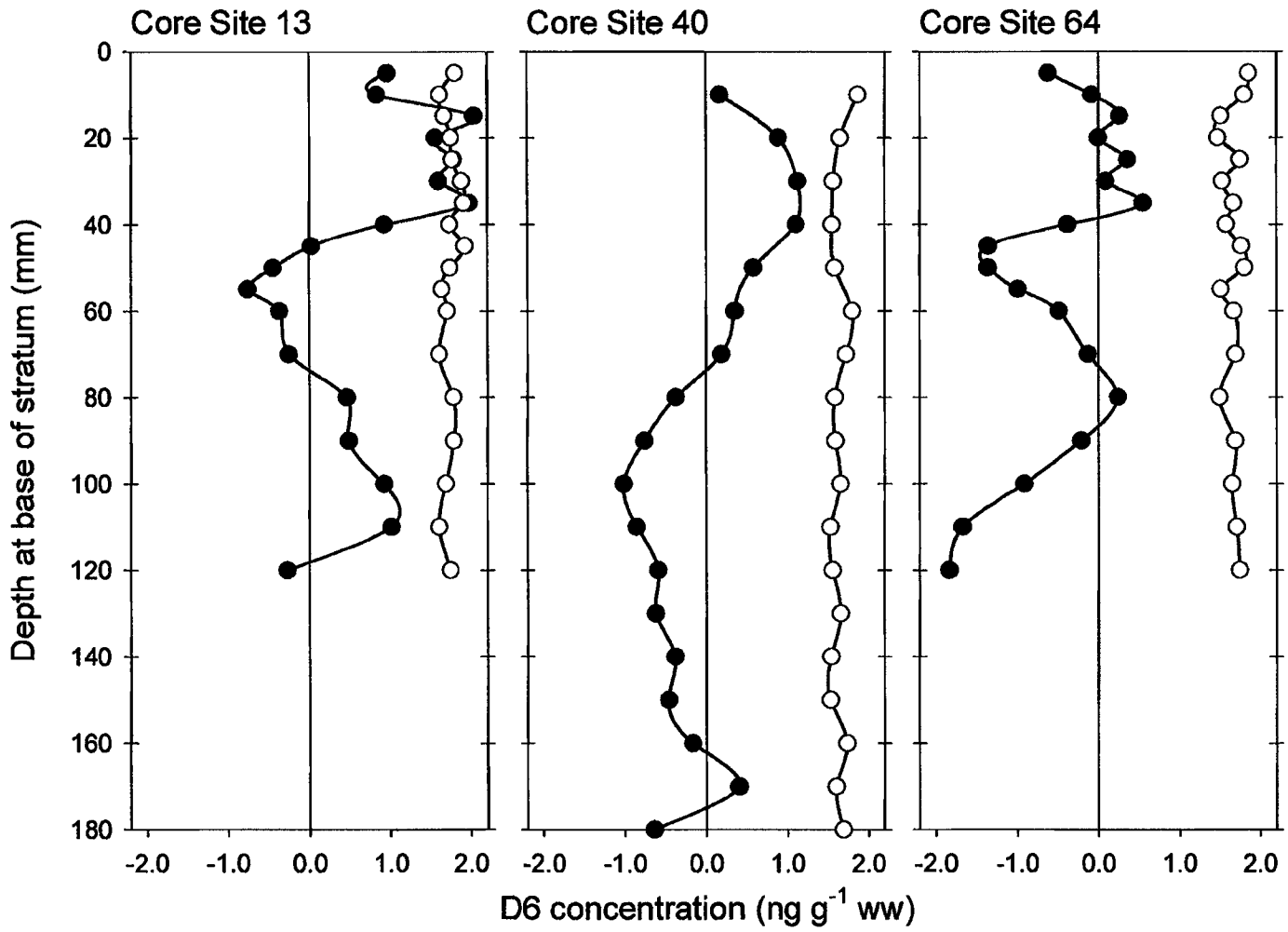

Figure 5. Background corrected concentrations (closed circles) and lower limits of detection (open circles) for D_6 measured in sediment cores collected form Lake Ontario 17-20 July 2006.

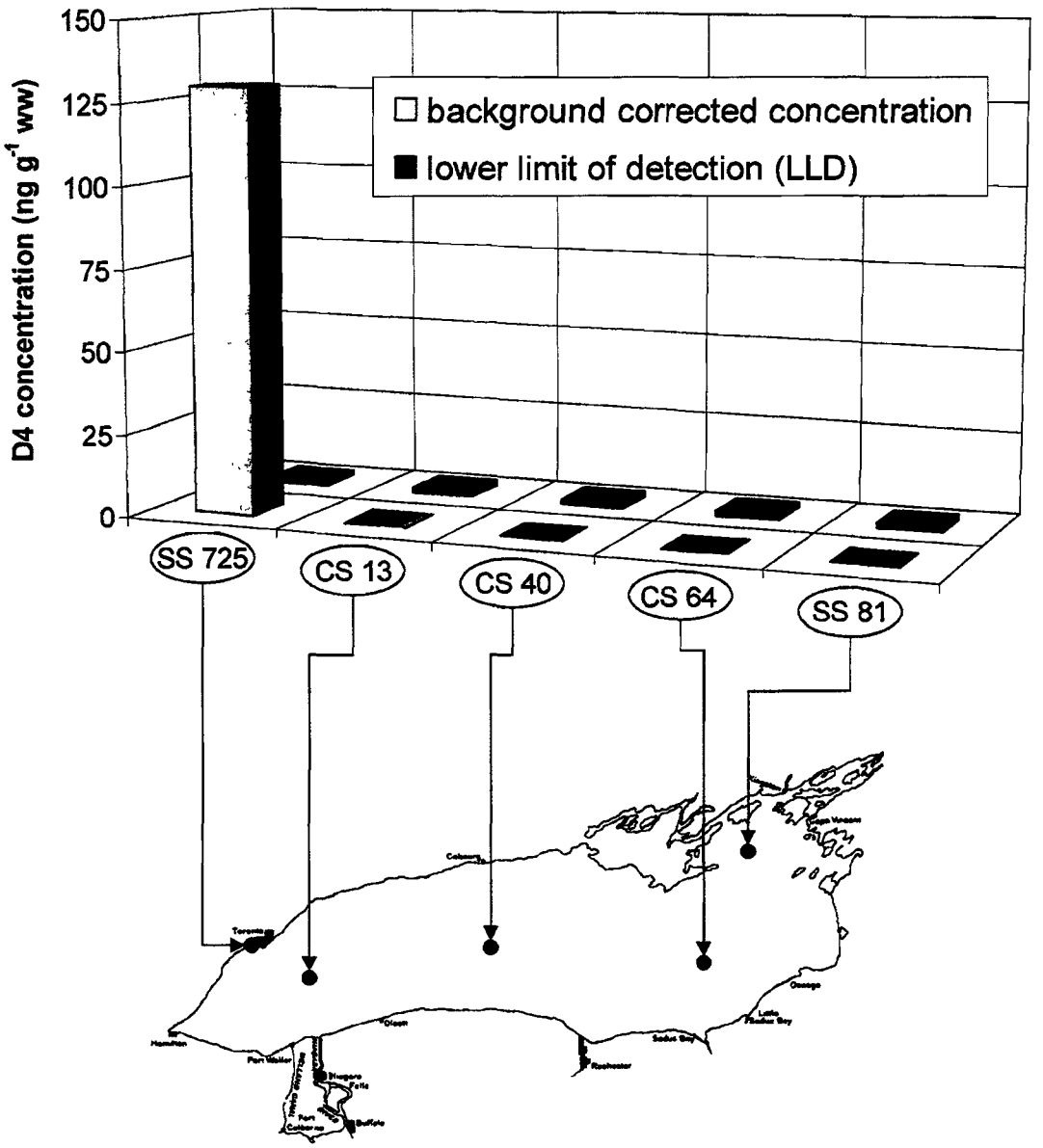

Figure 6. Background corrected concentrations and lower limits of detection (LLD) for D_4 measured in surface sediments collected form Lake Ontario 17-20 July 2006. Concentrations and LLD are expressed on the basis of wet weight.

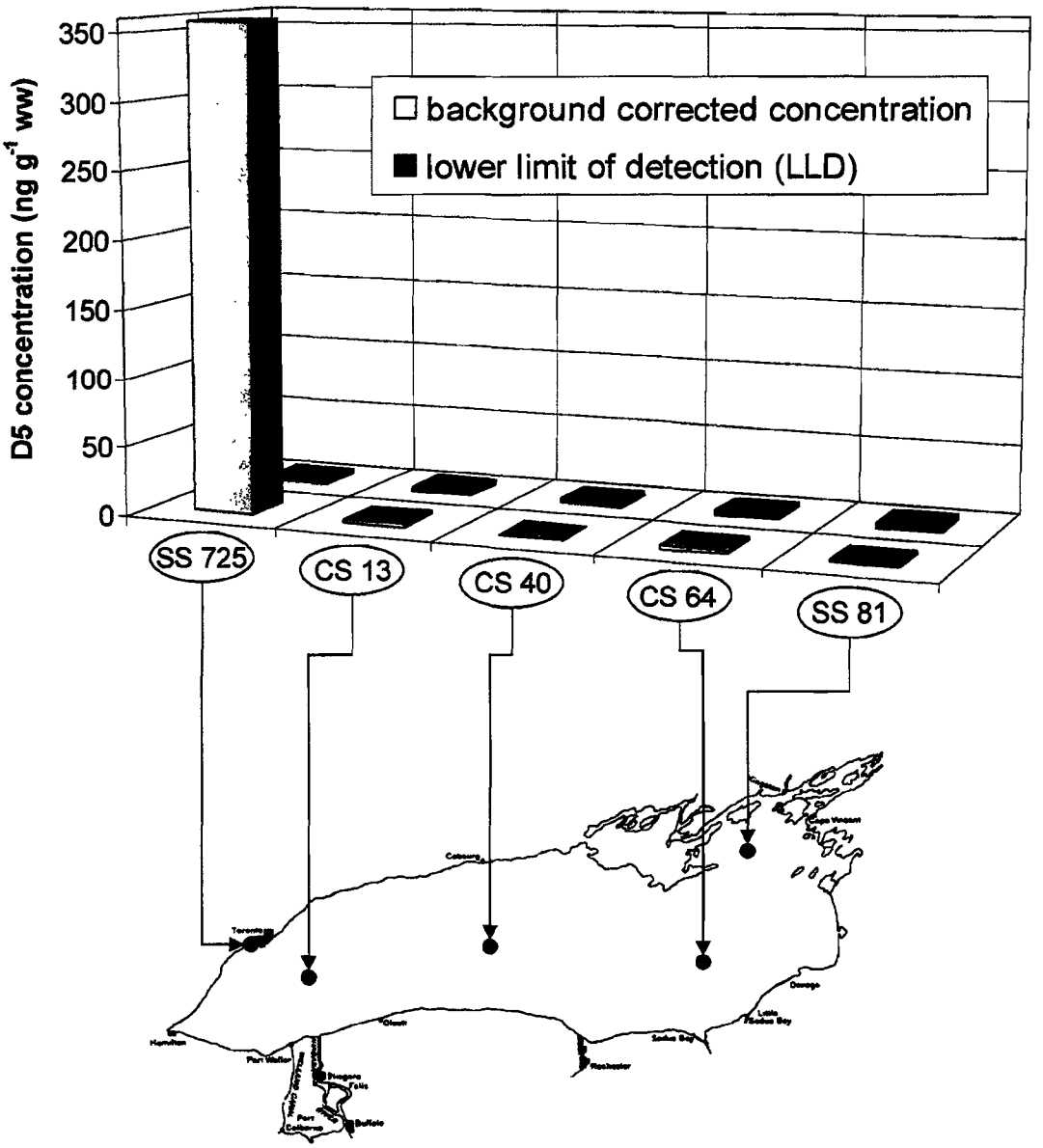

Figure 7. Background corrected concentrations and lower limits of detection for D_5 measured in surface sediments collected form Lake Ontario 17-20 July 2006. Concentrations and LLD are expressed on the basis of wet weight.

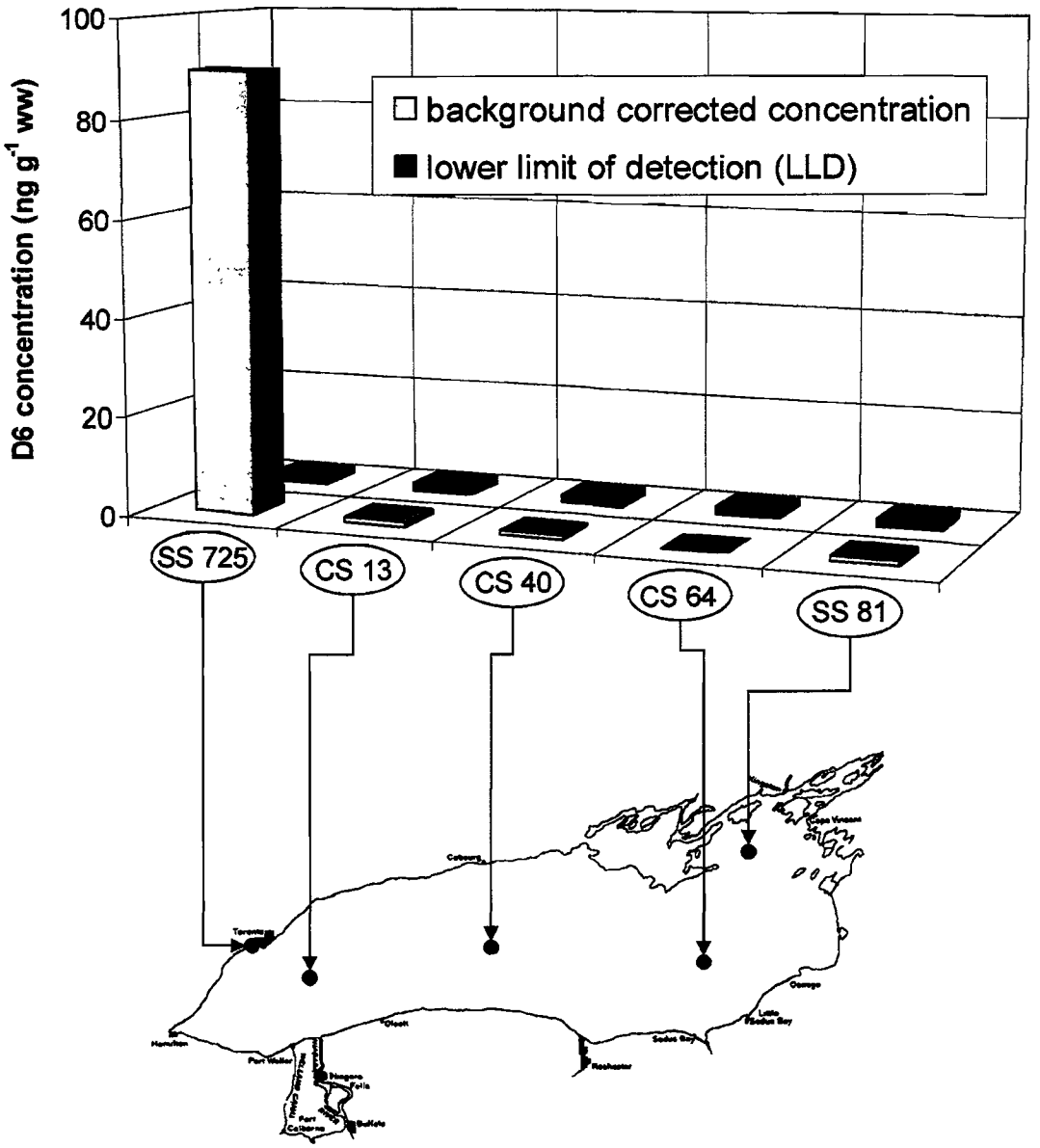

Figure 8. Background corrected concentrations and lower limits of detection for D_6 measured in surface sediments collected form Lake Ontario 17-20 July 2006. Concentrations and LLD are expressed on the basis of wet weight.

Study Title:	Trophic Dilution of Cyclic Volatile Methylsiloxane (cVMS) Materials in a Temperate Freshwater Lake.
HES Study No:	10771-108
Test Substances:	Octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2) Decamethylcyclopentasiloxane (D5; CAS No. 541-02-6) Dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6)
Authors:	David E. Powell Kent B. Woodburn
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Date:	18 May 2009

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ABSTRACT

The trophic transfer of cyclic methylsiloxane (cVMS) materials in aquatic ecosystems is an important criterion for assessing bioaccumulation and ecological risk. Food web magnification of octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6) was determined for a natural freshwater aquatic food web (Lake Pepin, Upper Mississippi River) using $\delta^{15}N$ as a continuous variable for assessing relative trophic levels (TL). The food web that was evaluated included surface sediments, 2 benthic macroinvertebrate species (2 genera, 2 families), and 15 fish species (14 genera, 9 families). Benthic detritivores (i.e., *Chironomous* sp. and *Hexagenia* sp.) occupied the lowest trophic level (TL ~2.0) and pelagic piscivores (i.e., largemouth bass and walleye) occupied the highest trophic level (TL ~3.7). 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 levels. Trophic magnification factors (TMFs) for the three cVMS materials were all < 1 (range 0.1 to 0.3) indicating trophic dilution across the aquatic food web. TMF values < 1 are indicative of materials that do not biomagnify and are considered to be non-bioaccumulative. Consequently, these results from Lake Pepin conclusively demonstrated that D4, D5, and D6 do not biomagnify in natural aquatic environments and confirmed that D4, D5, and D6 are <u>not</u> bioaccumulative materials.

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SIGNATURES and APPROVAL

This report consists of 61 pages with 11 tables and 10 figures. The undersigned have read and approved this report.

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INTRODUCTION

Cyclic volatile methylsiloxane (cVMS) materials, specifically octamethylcyclotetra-siloxane (D4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6), are widely used in industrial, personal care, and household applications (Horii and Kannan 2008), and the wastewater stream represents a major post-use disposal route. Generally, cVMS materials have relatively low molecular weight (297 to 445 amu), are volatile (vapor pressure 4.7 to 132 Pa at 25°C), have very low water solubility (5 to 56 μg/L), and are very lipophilic (Log K_{OW} 6.5 to 9.1). These properties are a consequence of the weak dispersion interactions in the neat liquid due to the low polarizability of the methyl siloxane materials, as reflected by their low molar refractivity, and their relatively large molecular size (Hirner et al. 2003; Ahmed et al. 2007). Because of these properties, cVMS materials occupy a somewhat unique chemical space and are expected to partition primarily to air during use and after disposal to wastewater. Multimedia modeling (Powell 2008) indicates that about 50-92% of the total emission of cVMS materials will partition to air and about 8-50% will be disposed to wastewater where they are efficiently removed during the treatment process. Less than 1-4% of the total cVMS emissions are expected to remain in wastewater effluents, which are the main sources of cVMS materials to surface waters.

Results of standard laboratory tests suggest that cVMS materials may meet regulatory screening criteria for bioaccumulation potential in Europe (Brooke et al. 2009a;b;c) and North America (Canada 2007a;b;c). Cyclic methylsiloxane materials have been identified as possible bioaccumulative chemicals in a number of categorization exercises (Environment Canada 2006; Muir and Howard 2006; Kaj et al. 2004, OSPAR 2005) due to their high Log K_{OW} values and laboratory-based bioconcentration factors (BCF 1660 to 12,400). However, relatively little data is currently available on the behavior of cVMS materials in the environment (reviewed by Brooke et al. 2009a;b;c). Cyclic volatile methylsiloxane materials have been measured in wastewater effluents (reviewed by Hirner et al. 2003; Brooke et al. 2009a,b,c). A Nordic survey (Kaj et al. 2005) found concentrations of cVMS materials ranging from < 0.1-6 μg/L in wastewater effluents with D5 predominating. However, the cVMS materials were not detected in urban or background surface waters. Urban sediments in Scandinavia had concentrations of cVMS materials ranging from <1 to 2200 ng/g dry weight (dw) while they were not detected at background sites. Schlabach et al. (2007) measured D4, D5, and D6 in wastewater effluent, surface water, sediment and biota from Inner Oslofjord. Concentrations of cVMS materials ranged from < 0.02-12 μg/L in wastewater and from < 4-920 ng/g dw in sediment, with D5 predominating, but were not detected in surface waters. Concentrations of cVMS materials in biota were 1.3-8.7 ng/g wet weight (ww) in mussels, 0.9-27 ng/g ww in livers of flounder, 70-2200 ng/g ww in livers of cod. Kaj et al. (2004, 2005) analyzed fish, seabird eggs, and marine mammals from Norway and Iceland for cVMS materials, finding D4, D5 and D6 in livers of fish (flounder, sculpin, dab) from urban areas and from several "background" marine locations. The cVMS materials were also detected in freshwater fish (pike, vendace) from Finland but not in

fish from background sites (arctic char and brown trout, Faroe Islands). Cyclic volatile methylsiloxane materials were not detected in seabird eggs (fulmar, herring gull). However, cVMS materials were reported at low ng/g concentrations in blubber of harbor seals from Denmark and pilot whale from the Faroe Islands. Knudsen et al. (2007) measured D5 residues ranging from 32.2-68.8 ng/g (wet weight; ww) in livers of dead or dying glaucous gulls from Bear Island, located midway between the mainland of Norway and the southern tip of Svalbard Archipelago. Kierkegaard et al. (2008) measured D5 residues averaging 10-12 ng/g ww in Arctic char taken from Lake Vattern, a large lake in Sweden receiving both industrial and wastewater discharge, while residues in a remote Swedish lake were detectable but below the limit of quantitation of 1 ng/g ww. While these limited measurements appear to suggest that cVMS materials may accumulate in top predator fish and marine mammals, it is unclear whether these results represent actual food web biomagnification or are simply a result of continuous exposure and rapid elimination or contamination due to the wide use of silicone based products.

Environmental exposure of aquatic organisms to highly lipophilic compounds may occur through both the water column and diet. Consumption of contaminated foodstuffs is thought to be the principal route of bioaccumulation for compounds with log K_{OW} values greater than about 5 (Bruggeman *et al.*, 1984; Muir *et al.*, 1985; Thomann, 1989; Nichols *et al.*, 2004). In the absence of metabolism, compounds with log K_{OW} values less that 5 tend to achieve concentrations that represent a thermodynamic equilibrium between the fish (predator or prey) and surrounding water. A compound is said to 'biomagnify' when lipid-normalized concentrations (or fugacity) of accumulated chemical residues in biological organisms increases with increasing trophic position (Fisk *et al.*, 2001; Hu *et al.*, 2006). It has been proposed (SETAC Pellston Workshop on Science-Based Guidance for the Evaluation and Identification of PBTs and POPs, Pensacola, FL, January 2008) that bioaccumulative substances be defined as substances which biomagnify in the food web - i.e., lipid-normalized concentrations (or fugacity) increase with increasing trophic position (Gobas *et al.*, 2008). Based on this definition, it was concluded that the most relevant criterion for assessing bioaccumulation was the Trophic Magnification Factor (TMF), and that the most conclusive evidence to demonstrate that a chemical substance biomagnifies was a TMF > 1.

Trophic magnification factors, which describe the change in chemical concentration from one trophic level to the other, are increasingly being used to assess bioaccumulation and biomagnification of chemicals in the environment (Muir *et al.*, 2004; Law *et al.*, 2006; Tomy *et al.*, 2007; Helm *et al.*, 2008; Houde *et al.*, 2008). Trophic magnification factors (TMFs) are derived from the slope of the regression of log lipid-normalized concentrations of the chemical in organisms from a food web versus their trophic level (TL), as determined by stable nitrogen isotope ratios ($\delta^{15}N$). As such, a TMF represents the trophic level increase of a chemical substance that is averaged across the food web rather than a single predator-prey relationship. Consequently, TMFs are preferable to single predator-prey relationships for comparing biomagnification between ecosystems. TMFs are particularly useful for comparing biomagnification of individual chemicals within a well defined food web of a single lake

or marine ecosystem. In addition, TMFs may be broadly applied across systems that differ considerably in their location and characteristics (Houde *et al.*, 2008). TMFs can be compared not only across regions for freshwater food webs but also between marine waters and freshwaters or among arctic, temperate, and tropical systems.

The overall objective of this study was to determine if cVMS materials, specifically, D4, D5, and D6 undergo biomagnification in a freshwater ecosystem. Biomagnification of cVMS was determined for Lake Pepin, which is a natural flood-plain lake on the Mississippi River located approximately 80 km downstream from the Twin Cities of Minneapolis and Saint Paul, Minnesota USA. TMFs for the three cVMS materials were determined for the aquatic food web of Lake Pepin using the stable isotopes of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) to estimate trophic positions and carbon flow to consumers (Post 2002; Jardine *et al.*, 2006). The part of the Lake Pepin food web that was evaluated (Table 1) included surface sediment, macroinvertebrates (2 species; 2 genera, 2 families), and fish (15 species 14 genera, 9 families). The biological organisms were divided into four feeding guilds (based on feeding habits and preferred habitat; Table 2) and seven trophic guilds (based on food preference; Table 3). The feeding and trophic guilds were subjectively assigned using information provided in Becker (1983), Goldstein and Simon (1999), and Pflieger (1997). Benthic detritivores (i.e., *Chironomous* sp. and *Hexagenia* sp.) occupied the lowest trophic level (TL ~2) and pelagic piscivores (i.e., largemouth bass and white bass) occupied the highest trophic level (TL ~4).

MATERIALS and METHODS

Study Area

Lake Pepin is a large, natural flood-plain lake in Navigation Pool No. 4 (river kilometers 1205 to 1276) of the upper Mississippi River (Fig. 1). The lake has a surface area of 102.7 km^2, length of 33.5 km and a mean depth of 5.4 m. Mean annual flows of the Mississippi River above Lake Pepin are about 600 $m^3 s^{-1}$ (Strark et al. 1996), and hydraulic residence times in the lake range from about 6 days during high flow regimes to 47 days during low flow (Heiskary and Vavricka 1993). Lake Pepin is approximately 80 km downstream from the Twin Cities of Minneapolis and Saint Paul, MN, a metropolitan area with an estimated population of 3.2 million people in 2006 and ranked as the 13th most populous metropolitan statistical area in the U.S (U.S. Census Bureau, 2008). The Metropolitan Wastewater Treatment Plant in St. Paul is the largest facility in the Twin Cities metropolitan statistical area and discharges about 10 $m^3 s^{-1}$ of treated wastewater to the Mississippi River. Point-source discharges from the Twin Cities metropolitan area have historically degraded the water quality of the river downstream through Lake Pepin (Johnson and Aasen, 1989) and were responsible for reduction of pollution-sensitive benthic organisms in the lake (Fremling 1964, 1989). Subsequent improvements to the treatment of wastewater in the Twin Cities have resulted in the return of pollution-sensitive benthic invertebrates since the early 1980s (Fremling 1989, Johnson and Aasen, 1989; Fremling and Johnson 1990). Lake Pepin is an efficient

sediment trap (Maurer *et. al.,* 1995), acts as an effective sink for sediment-associated contaminants (Wiener *et. al.,* 1984; Bailey and Rada 1984; Rada *et. al.,* 1990), and reduces the exposure of downstream reaches of the river to potentially toxic contaminants, such as cadmium (Beauvais *et. al.,* 1995) and polychlorinated biphenyl (Steingraber *et. al.,* 1994). Sediment accumulation rates range from 20-30 kg m^{-2} yr^{-1} in the upstream end of the lake and decrease to 3-5 kg m^{-2} yr^{-1} in the downstream end of the lake (Engstrom *et. al.*, 2009). Sediments in the lake have been spatially characterized with regard to particle size, organic content, and concentrations of certain trace metals (Bailey and Rada 1984; Rada *et. al.,* 1990; Balogh et al 1999; Engstrom et al., 2009).

Sample Collection

Fish were collected from Lake Pepin 04-05 September 2007. Surface sediments and benthic macroinvertebrates were collected from Lake Pepin 20-22 May 2008. All samples were collected with guidance and assistance from the State of Minnesota Department of Natural Resources (MDNR) Lake City Field Station, located in Lake City, Minnesota.

Fish (Table 1) were collected by electrofishing in near shore areas of the lake (Fig. 1). Immediately after collection, fish were placed in an oxygenated tank for transport to the nearby MDNR Lake City Field Station where the fish were measured for fresh weight and total length, and scales were collected for age determination. Individual fish were placed into polyethylene food storage bags, frozen whole and stored in the dark at about -20°C in a conventional freezer. Small forage fish (emerald shiner and young-of-year gizzard shad) of similar size were pooled into composite samples (Table 4) by species (n=3 composite samples of shad; n=4 composite samples of shiner) and placed into pre-cleaned glass jars with Teflon-lined lids before freezing. All fish were stored in a conventional freezer and transported frozen to Dow Corning Corporation in Midland, Michigan on 06 September 2007. All fish remained frozen during transport and were transferred to a -80°C freezer where they were stored until further processed.

Surface sediments and associated quality control (QC) samples were collected from 25 locations along five shore-to-shore transects positioned perpendicular to the flow axis of Lake Pepin (Fig. 1). Five surface sediment samples were taken along each transect at the same locations (Table 5) where ^{210}Pb-dated sediment cores had been collected in previous years (Balogh et al 1999; Engstrom et al., 2009). The five transects were distributed at roughly equal distances from upper to lower reaches of the lake, with each transect located in a different depositional region of the lake. Position coordinates of each station (Table 5) were determined at the time of collection using a Magellan® ProMark V and Magellan® DBR real-time differential global positioning system (DGPS). Surface sediments were collected using a stainless steel mini-box core. The upper 5-cm of surface sediment was removed from the box core on deck using a pre-cleaned 10-cm i.d. stainless steel core tube, placed into individually labeled polyethylene food storage bags, and stored in the dark in a cooler. Surface sediment samples were

transported back to the MDNR Lake City Field Station within 4 hours after collection for processing. On the day of collection, sediment samples and associated QC samples were homogenized in the individual storage bags and sub-samples collected for characterization analyses and determination of cVMS concentrations. Sediment samples to be analyzed for water, total organic carbon, and organic matter content were weighed into plastic containers with screw-cap lids. Samples to be analyzed for cVMS materials were weighed into extraction vials and extraction solvents containing internal standards were added, as described below. Any sediment remaining after removing the sub-samples was transferred to pre-cleaned, 120-mL wide mouth glass jars with Teflon-lined lids. All sediment samples were then stored at about 4°C in the dark in a conventional refrigerator. The refrigerated samples were transferred to coolers, stored under ice, and transported to Dow Corning Corporation in Midland, Michigan on 23 May 2008, where they were transferred to refrigerated storage at about 4°C in the dark.

Benthic macroinvertebrates (Table 1) were collected using a standard Ponar dredge and were retained in a 500-µm mesh wash tray that was rinsed with river water to remove small-grained sediment and detritus. Macroinvertebrates were removed from the wash tray using stainless steel forceps, placed directly into pre-cleaned glass jars with Teflon-lined lids, and stored in the dark in a cooler. Because of low densities or complete absence of organisms, it was not possible to collect benthic macroinvertebrates from all of the locations where surface sediments were collected (Fig. 1). Midge larvae (***Chironomous*** sp.) were collected from at least one location along each of the five shore-to-shore transects. Burrowing mayfly nymphs (***Hexagenia*** sp.) were collected from at least one location along the two upstream shore-to-shore transects, but were not found at any locations along the three downstream shore-to-shore transects. Macroinvertebrates were pooled into composite samples (Table 4) by species and transect (n=5 composite samples of midge larvae; n=2 composite samples of mayfly nymphs), transported back to the MDNR Lake City Field Station within 4 hours after collection, frozen whole and stored in the dark at about -20°C in a conventional freezer. The frozen macroinvertebrate samples were transferred to coolers, stored under ice, and transported frozen to Dow Corning Corporation in Midland, Michigan on 23 May 2008. All samples remained frozen during transport and were transferred to a -20°C freezer where they were stored until further processed.

Sample Preparation

Benthic macroinvertebrates and fish were removed from frozen storage and allowed to come to refrigerated temperature of about 4°C prior to processing. The benthic macroinvertebrates (midge larvae and mayfly nymphs) and forage fish (emerald shiner and young-of-year gizzard shad) were processed as composites of whole individuals, whereas all other fish were processed as individual whole specimens. Composite samples (Table 4) were prepared by cutting up the contents of each storage container into small pieces using clean scissors. The contents of each storage container were then homogenized using a Polytron® homogenizer and placed into frozen storage at -35°C. Whole, individual fish were removed from the polyethylene storage bags and

processed using a Hobart grinder model 4822. A small piece (about 3 g) of skin-free dorsal muscle tissue was first removed from behind the pectoral fin above the lateral line of each individual fish for analysis of stable isotopes. Each fish was then cut into small sections using stainless steel knives, and the cut sections passed through the grinder three times using a 13-mm cutting plate. The ground fish was collected into a stainless steel bowl and mixed by hand using a stainless steel spoon after each pass through the grinder. The ground fish was then homogenized by passing through the grinder a fourth time using a 3.2-mm cutting plate. The whole-body fish homogenate was then transferred, depending on size of fish, to a 0.5 to 4-L glass jar with Teflon-lined lid for frozen storage at -20°C.

Characterization of Sediments

Sediment composition and characterization analyses were determined by the Limnological Research Center at the University of Minnesota in Minneapolis. Small aliquots (about 10 g) of each sediment sample in individual plastic containers were shipped under blue ice from Dow Corning to the University of Minnesota on 09 June 2008. Samples were received in good condition at the University of Minnesota on 11 June 2008, and placed into refrigerated storage at about 4°C in the dark until processed for analysis. The surface sediment samples were analyzed by *carbon coulometry* (total carbon, total inorganic carbon, and total organic carbon) and *loss-on-ignition* (total water content and total organic matter content).

Carbon Coulometry Analyses: Organic carbon and carbonate mineral content were determined on freeze-dried and ground samples by coulometric titration (Engleman et al. 1985), using a UIC model 5011 CO_2 coulometer. Results were obtained as total carbon (%TC) and total inorganic carbon (%TIC); with total organic carbon (%TOC) calculated by difference. Percent calcite was calculated by dividing %TIC by 0.12, the mole fraction of C in $CaCO_3$. Given the local geology and water chemistry of Lake Pepin, calcite was assumed to be the only carbonate mineral present. Identification of other carbonate phases in the lake sediments would lead to small corrections in this calculation.

Loss-on-Ignition Analyses: A small quantity (about 3 cm^3) of sediment from each sample was used to determine sediment composition by LOI analysis according to the recommendations of Heiri et al. (2001). The entire sediment sample was vigorously stirred until homogenized, then sub-sampled with a spatula into a pre-weighed ceramic crucible and weighed again. Samples were oven-dried at 100°C overnight, cooled completely, and weighed to determine water content. Samples were then ignited in a muffle furnace at 550°C for four hours, cooled, and weighed to determine organic matter content. Samples were finally burned at 1000°C for two hours, cooled, and weighed to determine $CaCO_3$ content. The sample mass remaining after the 1000°C burn was considered the "inorganic" content, i.e., silicate minerals, oxides, and silicate algal (diatom) remains.

Characterization of Fish and Benthic Macroinvertebrates

Fish and benthic macroinvertebrates were analyzed for water content, lipid content and for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) by the Biogeochemistry and Paleoproteomics Laboratory at Michigan State University in East Lansing. Surface sediments were also analyzed for $\delta^{15}N$ and $\delta^{13}C$. Small aliquots (about 3 g) of each sample in individual plastic containers were transported from Dow Corning to Michigan State University. The samples were taken by car in a cooler containing blue ice. The first set of fish samples was transported on 08 February 2008 with the main set of fish sent on 26 June 2008. The benthic samples were transported on 16 June 2008. The sediment samples were transported on 19 September 2008. All samples were immediately placed into refrigerated storage upon arrival at about 4°C in the dark until processed for analysis.

Water and Lipid Content: Water and lipid content of the benthic macroinvertebrates and fish were determined on whole-body homogenates of individual fish, homogenized composite samples of small forage fish (emerald shiner and young-of-year gizzard shad), and homogenized composite samples of benthic macroinvertebrates (midge larvae and mayfly nymphs). Water content was determined as weight loss during lyophilization to a constant weight. The remaining lyophilized material was then extracted with chloroform:methanol (87:13) and lipid content determined gravimetrically and expressed on both dry and wet weight basis. The precision (± standard deviation) for this technique, based on replicate analyses of a laboratory standard (rainbow trout, *Oncorhynchus mykiss*), was 0.2 % for water content and 1.25% for lipid content.

Stable Isotope Analysis: Sub-samples of biota, and sediment were analyzed for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$). Isotopic signatures of the benthic macroinvertebrates (midge and burrowing mayfly) and small forage fish (emerald shiner and young-of-year gizzard shad) were determined on whole-body homogenates of the composite samples. Isotopic signatures of the remaining fish species were determined on skinless dorsal muscle tissue that was collected from posterior to the pectoral fin above the lateral line of each individual specimen. Biological samples were first lyophilized to a constant weight and extracted with chloroform:methanol (87:13) to remove the lipids. Sediment samples were first lyophilized to a constant weight, acidified with 0.5 N hydrochloric acid to remove carbonates, and washed with distilled water to remove acid residues. All samples were then dried in a vacuum oven and homogenized to a fine powder with a mechanical mill. The samples (about 1.0 mg in tin capsules) were combusted with O_2 and Cr_2O_2 at about 1030°C in an elemental analyzer (Eurovector). NOx products were reduced with Cu at 650°C. The combustion products N_2, CO_2, and H_2O were separated on a packed column and the $^{15}N/^{14}N$ or $^{13}C/^{12}C$ isotopic ratios determined using an interfaced isotope ratio mass spectrometer (Elementar Americas, Inc). Stable isotope abundances were expressed in per mil notation (δ) as the deviation from standards in parts per thousand (‰) according to the equation:

$$\delta X = \left[\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right] \times 1000$$

where X is ^{15}N or ^{13}C and R is the abundance ratio of the heavy to light isotope (i.e., $^{15}N/^{14}N$ or $^{13}C/^{12}C$). The $R_{standard}$ values were based on atmospheric nitrogen gas for ^{15}N and PeeDee Belemnite (PDB) for ^{13}C. The precision (± standard deviation) for this technique, based on replicate analyses of laboratory standard (Atlantic salmon; *Salmo salar*), was ≤0.2 ‰ for ^{15}N and ^{13}C.

Analysis of Cyclic Volatile Methylsiloxane (cVMS) Materials

Surface sediments, fish, and benthic macroinvertebrates were analyzed for cVMS materials (specifically D4, D5, and D6) by Dow Corning Corporation in Midland, Michigan.

Reagents: Hexanes (Optima grade) and acetonitrile (HPLC grade) were obtained from Fisher Scientific and used without further purification for extraction of cVMS materials from sediments. Tetrahydrofuran (THF) anhydrous ≥99.9% was obtained from Sigma-Aldrich and used without further purification for extraction of cVMS materials from benthic macroinvertebrates and fish. Anhydrous magnesium sulfate, also from Fisher Scientific, was used for removing incidental water from all extracts. Isotopically enriched ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6, used as internal standards for the GC-MS determination of cVMS materials in sediment extracts, were synthesized and characterized at Dow Corning Corporation (Midland, MI).

Extraction of Surface Sediments: Sediment samples and associated QC samples were initially processed for extraction of cVMS materials at the MDNR Lake City Field Station. On the day of collection, a 6-g sub-sample of wet sediment was weighed into a single-use borosilicate glass vial (28 x 95 mm, ca. 40 mL capacity), followed by addition of 6 mL of acetonitrile. After brief manual agitation, 12 mL of hexanes was added to the vial. The hexanes solvent contained known concentrations of isotopically labeled ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6 to serve as internal standard surrogates. The vial with sediment was re-weighed after each solvent addition so that accurate internal standard amounts could be determined. The capped vials were placed on a vortex mixer for 30 min and the samples then stored in coolers, in the dark, for transport to Dow Corning Corporation, as previously described. Samples were further processed for cVMS analyses at Dow Corning Corporation. Capped vials were centrifuged to facilitate separation of the phases. The upper hexane layer was removed to a round-bottom glass tube (20 x 150 mm) containing anhydrous magnesium sulfate (ca. 0.25 g) for drying the extract. A second portion of hexanes without the internal standards was added to the extraction vial. The extraction process was repeated

and the hexanes were combined in the glass tube. The extract volume in each tube was reduced in volume to approximately 1-2 mL under a stream of high purity liquid nitrogen from a dewar in a 25 °C bath. A portion of the resulting concentrated extract was transferred to a crimp-cap vial for GC-MS analysis.

Extraction of Fish and Benthic Macroinvertebrates: Frozen whole-body homogenates of individual fish and composite samples of forage fish and benthic macroinvertebrates were thawed to 4°C in a refrigerator and stirred before sub-samples were collected for extraction. Sub-samples of each homogenate, about 6 g for whole body fish; were weighed into single-use borosilicate glass vials (28 x 95 mm, ca. 40 mL capacity). Composite young-of-year gizzard shad; about 3 g for composite emerald shiner; about 1.6 g for composite mayfly nymphs; were weighed into single-use borosilicate glass vials (28 x 59 mm, ca. 20 mL capacity) and about 0.4 g for midge larvae were weighed into single-use borosilicate glass vials (15 x 46 mm, ca. 4 mL capacity). Homogenates were then extracted using a 2:1 solvent-to-sample mass ratio of THF containing known concentrations of isotopically labeled ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6 to serve as internal standard surrogates. The appropriate amount of THF containing the internal standards was added to the glass vials by weight, and the capped vials were placed on a vortex mixer for 30 min. The samples were then centrifuged for 5 minutes to separate the solids and the THF extract transferred to a new 40 ml vial. A second portion of THF without the internal standards was added to the first extraction vial, the extraction process repeated, and the extracts combined in the second extraction vial. A portion of the extract was transferred to a round-bottom glass vial (12 x 33 mm) containing anhydrous magnesium sulfate (ca. 0.25 g) for drying the extract. A portion of the dried extract was transferred to a crimp-cap vial for GC-MS analysis.

Analysis of Extracts: Gas chromatograph coupled with mass selective detection (GC-MS) was used to measure the amounts of D_4, D_5, and D_6, and ^{13}C-D_4, ^{13}C-D_5 and ^{13}C-D_6 in the sample extracts. GC-MS analyses of the extracts were performed on an Agilent 6890 gas chromatograph interfaced to an Agilent 5973 mass selective detector with an electron impact (EI) ionization source, operated in selected ion monitoring (SIM) mode. The GC was configured with a conventional inlet (150 °C) for making split injections (5:1 split ratio); lower inlet temperatures were useful for minimizing the magnitude of instrument-related background, with only modest reduction in sensitivity. Analytes were separated on a DB-WAXetr capillary GC column (polyethylene glycol, 30 m x 0.25 mm x 0.25 μm df) with helium carrier gas (1 mL/min). Following a 3 min post-injection hold at 40 °C, the column oven temperature was increased to 190 °C over 6 min, followed immediately by a second ramp to 210 °C over 0.5 min. Typical retention times were 4.1, 5.7, and 7.0 min, respectively, for D_4, D_5, and D_6. The target ions used for quantitative analysis were: $D_4/^{13}C$-D_4, *m/z* 281 and 285; $D_5/^{13}C$-D_5, *m/z* 355 and 360; $D_6/^{13}C$-D_6, *m/z* 429 and 435. These ions are formed by loss of a single $-CH_3$ group from the parent molecule and have the highest abundance in the EI spectra, excluding the common $[Si(CH_3)_3]^+$ ion at *m/z* 73. Peak area ratios

obtained from the resulting single ion chromatograms were used to calibrate response ratio against amount ratio for each compound using standards prepared in hexanes, and covering an approximate concentration range of 2.1 to 2500 ng/mL. The amounts of cVMS materials in each extract were determined from the resulting 1/(peak area)^2-weighted linear regression calibration functions, from which concentrations in the original sample were calculated.

Quality Control

Cyclic VMS materials are widely used in consumer products and may be present in personal care products, commercial products, and lubricants. Given the significant potential for sample contamination during collection, processing, storage, and analysis for cVMS materials in environmental matrices, a rigorous quality control (QC) program was developed and implemented in the field and laboratory. To the extent possible, all equipment in direct contact with samples was decontaminated by washing with dishwashing detergent followed by consecutive rinses with deionized water, acetone, and hexane. Sediments in direct contact with equipment that could not be decontaminated before use (i.e., box core, ponar, etc.) were not retained. Benthic macroinvertebrates were separated from the sediment matrix using a stainless steel 500-µm mesh wash tray that was rinsed with subsurface river water to remove small-grained sediment and detritus. Macroinvertebrates were removed from the wash tray using stainless steel forceps and placed directly into pre-cleaned glass jars with Teflon-lined lids. Fish were collected during electrofishing using dip nets with nylon mesh and held live in the field in an oxygenated steel holding tank containing subsurface river water. Fish were placed into polyethylene food storage bags and frozen whole after processing. To minimize potential contamination from air, field processing of all samples (fish, macroinvertebrates and sediment) was conducted outdoors down wind of the lake and upwind from buildings or other potential sources of cVMS materials. To prevent cross-contamination of samples, stainless steel instruments used during field processing were rinsed with water during use.

A rigorous QC program was followed in the field and laboratory to evaluate detectability, bias, and precision, and to verify that samples were not contaminated by sample collection, handling, shipment, storage, and processing procedures, (Table 6). Standard reference materials were not available for D4, D5, or D6 in any matrix. Therefore, reference materials were prepared by Dow Corning for the sediment and fish matrices. Reference materials for the benthic macroinvertebrate matrix could not be prepared because sufficient sample masses were not available The reference material for the sediment matrix was prepared by adding known masses of D_4, D_5, and D_6 to natural sediment having non-detectable concentrations of the cVMS materials. The reference material for the fish matrix was prepared by feeding live rainbow trout (*Oncorhynchus mykiss*) a diet that was dosed with D_4, D_5, and D_6. Final concentrations of the cVMS materials in the fish were determined by the concentrations in the food, duration of feeding exposure, and feeding rate.

Analytical methods were developed and validated using reference materials dosed with isotopically labeled ^{14}C-D_4, ^{14}C-D_5, and ^{14}C-D_6. Concentrations of D4, D5, and D6 in the dosed reference materials were determined by radiometric analysis and by GC-MS analysis. Reference materials dosed with unlabeled D4, D5, and D6 were used to monitor for changes in cVMS concentrations resulting from processing and storage of samples, and day-to-day variability in background and analytical performance.

Reference Sediment: Reference sediment used for the field blanks and reference samples was collected from Sanford Lake, a reservoir created by impoundment of the Tittabawasee River at Sanford, Michigan. Surface sediment (upper 5-10 cm) having a sandy-silt texture was collected on 09 May 2008. Concentrations of the cVMS materials in the natural Sanford Lake sediments were below detection. Dosed sediment was prepared by adding known quantities of the cVMS materials directly to the natural sediment. Characteristics of the surface sediment collected from Sanford Lake and used as QC samples for this study are shown below:

Characteristic	Value
Classification	Clay Loam
Texture (%, dry wt)	
• Sand	29
• Silt	32
• Clay	39
Solids content (%, wet wt)	41.8
Water content (%, wet wt)	58.2
Total organic carbon (%, dry wt)[1]	1.80
LOI (organic matter content; % dry wt)	19.2
Bulk Density (g cm^{-3} wet sediment)[2]	1.16
cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
• Blank sediment	
o D4	0.5 ± 1.1
o D5	0.8 ± 0.9
o D6	0.6 ± 0.1
• Dosed sediment	
o D4	19.3 ± 9.4
o D5	24.9 ± 9.6
o D6	20.9 ± 5.6

[1] Determined by Walkley Black titration method.
[2] Calculated from loss on ignition, and water content assuming a particle density of 2.6 g cm^{-3} (Håkanson and Jansson 1983).

Reference Fish: Live rainbow trout (*Oncorhynchus mykiss*) used for the field blanks and reference samples were purchased from Rainbow Ranch Trout Farm, located in Tawas, MI. Concentrations of the cVMS materials in the blank fish were below detection. The reference material fish was dosed by feeding live rainbow trout a diet of Zeigler trout chow (Ziegler Brothers, Gardner, PA) that

was dosed with unlabelled D_4, D_5, and D_6. The fish were fed the dosed feed at a rate of 1 g/day for 5 days. Characteristics of the fish used as QC samples for this study are shown below:

Characteristic	Mean ± sd
Blank fish (n=1)	
• Fresh weight (g)	750
• cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
o D4	2.4 ± 1.0
o D5	3.4 ± 1.0
o D6	0.2 ± 0.6
Dosed fish (n=1)	
• Fresh weight (g)	700
• cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
o D4	15109 ± 775
o D5	11495 ± 556
o D6	7762 ± 319

For the purpose of this study, detection levels as defined by APHA (1999) were used since they were frequently identified in the field monitoring literature (Table 6). Although the terminology may differ from that provided in more definitive sources (ASTM 2003; IUPAC 1995, 2002) the definitions are analogous. Methods for determining detection levels are available in various publications (Analytical Methods Committee 1987; Taylor 1987; Kateman and Buydens 1993; IUPAC 1995; Berger et al. 1996; Smith 1997; Eurachem 1998; APHA 1999; IUPAC 2002). Of the different detection levels that are defined, the limit of detection (LOD), the method detection level (MDL), and the limit of quantification (LOQ), are the most valuable for field monitoring. The LOD, MDL, and LOQ are similar in concept to the signal-to-noise ratio. The LOD is based on the ability to distinguish between signal and noise of the instrument and is determined by repetitive analysis of matrix-free blanks. The MDL is a measure of a methods ability to quantify an analyte in a sample matrix and is determined by repetitive analysis of a sample having a known level of analyte that is at least equal to the MDL but no greater than 5 times the MDL. The MDL will be greater than the LOD because of additional background noise resulting form the sample matrix and variability introduced through processing the sample for analysis. The LOQ is the minimum level of target analyte in a sample that can be detected and accurately quantified, and was defined as 3 times the MDL.

The LOD, MDL, and LOQ were determined as a function of the variance associated with replicate analyses of matrix-free blanks (LOD) and replicate analyses of samples containing a small, but measurable amount of cVMS materials (MDL, LOQ). The LOD and MDL at 99% confidence were then defined as:

$$DL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses. For this study, the LOD was calculated using non-background corrected amounts of D4, D5, and D6 measured in reagent blanks that were carried through the entire analytical procedure. The MDL was calculated using non-background corrected amounts and concentrations of D4, D5, and D6 measured in samples. The MDL for sediment was based on replicate analyses (N=6; $t_{0.99}$ = 3.37) of reference sediment. The MDL for benthic macroinvertebrates was based on replicate analyses (N=3; $t_{0.99}$ = 6.97) of a pooled midge sample. The species-specific MDL for fish was based on replicate analyses (N=7; $t_{0.99}$ = 3.14) of an individual fish from each species. The MDL for fish was then obtained as the intercept of the regression of species-specific MDL on mean concentration, where mean concentration was at least equal to but less than 5 times the species-specific MDL.

A variable instrumental blank response was always present for D4, D5, and D6, which made quantification of the cVMS materials difficult in most samples. The background response could be minimized and stabilized, but not eliminated, by changing the glass injection port liner and rubber septum prior to every analytical run, followed by 5 or more injections of a blank solvent in order to clean the injection port as much as possible. In addition, a DB-WAXetr column was used since it was a polyethylene glycol based column, which was free of siloxane materials. Measured amounts of cVMS materials in the samples were corrected for background levels of cVMS using results from the reagent blanks. Results for the reagent blanks represented background levels of cVMS materials associated with extraction solvents or lab ware, as well as contamination incurred during handling or treatment (e.g. volume reduction) of the extracts.

Tabular summaries of the analytical results for the QC samples associated with this study are provided in Table 7. Method detection limits (MDLs, expressed on the basis of wet weight) across all matrices (sediment, macroinvertebrates, and fish) ranged from 1.4 to 8.5 ng/g ww for D4, from 0.9 to 21.1 ng/g ww for D5, and from 1.5 to 4.5 ng/g ww for D6. Comparison of the MDLs and LOQs (Table 5) to concentrations in the samples (Table 10) indicated that:

- Background corrected concentrations of D4 in sediments were all less than the MDL for D4. Background corrected concentrations of D5 and D6 in sediments were all greater than the MDL, but were less than the LOQ for D5 in 18 of 25 samples and less than the LOQ for D6 in 25 of 25 samples.
- Background corrected concentrations of D4, D5, and D6 in benthic macroinvertebrates were all greater than the MDL, but were less than the LOQ for D4 in both midge and mayfly and less than the LOQ for D6 in mayfly.
- Background corrected concentrations of D4 and D5 in fish were all greater than the MDL, but were less than the LOQ for D4 in 8 of 16 species. Background corrected concentrations of D6 in fish were less than the MDL for D6 in 6 of 16 species and less than the LOQ in 11 of 16 species.

For field monitoring, a measurement that is less than a specified detection level (DL) may be: 1) reported as "below detection", 2) reported as zero, 3) reported as less than (<) the value of the DL, 4) reported as some value between zero and the DL, for example one-half the DL, or 5) reported as the actual value (positive or negative), whether or not it is below the DL. The last option, the reporting of the actual value, is the recommended procedure (Clarke 1998; Frome and Wambach 2005; Antweiler and Taylor 2008); otherwise the data is considered to be "censored". For this project, measured concentrations that were less than the method detection limit (MDL) but greater than the limit of detection (LOD) were reported as the measured concentration (i.e., uncensored value). Measured concentrations that were less than the limits of detection (LOD) were reported as the LOD divided by the sample weight that was analyzed (i.e., censored value).

Recovery of cVMS from 59 procedural matrix spikes across all matrices ranged from 90.1% to 110% for D4, from 91.3% to 112% for D5, and from 92.5% to 109% for D6.

Units of Measure

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

Statistical Analyses

Statistical analyses were performed using the Data Analysis Tool Package, as provided with Microsoft Excel 2003 (ver 11.0). A Type I error (α) of 0.05 was used to judge the significance of all statistical tests. Single-factor analysis of variance (ANOVA) was performed to test for differences in mean masses and concentrations (wet weight basis) of cVMS materials measured in reagent blanks, field blanks, and reference samples associated with each analytical batch of field samples (surface sediments, benthic macroinvertebrates, and fish). Two-factor ANOVA (without replication) was performed to test for differences across shore-to-shore transects and across upstream-to-downstream locations for concentrations of cVMS materials (dry weight, wet weight, and TOC-normalized), TOC, $\delta^{15}N$, and $\delta^{13}C$ measured in surface sediments. If the omnibus *F* value indicated significant differences between the mean values, a Tukey HSD multiple comparisons test (for equal sample sizes) or a Tukey-Kramer multiple comparisons test (for unequal sample sizes) was used to compare individual means (Sheskin 2000).

Linear regression was used to determine the slope and significance of the regression line fit to lipid-normalized concentrations of D4, D5, and D6 on trophic levels estimated from $\delta^{15}N$. All cVMS concentration data was converted to lipid weight for regression analyses and for calculation of trophic magnification factors (TMFs). The Pearson product-moment correlation coefficient (r) was used to evaluate correlations between the following variables in surface sediments: concentrations of cVMS materials (D4, D5, and D6), total organic carbon (TOC), and total inorganic carbon (TIC). The Pearson product-moment correlation coefficient (r) was also used to evaluate correlations between cVMS materials (D4, D5, and D6) and lipid content of benthic macroinvertebrates and fish. Log transformation of concentration data was used to generate normally distributed data for regression and correlation analyses.

Trophic Magnification Factor, Predator/Prey BMF, and BSAF Calculations

Trophic magnification factors (TMFs) for the Lake Pepin aquatic food web were determined on the relationship between the log-transformed lipid-normalized concentrations of cVMS materials (D4, D5, and D6) and $\delta^{15}N$. Converting $\delta^{15}N$ values to relative trophic level (TL) was performed according to the following equation:

$$TL = 2 + \frac{\left(\delta^{15}N_{consumer} - \delta^{15}N_{midge}\right)}{3.4}$$

where 2 was the assumed trophic level of midge larvae and 3.4 was the trophic enrichment fact constant for $\delta^{15}N$ (Jardine et al 2006). Trophic magnification factors were calculated as the antilog value of the slope (*m*) of the regression line of the natural log concentration (lipid-normalized) on TL, where:

$$TMF = e^{m}$$

Bioaccumulation factors (BAFs) were calculated for each consumer in the Lake Pepin food web by dividing the mean lipid-normalized concentrations of cVMS materials (D4, D5, and D6) in the predator species by the mean lipid-normalized concentrations in the diet of the predator species, using the equation:

$$BAF = \frac{C_{pred}}{\overline{C}_{prey}}$$

where C_{pred} and C_{prey} were the mean lipid normalized concentrations of cVMS materials in the predator and diet, respectively. To account for the relative abundance of each prey species in the diet of a predator species, the lipid-normalized concentrations of cVMS materials in the diet (C_{prey}) were calculated as mean diet-weighted concentrations using the equation:

$$\overline{C}_{prey} = \sum_{i=1}^{n} w_i C_i$$

where w_i was the normalized fraction of the prey species in the diet of the consumer species (Table 8) and C_i was the concentration of cVMS materials in the prey species. In most cases, the $\delta^{15}N$ values of the predator species were not a full trophic level above the prey species. Therefore, BAF values were corrected for trophic level increase, using the equation (Fisk et al 2001):

$$BAF_{TL} = \frac{BAF}{TL_{pred} / \overline{TL}_{prey}}$$

where TL_{pred} and TL_{prey} were the mean trophic levels of the predator and prey species, respectively. To account for the relative abundance of each prey species in the diet of a predator species, the trophic level of the diet was calculated as a mean diet-weighted trophic level using the equation:

$$\overline{TL}_{prey} = \sum_{i=1}^{n} w_i TL_i$$

where w_i was the normalized fraction of the prey species in the diet of the consumer species (Table 8) and TL_i was the trophic level of the prey species. Because all species in the Lake Pepin food web were not collected, concentrations of the cVMS materials and trophic levels were not available for all prey species identified in Table 8. Therefore, low-biased estimations of missing concentrations in the prey species were used for the BAF calculations to obtain high-biased estimations of the true BAF values. Missing trophic levels and lipid-normalized concentrations of the cVMS materials were estimated for the following prey species as:

- Plankton and seston: trophic level was assumed to be equal to 1.0; cVMS concentrations were estimated to be equal to the TOC-normalized concentrations measured in sediment.
- Macroinvertebrates (other than midge larvae and mayfly nymphs): trophic level and cVMS concentrations were estimated to be equal to the trophic level and lipid-normalized concentrations measured in midge larvae.
- Eggs: trophic level was estimated to be equal to the mean trophic level across all fish species; concentrations of the cVMS materials were estimated to be equal to the MDL in fish normalized to a mean lipid content in eggs of 12% wet weight.
- Fry of gizzard shad and freshwater drum: trophic level and cVMS concentrations were estimated to be equal to the trophic level and lipid-normalized concentrations measured in emerald shiner.
- Forage fish (other than young-of-year gizzard shad and emerald shiner): trophic level and cVMS concentrations were estimated to be equal to the mean measured trophic level and lipid-normalized concentrations averaged across emerald shiner, bluegill sunfish, and young-of-year gizzard shad.

- Terrestrial insects: trophic level and cVMS concentrations were estimated to be equal to the mean measured trophic level and lipid-normalized concentrations averaged across midge larvae and mayfly nymphs.

Biota-sediment accumulation factors (BSAFs) were calculated to quantify the aquatic bioavailability of sediment-associated cVMS materials using the equation:

$$BSAF = \frac{C_{organism}}{C_{sed}/TOC}$$

where $C_{organism}$ was the lipid normalized concentrations of cVMS materials in the organism, C_{sed} was the concentrations of cVMS materials in the sediment (wet weight) and TOC was the concentration of total organic carbon in the sediment (wet weight). BSAF values for the benthic macroinvertebrate species were calculated using the concentrations of cVMS materials and TOC measured in the sediments from which the organisms were collected. BSAF values for the fish species were calculated using the mean concentrations of cVMS materials and TOC measured in the surface sediments of the lake basin.

RESULTS DISCUSSION

Solids content and percentages of total organic carbon (TOC), calcium carbonate, and inorganic matter in surface sediments of Lake Pepin varied spatially within the basin, generally in relation to flow. Solids content (Table 5a) was greatest in surface sediments in the upstream end of the lake (mean 32% wet weight; transect I) and progressively decreased ($p < 0.001$) to the downstream end of the lake (mean 16% dry weight; transect V). Solids content of sediments collected across a transect were not significantly different ($p > 0.05$). Similarly, total inorganic carbon content of the sediments (data not shown) were greatest in the upstream end of the lake (mean 1.5% dry weight; transect I) and progressively decreased ($p < 0.001$) to the downstream end of the lake (mean 1.1% dry weight; transect IV), with the exception that the greatest total inorganic carbon content was observed in transect V (mean 1.6 % dry weight). When expressed on the basis of dry weight, TOC content of the sediments (Table 5a) was lowest in the upstream end of the lake (mean 3.1% dry weight; transect I) and progressively increased ($p < 0.001$) to the downstream end of the lake (mean 4.3% dry weight; transect V). When expressed on the basis of wet weight, TOC was greatest in the upstream end of the lake (mean 1.0% wet weight; transect I) and progressively decreased ($p < 0.001$) to the downstream end of the lake (mean 0.7% wet weight; transect V). These patterns of sediment composition resulted from preferential sorting and deposition of suspended solids from the water column as the Mississippi River undergoes transition from a lotic ecosystem (i.e., flowing water) to a lentic ecosystem (i.e., non-flowing water). Generally, coarse-grained particles low in organic carbon (i.e., sand) are deposited in the upstream end of the lake whereas fine-grained particles high in organic carbon (i.e., silts and clays) and flocculent organic matter are deposited in the downstream end of the lake.

The isotopic signatures of the sediments ($\delta^{15}N$ and $\delta^{13}C$) in Lake Pepin also varied spatially within the lake basin (Table 5a). $\delta^{15}N$ was lowest in surface sediments in the upstream end of the lake (mean 7.1‰; transect I) and progressively increased ($p = 0.05$) to the downstream end of the lake (mean 9.0‰; transect V). In contrast to that observed for other sediment characterization parameters, $\delta^{15}N$ of sediments collected across a transect were generally greatest in near shore locations (mean range 8.5‰ to 8.7‰) and lowest in the middle locations (mean range 7.7‰ to 8.2‰), but the differences were not judged to be significant ($p > 0.05$). $\delta^{13}C$ was greatest in the upstream end of the lake (mean -25.6‰; transect I) and progressively decreased ($p < 0.001$) to the downstream end of the lake (mean -26.7‰; transect IV). Similarly, $\delta^{13}C$ were greatest on the Minnesota side of the lake (mean -25.8‰) and progressively decreased towards the Wisconsin side of the lake (mean -26.2‰), which was judged to be marginally significant ($p = 0.09$). These patterns in isotopic signature suggest that the source of organic material in the sediments shifts from being allochthonous in origin (i.e., derived from outside the system, from the terrestrial environment) to autochthonous (i.e., derived from within the system) as the Mississippi River flows downstream through the lake.

Concentrations of the cVMS materials in surface sediments of Lake Pepin (Table 5b) varied spatially within the basin, generally in relation to flow, depending if concentrations were expressed on the basis of dry mass or wet mass. When expressed on the basis of dry weight (dw), concentrations of D4 and D6 were lowest in the upstream end of the lake (mean 1.27 ng/g dw for D4, mean 20.6 ng/g dw for D6; transect I) and progressively increased ($p < 0.001$) to the downstream end of the lake (mean 2.16 ng/g dw for D4, mean 38.5 ng/g dw for D6; transect V). In contrast, dry weight concentrations of D5 showed no discernable trend from the upstream to the downstream end of the lake (mean range 107 to 130 ng/ dw). However, concentrations of D5 were significantly lower on the Wisconsin side of the lake (mean 89.0 ng/g dw) relative to the rest of the lake basin (mean range 120 to 130 ng/g dw). When expressed on the basis of wet weight (ww), concentrations of D4 and D6 showed no discernable trend from the upstream to the downstream end of the lake (mean range 0.337 to 0.403 ng/ ww for D4, mean range 6.12 to 6.53 ng/ ww for D6). In contrast, wet weight concentrations of D5 were greatest in the upstream end of the lake (mean 35.5 ng/g ww; transect I), progressively decreased ($p < 0.001$) to the downstream end of the lake (mean 20.3 ng/g ww; transect V), and were significantly lower on the Wisconsin side of the lake (mean 22.5 ng/g ww) relative to the rest of the lake basin (mean range 25.7 to 28.8 ng/g ww).

Dry weight concentrations of D4, D5, and D6 in the surface sediments (Table 5b) were strongly correlated ($r > 0.75$; $p < 0.001$) with TOC in the surface sediments (Table 5a). When normalized to TOC content of the sediments, concentrations of D4 and D6 (Table 5b) were lowest in the upstream end of the lake (mean 39.5 ng/g TOC for D4, mean 651 ng/g TOC for D6; transect I) and progressively increased ($p < 0.001$) to the downstream end of the lake (mean 50.2 ng/g TOC for D4, mean 896 ng/g TOC for D6; transect V). Concentrations of D5 (Table 5) showed no discernable trend from the upstream to the downstream end of the lake (mean range 2970 to 3580 ng/g TOC), but were

significantly lower on the Wisconsin side of the lake (mean 2700 ng/g TOC) relative to the rest of the lake basin (mean range 3360 to 3510 ng/g TOC).

Fish and macroinvertebrates collected from the Lake Pepin aquatic food web were classified into relative trophic levels, feeding guilds, and trophic guilds. Relative trophic levels in the aquatic food web were calculated using the stable isotopes of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) to estimate trophic positions and carbon flow to consumers. The food web diagram constructed from $\delta^{13}C$ and $\delta^{15}N$ results (Fig. 2) shows that the $\delta^{13}C$ and $\delta^{15}N$ signatures were significantly correlated ($r = 0.64$; $p < 0.01$). This indicates that both carbon and nitrogen were biologically fractionated with the heavier isotopes being enriched in the higher trophic level organisms, and that carbon flow through the food web originated from a common source of carbon. The $\delta^{13}C$ signature for the benthic macroinvertebrates was significantly heavier compared to the signature for $\delta^{13}C$ sediment ($p < 0.01$), suggesting that the benthic macroinvertebrates at the base of the food web were selectively feeding on an allochthonous carbon source. Four feeding guilds (based on feeding habits and preferred habitat; Table 2) and seven trophic guilds (based on food preference; Table 3) were identified for the Lake Pepin food web and subjectively assigned to each species based on information provided in Becker (1983), Goldstein and Simon (1999), and Pflieger (1997). Benthic detritivores (i.e., midge larvae and mayfly nymphs) occupied the lowest trophic level (TL ~2) and benthipelagic piscivores (i.e., largemouth bass) occupied the highest trophic level (TL ~4).

Midge larvae and burrowing mayfly nymphs play an important role in aquatic food webs, representing a major link between producers, such as phytoplankton and benthic algae, and secondary consumers, such as fish. These organisms occupy important positions in the trophic dynamics of aquatic ecosystems, due to their numeric abundance and role in nutrient cycling. In Lake Pepin, midge larvae and mayfly nymphs indiscriminately ingest large quantities of fine sediment and accompanying organic matter (Fremling 1967) along with detritus, which is the main food item ingested. Emerald shiners and young-of-year gizzard shad are the primary food base for carnivores in the lake. However, all of the species classified as carnivore or piscivore (Table 9) will feed on mayfly nymphs and midge larvae when they are available in large numbers. Depending on the habitat and forage availability, walleye and smallmouth bass can be as piscivorous as white bass and largemouth bass in the river. Gizzard shad (young-of-year and adult) in Lake Pepin were characterized as being pelagic planktivores based on the feeding habits observed in the Mississippi River in Illinois and Missouri (Pflieger 1997). However, adult gizzard shad may also be characterized as being benthipelagic detritivores (Becker 1983).

When expressed on the basis of wet weight (ww), concentrations of the cVMS materials were highly variable between species ($p < 0.001$; Table 10; Fig. 3). The highest concentrations were observed in the river carpsucker, which were 59.1 ng/g ww for D4, 447 ng/g ww for D5, and 26.9 ng/g ww for D6. Generally, the lowest concentrations were observed in the primary forage fish (young-of-year gizzard shad and emerald shiner) and the top predator species (largemouth bass, smallmouth bass, white bass,

and walleye). Concentrations in these species ranged from 2.8 to 5.3 ng/g ww for D4, from 7.5 to 58.3 ng/g ww for D5, and from 0.5 to 5.1 ng/g ww for D6. Mean concentrations were also variable between trophic guilds ($p < 0.001$), with the lowest concentrations being observed in the piscivorous and carnivorous species and the highest concentrations in the omnivorous species, followed by the detritivorous species (Fig. 3). Concentrations (mean ± SE) in the piscivorous species were 4.7 ± 0.6 ng/g ww for D4, 34.3 ± 7.6 ng/g ww for D5, and 1.0 ± 0.4 ng/g ww for D6. Mean concentrations in the carnivorous species were 4.1 ± 0.7 ng/g ww for D4, 24.0 ± 1.2 ng/g ww for D5, and 1.4 ± 0.5 ng/g ww for D6. Mean concentrations in the omnivorous species were 18.1 ± 8.7 ng/g ww for D4, 195.7 ± 53.3 ng/g ww for D5, and 9.1 ± 3.7 ng/g ww for D6. Mean concentrations in the detritivorous species were 7.5 ± 0.8 ng/g ww for D4, 138.3 ± 24.7 ng/g ww for D5, and 8.6 ± 1.7 ng/g ww for D6. These results indicate that concentrations of the cVMS materials were greatest in species that ingest large quantities of sediment detritus.

Mean lipid content was highly variable between species ($p < 0.001$) and ranged from 0.9% of wet weight mass in midge larvae to 16.8% in river carpsucker (Fig. 4). Similarly, mean lipid content was highly variable between trophic guilds ($p < 0.001$) and ranged from 1.3 ± 0.3 % (SE) of wet weight mass in the detritivorous species to 13.3 ± 0.8 % in the omnivorous species. However, concentrations of D4, D5, and D6 were not significantly correlated with lipid content, regardless if concentrations were expressed on the basis of wet weight mass, dry weight mass or log-transformed concentrations. These results indicated that biological accumulation of the cVMS materials was **not** due to simple water-to-lipid partitioning and that accumulation of D4, D5, and D6 was controlled by processes such as dietary uptake, metabolism, assimilation efficiencies, and bioavailability due to chemical sorption in the water/sediment phase(s).

Biota-sediment accumulation factors (BSAF values) for the three cVMS materials were greatest in macroinvertebrate species living and feeding in the sediments (i.e., the benthic detritivores), and generally decreased with increasing trophic level in the food web (Table 11; Fig. 5). BSAF values for the three cVMS materials in fish were greatest in species that feed on invertebrates and organic material in the bottom sediments (i.e., the benthic and suprabenthic omnivores and invertivores). The smallest BSAF values were observed in fish species that feed on smaller fish in the water column (i.e., the pelagic carnivores and piscivores). The fact that BSAF values were greatest in organisms having a close association with the sediment compartment clearly indicates that the source of the three cVMS materials in the Lake Pepin food web was sediment.

The greatest BSAF values were observed for D4 (range 0.8 to 19.2), with values >1.0 for 16 of 18 species (Table 11; Fig. 5). However, the large BSAF values for D4 may reflect an analytical bias associated with analysis of the sediments and should be considered with caution. Measured concentrations of D4 in the surface sediments (Table 5) were all considerably less than the analytical method detection limit (MDL) of 8.5 ng/g ww because of high background levels of D4 encountered during the analysis of the sediment samples. Instead of using censored data (e.g., the MDL) to calculate BSAF values for D4, actual measured concentrations of D4 were used even though

they were less than the MDL. As a result, the BSAF values for D4 are likely over estimated because concentrations of D4 in the surface sediments were overcorrected for background.

In contrast to that observed for D4, BSAF values were much smaller for D5 (range 0.1 to 5.3) and even smaller for D6 (range < 0.1 to 1.6), with values >1.0 only being observed in the two benthic macroinvertebrate species. These results indicated that the relative bioavailability of the three cVMS materials in sediment was greatest for D4 and smallest for D6. This trend of decreasing bioavailability was also apparent from within-species comparisons of the BSAF values for the three cVMS materials. For all 18 species, the BSAF values for the three cVMS materials within a species always followed the order D4 > D5 > D6. Within a species, the BSAF values also decreased with increasing Log K_{OW} of the cVMS materials, indicating that bioavailability of the cVMS materials in sediment decreased with increasing Log K_{OW}. Presumably, the decreased bioavailability of the cVMS materials was related to increased binding affinity to organic material in the sediment and/or decreased uptake efficiency of the materials across the gut.

Similar to that observed for BSAF values, trophic level corrected predator-prey bioaccumulation factors (BAF_{TL} values) for the three cVMS materials were greatest in macroinvertebrate species living and feeding in the sediments (Table 11; Fig. 6). However, in contrast to the BSAF values the BAF_{TL} values for the three cVMS materials in fish were all < 1.0. As previously discussed, the source of cVMS in the aquatic food web of Lake Pepin is from the sediment compartment. Consequently, BAF_{TL} values < 1.0 indicate that the three cVMS materials do not bioconcentrate and do not biomagnify in the food web of the lake.

Lipid-normalized concentrations of the three cVMS materials were greatest in the lowest trophic levels and significantly **decreased** up the food web to the higher trophic levels in Lake Pepin (Figs. 7-9). Trophic magnification factors (TMFs) for the three cVMS materials were all < 1 (range 0.3 to 0.1) indicating trophic dilution within the food web. TMF values < 1 are indicative of materials that do not biomagnify and are considered to be non-bioaccumulative (Gobas *et al.*, 2008).

The decline of the D4, D5, and D6 lipid-equivalent fish concentrations with increasing trophic level indicated that accumulation of these compounds was **not** due to simple water-to-lipid partitioning, *i.e.*, bioconcentration via the gills. If bioconcentration was the dominant process for accumulation of such residues, the lipid-normalized concentrations should be approximately equal across the various organisms of the food web. Instead, accumulation of D4, D5, and D6 by aquatic organisms was controlled by dietary uptake and associated mitigation processes such as metabolism, growth dilution, low uptake and assimilation efficiencies, and reduced bioavailability due to chemical sorption in the water/sediment phase(s). As a result, the field data demonstrated that bioconcentration processes were not pertinent to uptake of D4, D5, and D6 into aquatic organisms in the Lake Pepin ecosystem. Rather, accumulation of

the three cVMS materials occurred via uptake from food and the field data clearly show trophic dilution for D4, D5, and D6.

Calculation of a single TMF value from the regression of chemical concentration on trophic level assumes that biomass transfer and biotransformation efficiencies are similar for all the organisms at all the trophic levels. The amount of scatter about the fitted regression line reflects the deviation from these assumptions. Grouping individual species of the food web into feeding and trophic guilds (defined in Tables 2 and 3) tends to minimize the scatter and better represents the net transfer of a chemical through the food web. Comparison of lipid-normalized concentrations across the feeding and trophic guilds (Figs. 7-9) indicated that D4, D5, and D6 were greatest in macroinvertebrate species living and feeding in the sediments (i.e., the benthic detritivores). Similarly, lipid-normalized concentrations of the three cVMS materials in fish were greatest in species that feed on invertebrates and organic material in the bottom sediments (i.e., the benthic and suprabenthic invertivores, omnivores and detritivores). In contrast, the lowest lipid-normalized concentrations of D4, D5, and D6 were observed in fish species that feed on smaller fish and organisms in the water column (i.e., the pelagic/benthipelagic carnivores and piscivores). These results further demonstrated that the source of the three cVMS materials in the Lake Pepin food web was sediment (as previously discussed for the BSAF values) and that the water column did not appear to represent a significant source of exposure.

The Lake Pepin field data indicated that diet was the primary route of biological uptake for the three cVMS materials in the food web, and that uptake and assimilation efficiency were related to the trophic status of the organisms. Intestine length in fishes tends to be longest in herbivorous species and decreases in length as trophic status shifts from a low quality diet (i.e., low protein and high roughage) to a high-quality diet (i.e., high protein and low roughage). Generally, lipid-normalized concentrations of the three cVMS materials were greatest in fish species having lower-quality diets and decreased as trophic status shifted to higher-quality diets. Presumably, uptake and assimilation of the three cVMS materials was more efficient in species with longer intestines, which serve to maximize digestion and absorption. Most of the enzymatic digestion of food materials occurs in the intestine, and differences in the ability to secrete various enzymes are related to differences in food habitats. The gastrointestinal tract has been shown to play an important role in metabolizing some chemicals (i.e., some PAHs) by fish, altering their form and limiting systemic bioavailability (Kleinow *et al.*, 1998; Nichols *et al.*, 2004). Operating in series with first-pass metabolism in the liver, this activity can substantially reduce bioaccumulation of contaminant residues (Kleinow and James, 2001; Nichols *et al.*, 2004).

Lipophilic substances may be transferred along the food web with the lipid flow or energy transfer to higher trophic level consumers. TMF studies of aquatic food webs have shown that concentrations of persistent and bioaccumulative chemicals in aquatic biota are significantly related to their trophic position. Similarly, TMF values for persistent and bioaccumulative chemicals appear to be related to the octanol-water partition coefficient (K_{OW}), which is widely used as a measure of the bioaccumulation

potential of persistent chemicals. For example, TMF values for persistent hydrophobic chemicals in 17 lakes in Canada and the northeastern United States were significantly correlated with log K_{OW} (Houde *et al.*, 2008), implying that the rate of accumulation along the food web was dependant on hydrophobicity and recalcitrance to degradation. However, trophic magnification (i.e., bioaccumulation and biomagnification) is also dependant on the metabolic capacity of each organism at the different trophic levels as well as the physiological properties of the chemical substance. The decline of the lipid-equivalent concentrations of D4, D5, and D6 with increasing trophic position in the Lake Pepin food web (Figs. 7-9) was not consistent with bioaccumulation and biomagnification of persistent hydrophobic chemicals such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). In contrast to the observation that lipophilic substances such as PCBs and OCPs biomagnify (TMF>1) in aquatic food webs and that TMF values increased with log K_{OW}, the three cVMS materials (log K_{OW} range 6.5 to 9.1) did not biomagnify in the Lake Pepin food web (TMF range 0.3 to 0.1) and TMF values decreased with log K_{OW} (Fig. 10). The lack of biomagnification of the cVMS materials indicates that K_{OW} was not a pertinent factor to determine accumulation of the three cVMS materials in the Lake Pepin food web.

The Lake Pepin results indicate that laboratory BCF values of the three cVMS materials are not appropriate measures for evaluating the bioaccumulation potential of these chemicals, since the process of bioconcentration was not significant to uptake or trophic transfer in the aquatic food web. Bioaccumulation of the three cVMS materials in the Lake Pepin aquatic food web occurred via biomagnification processes, not bioconcentration. The field data showed that biomagnification factors (BMFs; the lipid-normalized concentration in a predator relative to the lipid-normalized concentration in prey) were significantly less than 1.0 for D4, D5, and D6 for all single predator-prey relationships in the Lake Pepin food web. The field data also showed that food web trophic dilution was occurring for D4, D5, and D6, as all three compounds had TMF values that were significantly less than 1 (range 0.3 to 0.1). TMF values < 1 are indicative of materials that do not biomagnify and are considered to be non-bioaccumulative (Gobas *et al.*, 2008).

Steady-state, mass balance bioaccumulation models (for example, see Gobas 1993; Gobas *et al.*, 1998; Arnot and Gobas 2003, 2004; all models available for download at: http://www.rem.sfu.ca/toxicology/models/models.htm) do not account for biotransformation or an absence of bioavailability in the gastrointestinal tract. Moreover, these models utilize a conservative assumption regarding the assimilation efficiency of a chemical in the diet across a wide range of substances. The models assume that low trophic level fish feed on diets that are in equilibrium with exposure water concentrations and, combined with the presumed dietary uptake of chemicals, may permit accumulation of a compound far in excess of observed concentrations if gut metabolism or reduced dietary transfer is operational. Attempts to use these bioaccumulation models to simulate trophic dilution of D4, D5, and D6 in the Lake Pepin food web have not been successful, even when laboratory-measured metabolism rate constants are incorporated. The failure of the models to predict trophic dilution in the Lake Pepin food web appears to be related to the model assumptions of an excessive dietary uptake rate

that is based on lipophilicity (i.e., log K_{OW}). However, K_{OW} as a surrogate measure of lipophilicity is unable to represent many of the biological and environmental phenomena that control the degree to which chemicals bioaccumulate. As a result, modeling based on K_{OW} will overestimate the bioaccumulative nature of many chemicals, including the cyclic methylsiloxane materials, in aquatic ecosystems. The assumption that dietary uptake rate is based solely on log K_{OW} as a measure of lipophilicity resulted in erroneously elevated body burdens of the cVMS materials in lower trophic level fish that are efficiently transferred through the model food web producing trophic level magnification, which is inconsistent with field data collected from Lake Pepin.

CONCLUSIONS

The trophic transfer of cyclic methylsiloxane (cVMS) materials in aquatic ecosystems is an important criterion for assessing bioaccumulation and ecological risk. Food web magnification of the cVMS materials (specifically D4, D5, and D6) was determined for the Lake Pepin food web using $\delta^{15}N$ as a continuous variable for assessing trophic levels (TL). The food web that was evaluated included surface sediments, 2 benthic macroinvertebrate species (2 genera, 2 families), and 15 fish species (14 genera, 9 families). The biological organisms were divided into 4 feeding guilds (based on feeding habitat) and 7 trophic guilds (based on food preference). Benthic detritivores (i.e., *Chironomous* sp. and *Hexagenia* sp.) occupied the lowest trophic level (TL ~2) and pelagic piscivores (i.e., largemouth bass and white bass) occupied the highest trophic level (TL ~4).

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 levels. Trophic magnification factors (TMFs) for the three cVMS materials were all < 1 (range 0.1 to 0.3) indicating trophic dilution across the food web. The TMF values for D4, D5, and D6 also decreased with increasing octanol-water partition coefficient (log K_{OW}), which is widely used as a surrogate measure of lipophilicity and bioaccumulation potential. However, attempts to use available bioaccumulation models to simulate trophic dilution of D4, D5, and D6 in an aquatic food web were not successful. This failure to simulate trophic dilution appears to be related to model assumptions of an excessive dietary uptake rate that is based on lipophilicity (i.e., log K_{OW}). Clearly, K_{OW} as a surrogate measure of lipophilicity is unable to represent many of the biological and environmental phenomena that control the degree to which cVMS materials bioaccumulate. As a result, modeling based on K_{OW} will overestimate the bioaccumulative nature of D4, D5, and D6 in aquatic ecosystems.

The decline of the D4, D5, and D6 lipid-equivalent fish concentrations with increasing trophic level indicated that accumulation of these compounds was not due to simple water-to-lipid partitioning, *i.e.*, bioconcentration across the gills. If bioconcentration was the dominant process for accumulation of such residues, the lipid-normalized concentrations should be approximately equal across the various organisms of the food web. The Lake Pepin data show that simple water-to-lipid partitioning was not the key

process for accumulation, thereby demonstrating that the bioconcentration process was not pertinent to uptake of D4, D5, and D6 into aquatic organisms in the environment. Accumulation of D4, D5, and D6 in the Lake Pepin food web occurred via processes controlled by dietary uptake and associated mitigation processes such as metabolism, growth dilution, low uptake and assimilation efficiencies, and reduced bioavailability due to chemical sorption in the water/sediment phase(s). Consequently, the Lake Pepin field data indicate that laboratory BCF values for the three cVMS materials are not appropriate measures for regulation of the 'B' potential of these chemicals.

The results from Lake Pepin showed that cVMS materials undergo trophic dilution in aquatic food webs and conclusively demonstrated that D4, D5, and D6 do not biomagnify. TMF values for persistent and bioaccumulative substances, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are >1 and increase with increasing lipophilicity. In contrast, TMF values < 1 are indicative of materials that do not biomagnify and are considered to be non-bioaccumulative. Consequently, field data from the Lake Pepin food web confirm that D4, D5, and D6 are <u>not</u> bioaccumulative materials in aquatic environments.

FUTURE WORK

This report evaluates and summarizes the biomagnification and bioaccumulation of D4, D5, and D6 in the freshwater aquatic food web of Lake Pepin. The terrestrial component of the Lake Pepin food web will be evaluated by collection and analysis of American mink (*Mustela vison*). Mink were collected from backwater areas of Lake Pepin in November 2008. Concentrations of D4, D5, and D6 will be measured in the fat, muscle, and liver. Relative trophic level of mink in the food web will be determined using $\delta^{15}N$ and $\delta^{13}C$.

A separate but related project is being conducted to evaluate biomagnification and bioaccumulation of D4, D5, and D6 in the marine food web of Oslofjord, Norway. The experimental design for the Oslofjord project was based on the design that was used for the aquatic component of the Lake Pepin food web. Samples were collected from Oslofjord in November 2008 and included surface sediments, macroinvertebrates, and fish. Concentrations of D4, D5, and D6 will be measured in whole-body homogenates of each collected specimen. Relative trophic levels of the collected specimens will be determined using $\delta^{15}N$ and $\delta^{13}C$.

ACKNOWLEDGEMENTS

Samples were collected from Lake Pepin with guidance and assistance from the Minnesota Department of Natural Resources (DNR). We are especially grateful for the technical guidance and assistance provided by Steve DeLain, Daniel Dieterman, and Walter Popp at the DNR Lake City Field Station. Technical oversight during analysis of samples for water content, lipid content and for isotopic signatures of nitrogen (N; $\delta^{15}N$)

and carbon (C; $\delta^{13}C$) was provided by Hasand Gandhi (Biogeochemistry and Paleoproteomics Laboratory, Michigan State University). Technical oversight during characterization of the sediment samples was provided by Amy Myrbo (National Lacustrine Core Repository, Limnological Research Center, University of Minnesota).

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Table 1. Species collected to evaluate biomagnification and bioaccumulation of cyclic methylsiloxane materials (cVMS; specifically, D4, D5, and D6) in the freshwater aquatic food web of Lake Pepin, Minnesota. Aquatic food web samples included fish (collected using electrofishing, September 2007), macroinvertebrates and associated surface sediments (collected using VanVeen dredge or box core, May 2008).

Common Name	Family	Genus species	Feeding Guild	Trophic Guild	Typical Food Items
Midge	Chironomidae	*Chironomous sp.*	benthic	detritivore	sediment detritus, diatoms, small plants, and animals; ingest fine sediment and associated organic matter
Burrowing mayfly	Ephemeridae	*Hexagenia sp.*	benthic	detritivore	sediment detritus; nymphs ingest large quantities of fine sediment and associated organic matter
River carpsucker	Catosomidae	*Carpiodes carpio*	suprabenthic	omnivore	suction and filter feeder; consumes insect larvae and other organisms in the sediment, including periphyton, invertebrate eggs, filamentous and single-celled algae, protozoans, small crustaceans, oligochaetes, mollusks
Quillback	Catosomidae	*Carpiodes cyrinus*	suprabenthic	omnivore	filter feeder and grazer; consumes insect larvae and other organisms in the sediment, including sediment detritus
White sucker	Catosomidae	*Catostomus commersoni*	suprabenthic	invertivore	filter feeder and grazer; consumes small invertebrates (zooplankton, insects, crustaceans, mollusks) and plant matter.
Silver redhorse	Catosomidae	*Moxostoma anisurum*	suprabenthic	invertivore	sucker; consumes primarily mollusks, immature insects, and other small organisms in the sediment
Shorthead redhorse	Catosomidae	*Moxostoma macrolepidotum*	suprabenthic	invertivore	sucker; consumes mollusks, immature insects, crustaceans, algae, and detritus in the sediment
Bluegill sunfish	Centrarchidae	*Lepomis macrochirus*	benthipelagic	carnivore	drift feeder; consumes aquatic insects and other small invertebrates, including, crustaceans, crayfish; diet may include very small fish.
Smallmouth bass	Centrarchidae	*Micropterus dolomieu*	benthipelagic	carnivore	carnivorous; consumes fish, crayfish, and insects
Largemouth bass	Centrarchidae	*Micropterus salmoides*	benthipelagic	piscivore	carnivorous; adults preferentially consume smaller fish; diverse diets may also include crayfish, large insects, frogs, snakes, salamanders, small birds and mammals

Black crappie	Centrarchidae	*Pomoxis nigromaculatus*	pelagic	piscivore	carnivorous; diverse diets include smaller fish, zooplankton, insects, and crustaceans
Gizzard shad (young of year)	Clupeidae	*Dorosoma cepedianum*	pelagic	planktivore	begin life feeding on zooplankton; at about 3 cm in length they become filter feeders, consuming both small invertebrates and phytoplankton, as well as sand for the gizzard.
Gizzard shad (adult)	Clupeidae	*Dorosoma cepedianum*	benthipelagic	planktivore	filter feeder; consume small (microscopic) invertebrates (zooplankton, micro-crustaceans), phytoplankton, and sediment detritus
Common carp	Cyprinidae	*Cyprinus carpio*	suprabenthic	omnivore	filter feeder and grazer; omnivorous diet of plant matter, insects, crustaceans (including zooplankton), mollusks, and sediment detritus
Emerald shiner	Cyprinidae	*Notropis atherinoides*	pelagic	planktivore	particulate feeder; pelagic feeding at mid-water and surface; consumes mostly zooplankton, small insects, and small crustaceans
White bass	Percichthyidae	*Morone chrysops*	pelagic	carnivore	carnivorous; adults primarily consume smaller fish (predominantly gizzard shad); diverse diet may also include zooplankton, insects, and crustaceans
Walleye	Percidae	*Stizostedion vitreum*	benthipelagic	piscivore	carnivorous; primarily consume fish of all species; diverse diet also includes crayfish, leeches, large insects, and worms
Freshwater drum	Sciaenidae	*Aplodinotus grunniens*	suprabenthic	invertivore	carnivorous; diverse diet includes mussels, crustaceans, fish, mollusks, insects and insect larvae, and crayfish

Table 2. Feeding guilds defined for the aquatic food web in Lake Pepin. The feeding guilds were defined on the basis of feeding habits and preferred habitat in the water column (Becker 1983; Goldstein and Simon 1999; Pflieger 1997).

Guild	Definition
Pelagic	Prefer to live and feed in the water column; usually do not feed or search for food in the bottom sediments
Benthipelagic	Feeds and searches for food anywhere in the water column from surface to the bottom sediments
Suprabenthic	Prefer to live and feed on or near the bottom sediments; usually do not feed or search for food in the water column
Benthic	Lives and feeds in the bottom sediments

Table 3. Trophic guilds defined for the aquatic food web in Lake Pepin. The trophic guilds were defined on the basis of primary diet (Becker 1983; Goldstein and Simon 1999; Pflieger 1997).

Guild	Diet
Detritivore	Primarily detritus (organic debris, seston); > 75% of diet consists of detritus.
Omnivore	Generalized diet (may include detritus, plant matter, invertebrates, seston); > 20% of diet consists of detritus and seston; < 70% of diet consists of macroinvertebrates.
Planktivore	Primarily plankton (zooplankton, seston, insect larvae, crustaceans); > 75% of diet consists of plankton.
Carnivore	Primarily macroinvertebrates and vertebrates (smaller fish, amphibians, etc); 25-75% of diet consists of macroinvertebrates; 25-75% of diet consists of fish.
Invertivore	Specialized carnivore that feeds primarily on macroinvertebrates (insects, mussels, crustaceans); > 75% of diet consists of macroinvertebrates.
Piscivore	Specialized carnivore that feeds primarily on smaller fish; > 75% of diet consists of fish.

Table 4. Benthic macroinvertebrates and forage fish collected from Lake Pepin that were pooled into composite samples for analysis.

Matrix	Composite	Individuals	Mean Total Length (cm)	Mean Fresh Weight (g)
Midge larvae	1			10.1
	2			1.12
	3			1.15
	4			3.46
	5			6.87
Mayfly nymphs	1			5.09
	2			5.05
Emerald shiner	1	9	7.2	2.32
	2	19	5.3	0.93
	3	20	4.0	0.44
	4	48		0.60
YOY Gizzard shad	1	3	15.0	29.8
	2	10	15.1	31.3
	3	10	14.9	30.1

Table 5a. Physical and chemical characteristics of surface sediments collected from Lake Pepin.

	Coordinates (dd mm ss.s)[1]		Solids	Total Organic Carbon			
Location	Latitude	Longitude	(% ww)	(% dw)	(% ww)	$\delta^{13}C$	$\delta^{15}N$
I.1	44 32 40.9	92 21 42.3	30.72	3.26	1.00	-25.50	7.78
I.2	44 32 53.9	92 22 26.2	28.55	3.31	0.94	-25.61	7.92
I.3	44 33 18.2	92 22 55.5	30.16	3.22	0.97	-25.61	7.57
I.4	44 33 44.3	92 23 24.4	30.64	3.07	0.94	-25.75	6.09
I.5	44 34 06.9	92 24 11.7	38.90	2.89	1.12	-25.84	6.13
II.1	44 31 41.5	92 19 28.8	24.32	3.43	0.83	-25.57	7.87
II.2	44 32 17.2	92 19 33.2	24.64	3.57	0.88	-25.85	7.86
II.3	44 32 39.7	92 19 15.8	23.98	3.50	0.84	-25.89	9.49
II.4	44 32 56.0	92 18 59.1	25.01	3.41	0.85	-25.99	8.55
II.5	44 33 06.5	92 18 34.2	34.59	2.50	0.86	-26.24	8.24
III.1	44 29 48.8	92 18 22.4	20.63	3.73	0.77	-25.90	8.64
III.2	44 29 54.2	92 18 19.0	20.78	3.67	0.76	-25.83	8.68
III.3	44 29 59.6	92 17 58.2	23.45	3.61	0.85	-25.71	8.06
III.4	44 29 58.8	92 17 38.7	18.91	3.73	0.71	-25.69	7.79
III.5	44 30 02.6	92 17 32.2	20.96	3.74	0.78	-25.90	7.86
IV.1	44 25 42.9	92 14 07.2	27.88	2.93	0.82	-25.76	9.66
IV.2	44 26 56.5	92 14 46.7	18.56	3.91	0.73	-26.06	7.38
IV.3	44 27 04.3	92 14 23.0	18.31	3.99	0.73	-26.09	7.50
IV.4	44 27 05.2	92 14 06.1	16.36	4.17	0.68	-26.30	7.91
IV.5	44 27 08.9	92 13 16.6	23.91	2.89	0.69	-26.57	10.22
V.1	44 24 56.3	92 09 16.2	16.81	4.22	0.71	-26.42	9.68
V.2	44 25 22.4	92 09 35.8	15.45	4.47	0.69	-26.35	9.22
V.3	44 25 43.1	92 09 36.4	16.43	4.30	0.71	-27.05	7.79
V.4	44 26 04.4	92 09 32.9	15.23	4.26	0.65	-27.02	8.35
V.5	44 26 13.4	92 09 32.9	15.48	4.22	0.65	-26.43	9.79

[1] Coordinates are based on projection NAD 83 Zone 15.

Table 5b. Concentrations of D4, D5, and D6 measured in surface sediments collected from Lake Pepin.

	Concentration (ng/g ww)[1]			Concentration (ng/g dw)[2]			Concentration (ng/g TOC)[2]		
Location	D4	D5	D6	D4	D5	D6	D4	D5	D6
I.1	(0.451)	40.4	6.81	1.47	131.5	22.2	45.0	4033	680
I.2	(0.354)	34.3	5.93	1.24	120.3	20.8	37.6	3639	628
I.3	{0.346}	35.2	7.13	1.15	116.6	23.6	35.6	3620	734
I.4	(0.351)	33.1	5.90	1.15	107.9	19.3	37.3	3516	627
I.5	(0.514)	34.6	6.61	1.32	89.0	17.0	45.8	3078	588
II.1	(0.357)	35.3	7.61	1.47	145.3	31.3	42.8	4236	912
II.2	{0.341}	29.7	6.48	1.38	120.5	26.3	38.7	3375	736
II.3	(0.352)	28.6	7.01	1.47	119.2	29.3	41.9	3407	836
II.4	{0.299}	24.0	5.90	1.20	96.0	23.6	35.1	2814	692
II.5	{0.335}	18.3	5.65	0.97	52.8	16.3	38.8	2118	655
III.1	{0.343}	26.0	6.18	1.66	125.9	29.9	44.6	3376	803
III.2	{0.343}	25.9	6.30	1.65	124.9	30.3	45.0	3402	826
III.3	(0.350)	31.4	6.57	1.49	133.8	28.0	41.3	3705	776
III.4	{0.327}	27.5	6.66	1.73	145.5	35.2	46.4	3902	944
III.5	{0.338}	25.5	6.06	1.61	121.9	28.9	43.1	3258	773
IV.1	(0.415)	20.2	5.90	1.49	72.4	21.2	50.8	2472	722
IV.2	(0.357)	27.1	7.25	1.93	146.2	39.0	49.2	3740	999
IV.3	{0.330}	26.2	6.61	1.80	142.9	36.1	45.2	3581	905
IV.4	(0.377)	25.1	6.62	2.30	153.2	40.5	55.2	3673	970
IV.5	{0.325}	16.5	4.91	1.36	69.2	20.5	47.0	2394	710
V.1	{0.340}	21.2	6.26	2.03	126.1	37.3	48.1	2991	884
V.2	{0.341}	21.4	6.66	2.21	138.3	43.1	49.4	3095	965
V.3	{0.344}	22.7	6.76	2.09	138.1	41.1	48.7	3211	956
V.4	{0.344}	18.9	5.50	2.26	124.0	36.1	53.0	2912	848
V.5	{0.339}	17.4	5.41	2.19	112.4	34.9	51.9	2663	828

[1] Measured concentrations of D4 in surface sediments were all < MDL (8.5 ng/g ww). Values in ( ) are concentrations that were < MDL but > LOD, and are reported as the actual measured concentration. Values in { } are concentrations that were < LOD, and are reported as the LOD divided by the sample weight that was analyzed.

[2] Concentrations cVMS materials expressed on the basis of dry weight (ng/g dw) and total organic carbon (ng/g TOC) were calculated from measured concentrations of cVMS materials, which were determined on wet samples.

Table 6. Summary of the quality control (QC) program that was implemented in the field and laboratory for the Lake Pepin monitoring project. The QC samples were collected and analyzed to evaluate detectability, bias, and precision, and to verify that samples were not contaminated by sample collection, handling, shipment, storage, and processing procedures.

QC Sample	Description	Available Matrices
Detection limits	• Limit of detection (LOD): The minimum level of analyte that can be detected and reported with 99% probability that it is different from a matrix–free blank. Determined by repetitive analysis of reagent blanks. • Method detection limit (MDL): The level of analyte in a sample matrix, that when processed through the complete analytical method, can be measured and reported with 99% probability that it is different from a blank. Determined by repetitive analysis of samples. • Limit of quantification (LOQ): The minimum level of analyte in a sample matrix that can be measured and accurately quantified with an estimation error no greater than 30% with 99% probability. Defined as 3 times the MDL.	• sediment • macroinvertebrates • fish
Reagent blanks	Extraction solvents dispensed directly into an empty extraction vial. Used to evaluate contamination from solvents, containers, and analytical operations, for blank-correction of sample data, and for calculation of detection limits (LOD and LOQ).	• sediment • macroinvertebrates • fish
Field blanks	Reference sample having very low or non-detectable concentrations of cVMS materials that was taken into the field and processed like a field sample. Used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples.	• sediment
Laboratory blanks	Reference sample having very low or non-detectable concentrations of cVMS materials that was processed in the laboratory like a field sample. Used to evaluate contamination bias resulting from storage, processing, and analysis of samples.	• sediment • fish

Field replicates	Replicate field samples that were processed, extracted, and analyzed as individual samples. Used to evaluate between-sample variability (precision).	• sediment • macroinvertebrates • fish
Laboratory replicates	Replicate sub-samples of a processed field sample that were extracted and analyzed as individual samples. Used to evaluate within-sample variability, for calculation of detection limits (MDL), and to evaluate analytical precision.	• sediment • macroinvertebrates • fish
Extract replicates	Replicate analyses of a sample extract. Used to evaluate instrument precision.	• sediment • macroinvertebrates • fish
Field spikes	Field samples spiked in the field with known amounts of cVMS materials. Used to evaluate loss of cVMS from during collection, processing, transport, storage, and analysis of samples, and to evaluate analytical bias.	• sediment
Laboratory spikes	Processed field samples spiked in the laboratory with known amounts of cVMS materials. Used to evaluate analytical bias.	• macroinvertebrates • fish
Reference Samples	Control samples having known concentrations of cVMS materials (reference samples having very low or non-detectable concentrations of cVMS materials were used for field blanks and laboratory blanks). Used to evaluate contamination or loss of cVMS from samples during collection, transport, processing, storage, and analysis, for calculation of detection limits (MDL), and to evaluate analytical bias and precision.	• sediment • fish
Internal standards	Stable isotopes (^{13}C) of D4, D5, and D6 added to assess and correct for instrument variability.	• sediment • macroinvertebrates • fish

Table 7. Results for quality control (QC) samples that were collected and analyzed with samples from Lake Pepin.

Matrix	N[1]	D4	D5	D6
Sediment				
• Background (reagent blanks; ng)	8	6.8	19.0	1.3
• LOD (reagent blanks; ng)	8	2.1	8.7	0.7
• MDL (reference sediment; ng/g wet wt)[2]	5	8.5	10.4	4.5
• LOQ (3 × MDL; ng/g wet wt)	5	25.6	31.1	13.4
• Precision				
o reference sediment (mean RSD %)	6	17.3	13.7	9.5
o field replicates (RSD; %)	25	< MDL[3]	23.9	9.8
o laboratory replicates (mean RPD ± sd; %)	6	< MDL[3]	3.2 ± 3.7	3.4 ± 4.9
• Bias				
o field blanks (mean concentration ± sd; ng/g ww)	6	0.5 ± 1.1	0.8 ± 0.9	0.6 ± 0.1
o reference sediment (mean recovery ± sd; %)	6	97.7 ± 15.8	104 ± 10.9	105 ± 9.9
o field spikes (mean recovery ± sd; %)	5	110 ± 0.3	112 ± 0.6	109 ± 1.0
Benthic macroinvertebrates				
• Background (reagent blanks; ng)	9	1.0	5.4	-1.3
• LOD (reagent blanks; ng)	9	1.5	7.1	0.2
• MDL (laboratory replicates; ng/g wet wt)[1]	3	3.3	21.1	1.8
• LOQ (3 × MDL; ng/g wet wt)	3	10.0	63.3	5.3
• Precision (midge larvae)				
o field replicates (RSD; %)	5	35.6	47.3	34.8
o laboratory replicates (mean RPD ± sd; %)	7	16.5 ± 12.6	20.4 ± 27.7	10.8 ±18.8
o extract replicates (mean RPD ± sd; %)	6	1.6 ± 0.2	0.8 ± 0.7	3.8 ± 1.3
• Precision (mayfly nymphs)				
o field replicates (RPD; %)	2	3.0	1.2	13.2
o laboratory replicates (mean RPD ± sd; %)	2	11.6 ± 2.7	10.0 ± 4.7	14.1 ± 5.2
• Bias (midge larvae)				
o laboratory spikes (mean recovery ± sd; %)	3	98.2 ± 0.4	92.6 ± 1.1	105 ± 0.7

Fish				
• Background (reagent blanks; ng)	28	13.1	9.3	6.4
• LOD (reagent blanks; ng)	28	9.6	9.6	12.3
• MDL (laboratory replicates; ng/g wet wt) [1]	10	1.4	0.9	1.5
• LOQ (3 × MDL; ng/g wet wt)	10	4.1	2.7	4.6
• Precision				
o reference fish (RSD; %)	18	5.5	5.2	4.4
o field replicates (mean RSD ± sd; %)	16	32.8 ± 22.3	27.8 ± 19.5	73.8 ± 41.4
o laboratory replicates (mean RSD ± sd; %)	41	13.8 ± 8.5	7.3 ± 7.4	6.9 ± 6.7
o extract replicates (mean RPD ± sd; %)	76	18.5 ± 14.9	3.7 ± 3.9	21.5 ± 18.4
• Bias				
o laboratory blanks (mean concentration ± sd; ng/g ww)	18	2.4 ± 1.0	3.4 ± 1.1	0.2 ± 0.6
o reference fish (mean recovery ± sd; %)	18	95.1 ± 5.2	95.4 ± 4.9	96.1 ± 4.2
o laboratory spikes (mean recovery ± sd; %)	51	90.1 ± 4.7	91.3 ± 6.5	95.2 ± 4.8

[1] N is the number of individual samples or sets of sample replicates (2 or more samples) that were analyzed.

[2] The MDL was based on analysis of replicate samples (N=7) containing concentrations of cVMS that were at least equal to the MDL but less than 5 times the MDL. The MDL for fish was based on regression of MDL on mean concentration.

[3] Precision estimates for D4 in sediment are not reported because concentrations of D4 in the field replicate samples and laboratory replicate samples were all less than the MDL.

Table 8. Feeding matrix for the aquatic food web in Lake Pepin (Daniel Dieterman, Minnesota Department of Natural Resources Lake City Field Station, personal communication), sorted on increasing trophic level.

			Forage-Prey Species												
	Species	Mean trophic level	Sediment detritus	Plankton	Midge	Burrowing mayfly	Other macroinvertebrates[1]	Fish eggs	Gizzard shad (fry)	Freshwater drum (fry)	Gizzard shad (YOY)	Emerald shiner	Other forage fish[2]	Terrestrial insects	Total Fraction
Predator Species	Midge	2.0	0.80	0.20											1.00
	Burrowing mayfly	2.0	0.75	0.25											1.00
	White sucker	2.6	0.10		0.15	0.15	0.50	0.10							1.00
	Common carp	2.8	0.15	0.10	0.45	0.15	0.15								1.00
	Gizzard shad	2.8		0.95	0.05										1.00
	Gizzard shad (YOY)	2.9		1.00											1.00
	Silver redhorse	3.0	0.10		0.20	0.15	0.55								1.00
	Bluegill sunfish	3.1	0.05	0.10	0.10	0.10	0.10		0.10	0.05	0.10	0.10	0.10	0.10	1.00
	River carpsucker	3.3	0.10	0.10	0.20	0.20	0.30	0.10							1.00
	Shorthead redhorse	3.3	0.10		0.25	0.20	0.45								1.00
	Freshwater drum	3.4		0.05	0.25	0.50					0.10	0.10			1.00
	Emerald shiner	3.4		0.70	0.05	0.05		0.15	0.05						1.00
	Black crappie	3.4		0.05	0.10	0.10			0.05	0.05	0.25	0.20	0.20		1.00
	White bass	3.5		0.10	0.15	0.15				0.10	0.30	0.20			1.00
	Smallmouth bass	3.5		0.05	0.05	0.10			0.05	0.05	0.20	0.20	0.20	0.10	1.00
	Walleye	3.6			0.05	0.10				0.15	0.40	0.30			1.00
	Quillback carpsucker	3.6	0.10	0.10	0.30	0.20	0.20	0.10							1.00
	Largemouth bass	3.8		0.05	0.05	0.10			0.05		0.25	0.25	0.20	0.05	1.00

[1] Other macroinvertebrate species predominately include caddisfly (Trichoptera) and stonefly (Plecoptera) larvae, but also crustaceans (Cladocerans and Amphipods), snails, and mollusks.

[2] Other forage fish include small minnow (Cyprinid) species such as bullhead minnow (*Pimephales vigilax*).

Table 9. Species characteristics of samples analyzed from the Lake Pepin food web, sorted on increasing $\delta^{15}N$.

Species	N[1]	Age Mean	Age SD	Weight (g) Mean	Weight (g) SD	Length (cm) Mean	Length (cm) SD	Lipid (% ww)[2] Mean	Lipid (% ww)[2] SD	$\delta^{13}C$ Mean	$\delta^{13}C$ SD	$\delta^{15}N$ Mean	$\delta^{15}N$ SD	Trophic Level Mean	Trophic Level SD
Surface sediment[3]	25							0.8	0.1	-26.0	0.4	8.2	1.0	0.7	0.3
Surface sediment[4]	5							0.8	0.2	-26.1	0.6	7.9	1.2	0.6	0.4
Midge	5							0.8	0.2	-29.4	1.6	12.8	0.5	2.0	0.1
Burrowing mayfly	2							2.5	0.2	-28.1	0.6	12.9	0.6	2.0	0.2
White sucker	1	3.0		744.0		42.2		2.0		-27.5		14.9		2.6	
Common carp	3	8.3	1.5	2795.0	100.5	59.0	1.1	12.9	0.9	-27.2	0.4	15.5	0.3	2.8	0.1
Gizzard shad	4	2.3	0.5	383.0	225.9	31.6	4.9	8.4	1.6	-26.9	0.3	15.6	0.3	2.8	0.1
Gizzard shad (YOY)	3	0.0	0.0	30.4	0.8	15.0	0.1	3.7	0.2	-26.4	0.3	16.0	0.1	3.0	0.0
Silver redhorse	3	4.3	0.6	1969.3	109.4	55.0	1.1	7.2	1.5	-26.1	0.3	16.0	0.5	3.0	0.1
Bluegill sunfish	3	4.0	0.0	142.0	3.0	18.3	0.2	4.8	0.5	-26.0	0.2	16.5	0.5	3.1	0.1
River carpsucker	1	4.0		2807.0		56.6		16.8		-26.8		17.0		3.3	
Shorthead redhorse	3	1.0	0.0	135.3	17.9	23.6	1.2	6.3	0.7	-25.9	0.5	17.3	0.8	3.3	0.2
Freshwater drum	3	4.3	0.6	668.3	97.5	37.6	2.8	4.7	0.1	-25.7	0.7	17.5	0.5	3.4	0.2
Emerald shiner	4			1.1	0.8	5.3	1.4	3.5	1.3	-27.2	0.3	17.6	1.4	3.4	0.4
Black crappie	3	4.0	0.0	466.3	12.3	30.0	0.5	7.0	0.2	-26.6	0.3	17.6	0.1	3.4	0.0
White bass	3	3.0	0.0	255.0	17.4	27.4	0.7	6.6	0.8	-26.0	0.6	17.8	1.0	3.5	0.3
Smallmouth bass	3	2.7	0.6	359.7	63.1	29.1	1.9	5.7	0.4	-25.9	0.1	18.0	0.1	3.5	0.0
Quillback carpsucker	2	3.0	0.0	1443.0	222.0	47.0	0.8	12.3	1.8	-25.7	1.4	18.2	0.3	3.6	0.1
Walleye	3	4.0	0.0	888.0	32.9	47.6	1.0	6.9	1.0	-26.3	0.7	18.2	0.8	3.6	0.2
Largemouth bass	3	5.0	1.0	819.3	234.9	36.7	2.8	4.4	1.5	-26.4	0.5	19.0	0.1	3.8	0.0

[1] N is the number of samples analyzed. For midge, mayfly, young-of-year (YOY) gizzard shad, and emerald shiner N is equal to the number of pooled samples analyzed.

[2] For sediment samples % total organic carbon (TOC, % ww) is reported rather than lipid content.

[3] Sample means and standard deviations represent whole lake values, based on analysis of n=25 sediment samples.

[4] Sample means and standard deviations were based on analysis of n=5 sediment samples from where benthic macroinvertebrate species were collected.

Table 10. Mean concentrations of cVMS materials (D4, D5, and D6) measured in samples analyzed from the Lake Pepin food web, sorted on increasing trophic level.

Species	N[1]	Trophic Level Mean	D4 (ng/g ww)[2] Mean	D4 (ng/g ww)[2] SD	D5 (ng/g ww)[2] Mean	D5 (ng/g ww)[2] SD	D6 (ng/g ww)[2] Mean	D6 (ng/g ww)[2] SD	D4 (ng/g lipid)[3] Mean	D4 (ng/g lipid)[3] SD	D5 (ng/g lipid)[3] Mean	D5 (ng/g lipid)[3] SD	D6 (ng/g lipid)[3] Mean	D6 (ng/g lipid)[3] SD
Surface sediment[4]	25	0.7	(0.4)	0.0	26.7	6.4	6.3	0.6	48	5	3289	522	800	121
Surface sediment[5]	5	0.6	(0.4)	0.1	28.2	6.7	6.6	0.7	46	2	3433	566	821	142
Midge	5	2.0	7.3	2.6	154.1	72.9	10.5	3.7	888	304	18114	8860	1305	550
Burrowing mayfly	2	2.0	7.8	0.2	98.7	0.9	3.7	0.3	309	36	3895	341	148	28
White sucker	1	2.6	6.4		58.5		(0.3)		314		2865		13	
Common carp	3	2.8	4.9	0.6	136.8	64.8	9.4	7.1	38	3	1050	467	71	52
Gizzard shad	4	2.8	10.0	2.0	69.2	25.4	1.7	2.5	118	4	816	222	19	26
Gizzard shad (YOY)	3	3.0	2.8	1.1	15.1	2.5	3.7	4.0	76	31	402	40	99	111
Silver redhorse	3	3.0	10.9	1.7	249.9	105.3	5.8	4.9	160	56	3412	804	74	49
Bluegill sunfish	3	3.1	3.6	0.6	27.4	5.2	(1.2)	0.8	78	18	580	132	23	14
River carpsucker	1	3.3	59.1		446.5		26.9		351		2654		160	
Shorthead redhorse	3	3.3	6.1	4.1	58.4	5.5	(1.4)	1.3	101	79	927	124	22	19
Freshwater drum	3	3.4	1.7	1.1	24.2	18.8	4.9	4.0	36	24	513	399	103	84
Emerald shiner	4	3.4	3.0	1.9	34.9	9.6	5.1	4.3	98	62	1087	467	166	130
Black crappie	3	3.4	6.7	1.5	36.9	3.2	(0.7)	0.0	97	24	531	49	10	0
White bass	3	3.5	3.4	1.4	21.8	4.1	(1.1)	1.1	49	16	332	77	17	20
Smallmouth bass	3	3.5	5.3	3.5	22.9	4.1	2.0	2.5	91	57	398	43	36	47
Quillback carpsucker	2	3.6	17.5	6.8	158.6	27.4	6.9	4.1	140	35	1283	35	54	26
Walleye	3	3.6	4.4	0.6	58.3	10.1	1.8	1.8	64	14	848	92	25	21
Largemouth bass	3	3.8	3.1	0.3	7.5	3.0	(0.5)	0.1	78	30	175	38	13	4

[1] N is the number of individual samples analyzed. For midge, mayfly, young-of-year (YOY) gizzard shad, and emerald shiner N is equal to the number of pooled samples analyzed.

[2] Values in ( ) are concentrations that were < MDL but > LOD, and are reported as the actual measured concentration.

[3] For sediment samples, concentrations are normalized and reported on the basis of total organic carbon (TOC) rather than lipid content.

[4] Sample means and standard deviations represent whole lake values, based on analysis of n=25 sediment samples.

[5] Sample means and standard deviations were based on analysis of n=5 sediment samples from where benthic macroinvertebrate species were collected.

Table 11. Mean biota-sediment accumulation factors (BSAF) and mean predator-prey bioaccumulation factors (BAF) for D4, D5, and D6 in the Lake Pepin food web, sorted on increasing trophic level.

					Predator-Prey Bioaccumulation Factors					
		Biota-Sediment Accumulation Factors[1]			BAF (not corrected for trophic level)[2]			BAF_{TL} (corrected for trophic level)[3]		
BAF Predator Species	TL	D4	D5	D6	D4	D5	D6	D4	D5	D6
Midge larvae	2.0	19.2	5.3	1.6	19.2	5.3	1.6	6.4	1.8	0.5
Mayfly nymphs	2.0	6.7	1.1	0.2	6.7	1.1	0.2	2.3	0.4	0.1
White sucker	2.6	6.8	0.8	< 0.1	0.9	0.5	< 0.1	0.7	0.4	< 0.1
Common carp	2.8	0.8	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1
Gizzard shad	2.8	2.6	0.2	< 0.1	2.0	0.2	< 0.1	0.7	0.1	< 0.1
Gizzard shad (YOY)	2.9	1.7	0.1	0.1	1.7	0.1	0.1	0.6	< 0.1	< 0.1
Silver redhorse	3.0	3.5	1.0	0.1	0.4	0.6	0.2	0.3	0.4	0.1
Bluegill sunfish	3.1	1.7	0.2	< 0.1	0.2	0.1	0.1	0.2	0.1	< 0.1
River carpsucker	3.3	7.6	0.8	0.2	1.0	0.4	0.3	0.6	0.2	0.2
Shorthead redhorse	3.3	2.2	0.3	< 0.1	0.3	0.1	< 0.1	0.1	0.1	< 0.1
Freshwater drum	3.4	0.8	0.1	0.1	0.1	< 0.1	0.1	< 0.1	< 0.1	0.1
Emerald shiner	3.4	2.1	0.3	0.2	0.9	0.3	0.3	0.4	0.1	0.1
Black crappie	3.4	2.1	0.2	< 0.1	0.3	0.1	< 0.1	0.3	0.1	< 0.1
White bass	3.5	1.1	0.1	< 0.1	0.2	0.1	0.1	0.1	< 0.1	< 0.1
Smallmouth bass	3.5	2.0	0.1	< 0.1	0.3	0.1	0.1	0.2	0.1	0.1
Quillback carpsucker	3.6	3.0	0.4	0.1	0.4	0.2	0.1	0.2	0.1	0.1
Walleye	3.6	1.4	0.2	< 0.1	0.2	0.2	0.2	0.2	0.2	0.1
Largemouth bass	3.8	1.7	0.1	< 0.1	0.3	< 0.1	0.1	0.2	< 0.1	< 0.1

[1] BSAF values for the benthic macroinvertebrate species (midge larvae and mayfly nymphs) were calculated using the concentrations of cVMS materials and TOC measured in the sediments from which the organisms were collected. BSAF values for the fish species were calculated using the mean concentrations of cVMS materials and TOC measured in the surface sediments of the lake basin.

[2] BAF is the predator-prey bioaccumulation factor, which has not been corrected for trophic level increase.

[3] BAF_{TL} is the predator-prey bioaccumulation factor, which has been corrected for trophic level increase. Predator-prey bioaccumulation factors were corrected for trophic level increase because the $\delta^{15}N$ values of the predator species were not always a full trophic level above the prey species.

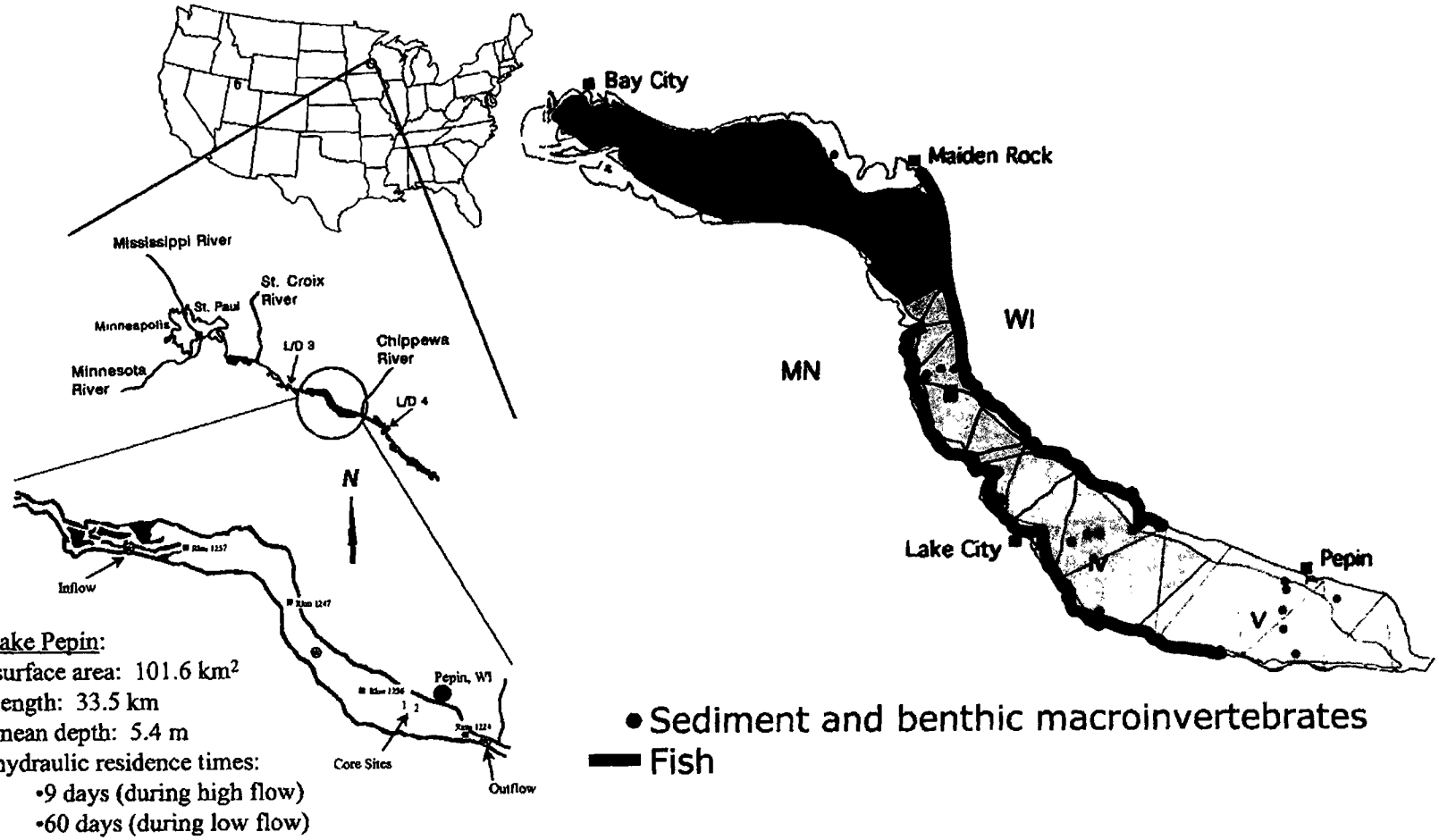

Figure 1. Map of Lake Pepin showing depositional regions (I-V) and locations where surface sediments (red circles), benthic macroinvertebrates (red circles), and fish (blue lines) were collected.

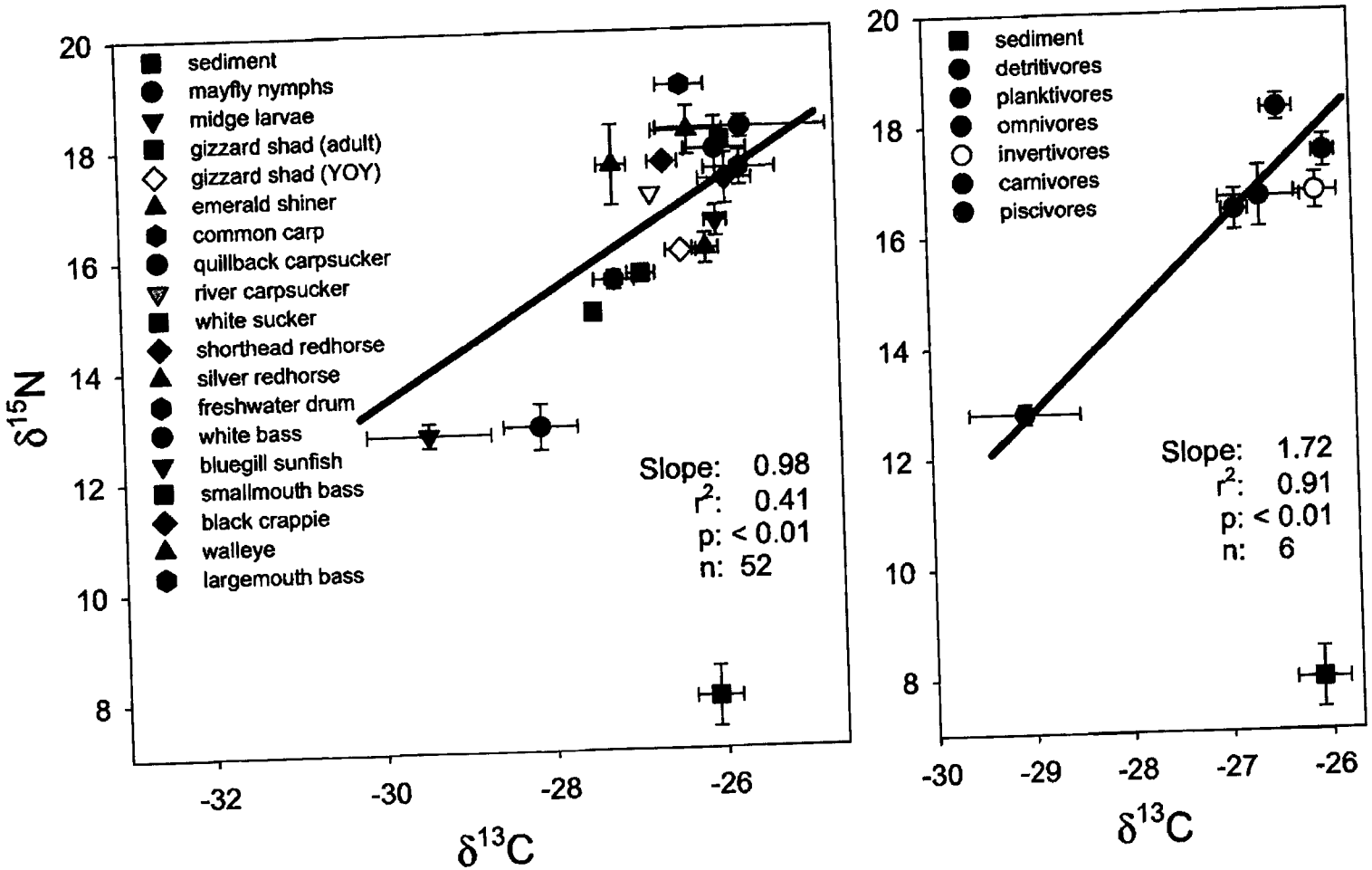

Figure 2. Food web diagram for Lake Pepin, based on stable isotope analysis of samples. Data represent mean isotopic ratios ± SE (standard error) by individual species or by trophic guild. Regression for species was based on all data (n=52 observations across 18 species). Regression for trophic guilds was based on mean values (n=6 means across 6 trophic guilds).

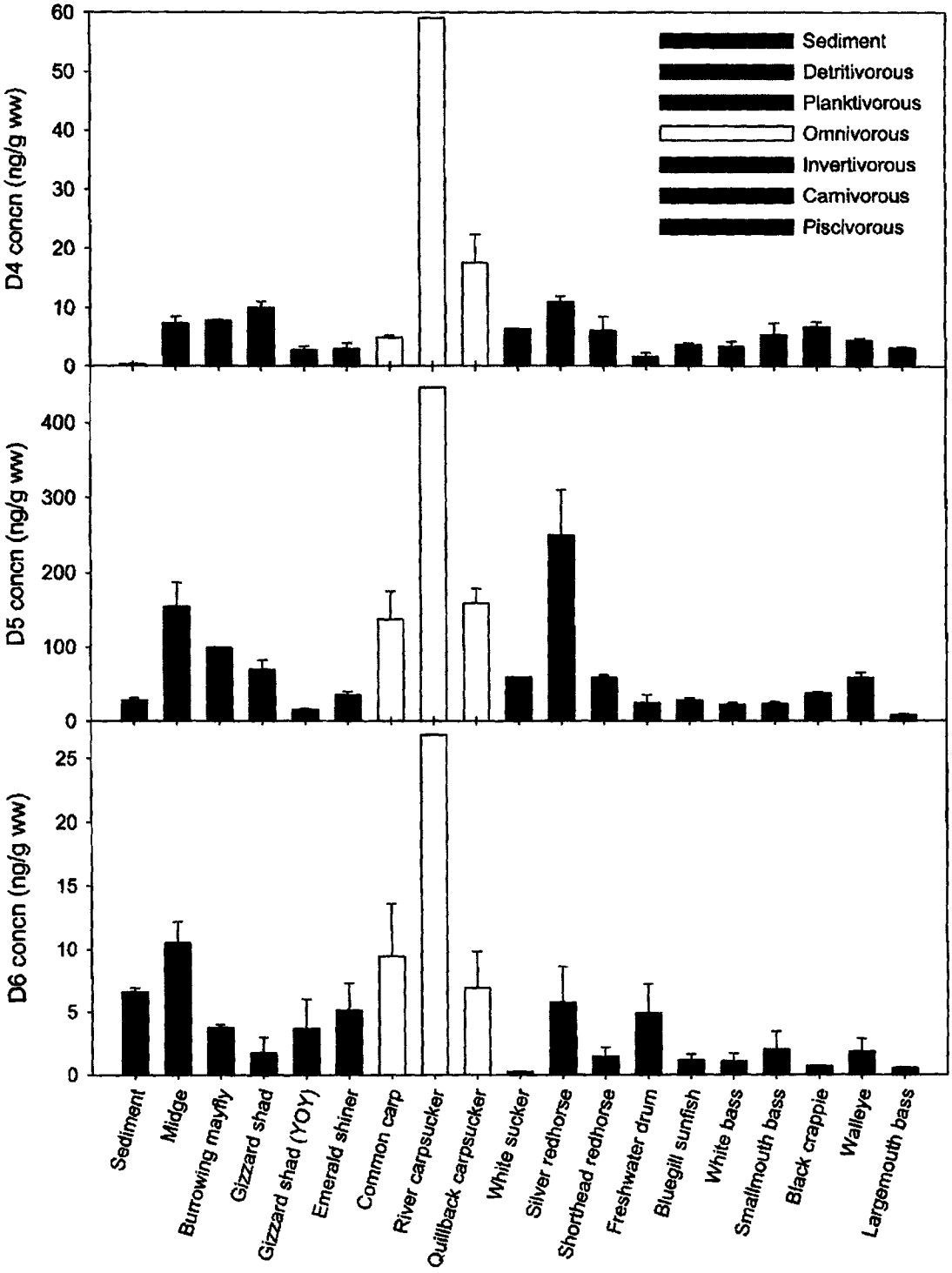

Figure 3. Mean whole-body concentrations of D4, D5, and D6 in the food web of Lake Pepin. Bars represent mean concentrations ± SE (standard error) for each individual species, grouped by trophic guild.

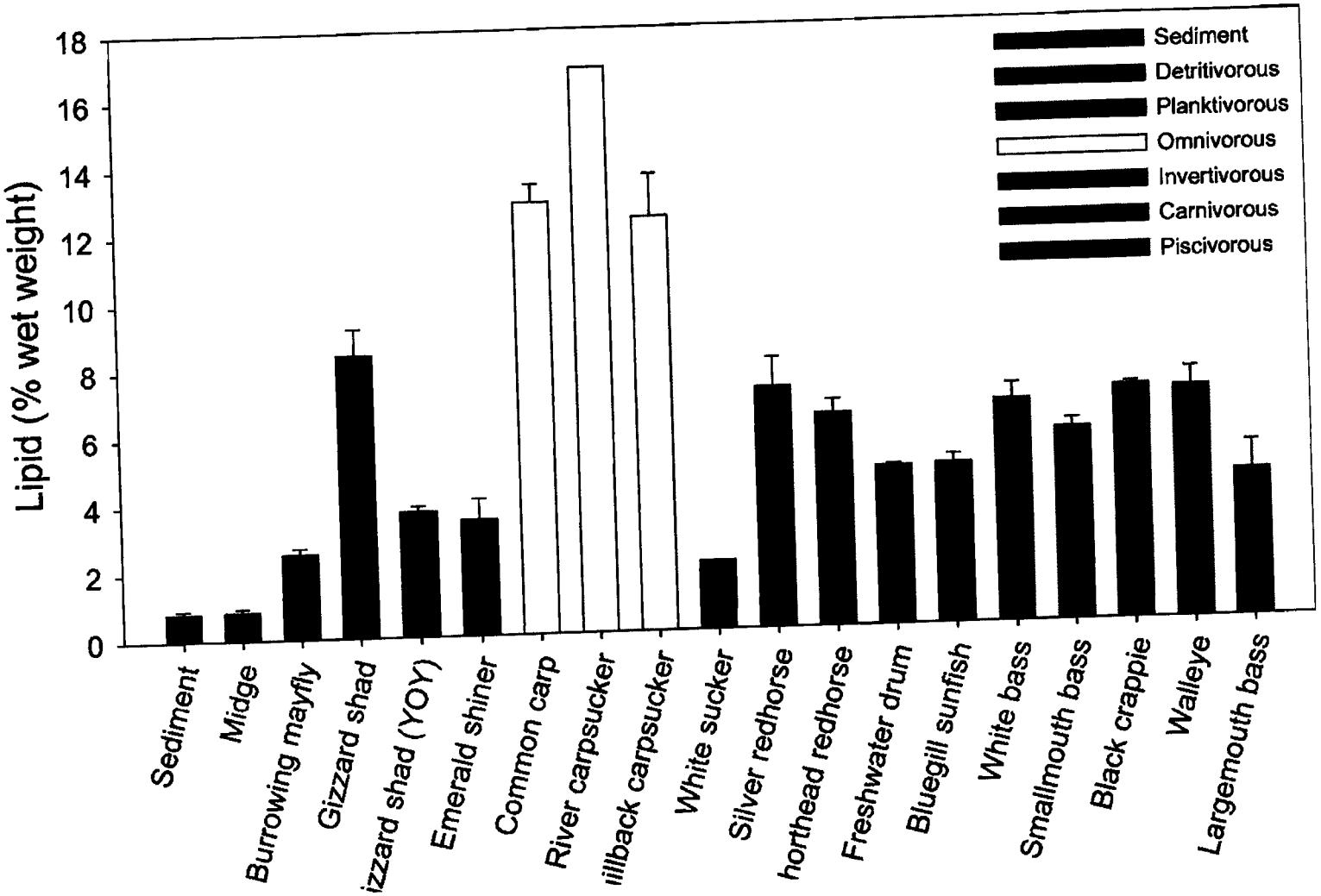

Figure 4. Mean whole-body lipid content in the food web of Lake Pepin. Bars represent mean lipid content ± SE (standard error) for each individual species, grouped by trophic guild.

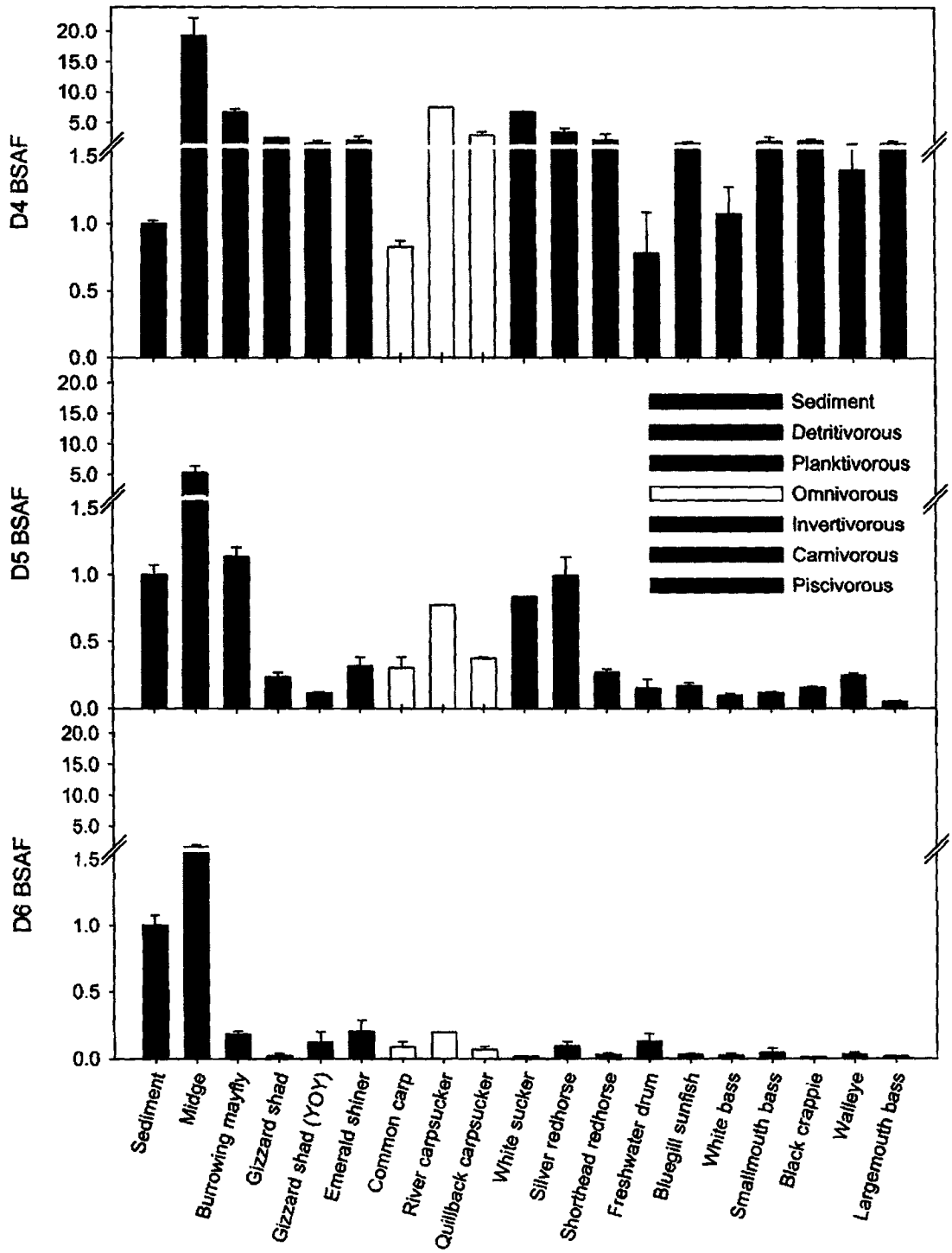

Figure 5. Mean biota-sediment accumulation factors (BSAF) for D4, D5, and D6 in the food web of Lake Pepin. Bars represent mean BSAF ± SE (standard error) for each individual species, grouped by trophic guild.

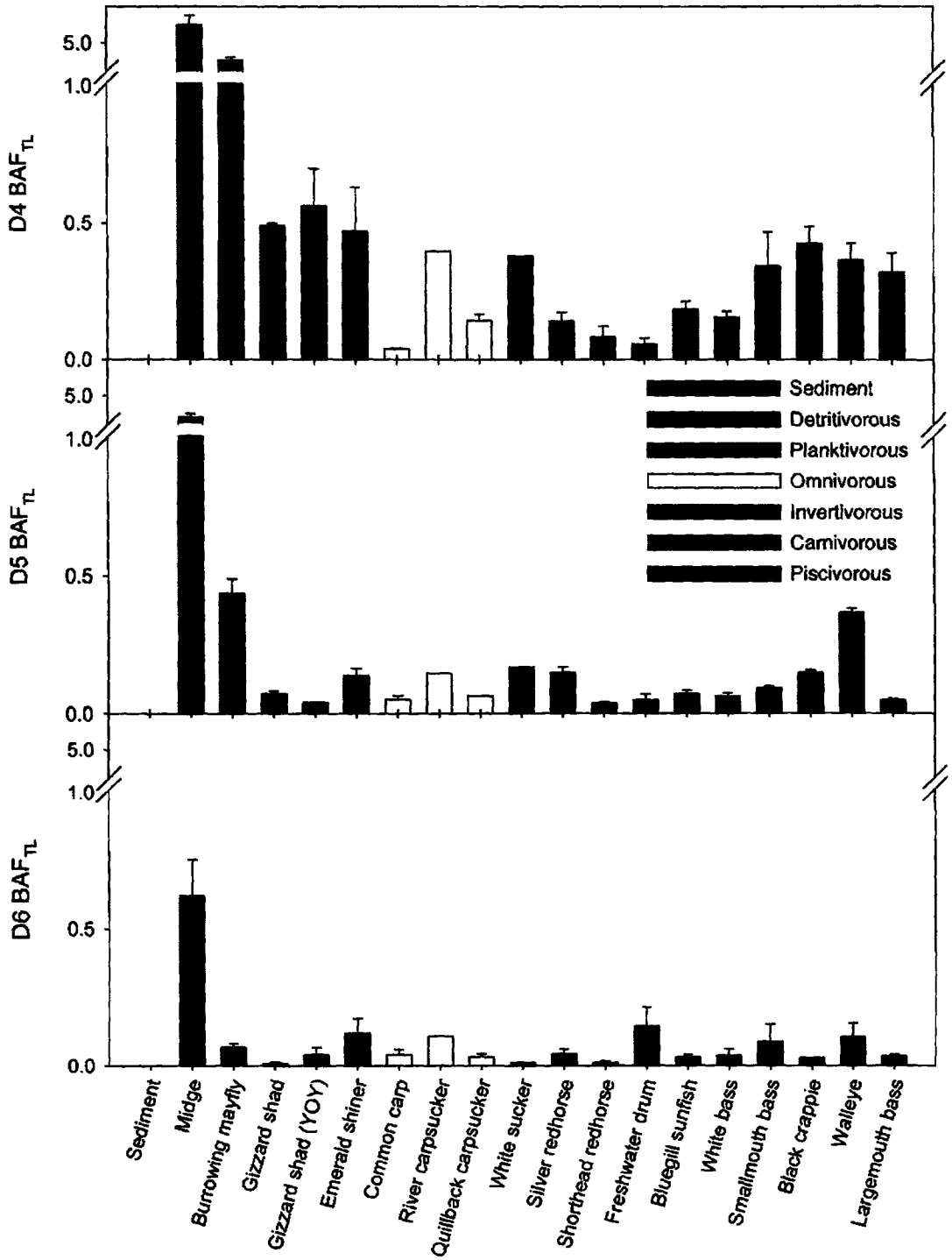

Figure 6. Mean trophic level corrected predator-prey accumulation factors (BAF_{TL}) for D4, D5, and D6 in the food web of Lake Pepin. Bars represent mean $BAF_{TL} \pm SE$ (standard error) for each individual species, grouped by trophic guild.

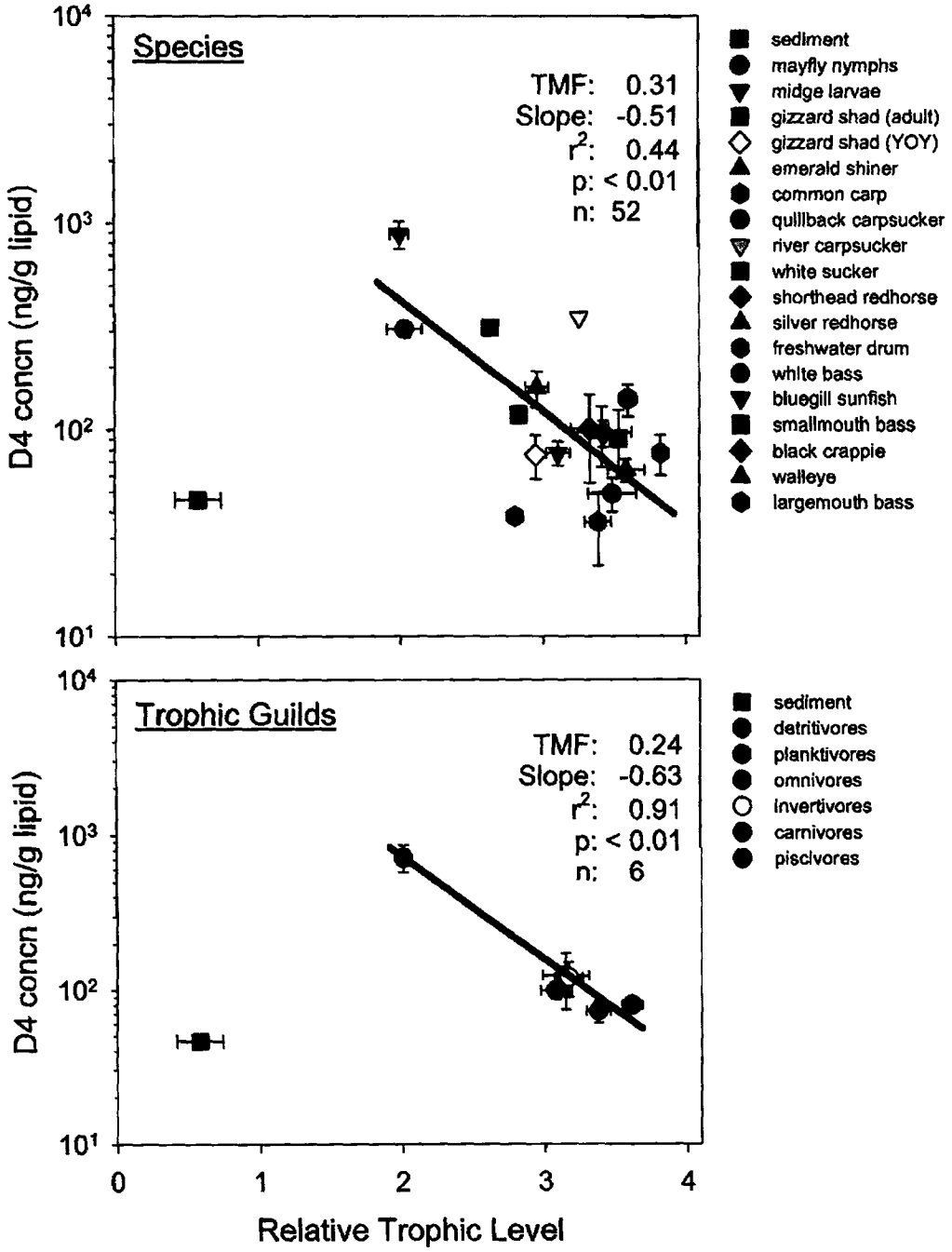

Figure 7. Lipid-normalized whole-body concentrations of D4 and trophic level relationships for the aquatic food web in Lake Pepin. Data represent mean concentrations ± SE (standard error) by individual species or by trophic guild. TMF regression for species was based on all data (n=52 observations across 18 species). TMF regression for trophic guilds was based on mean values (n=6 means across 6 trophic guilds).

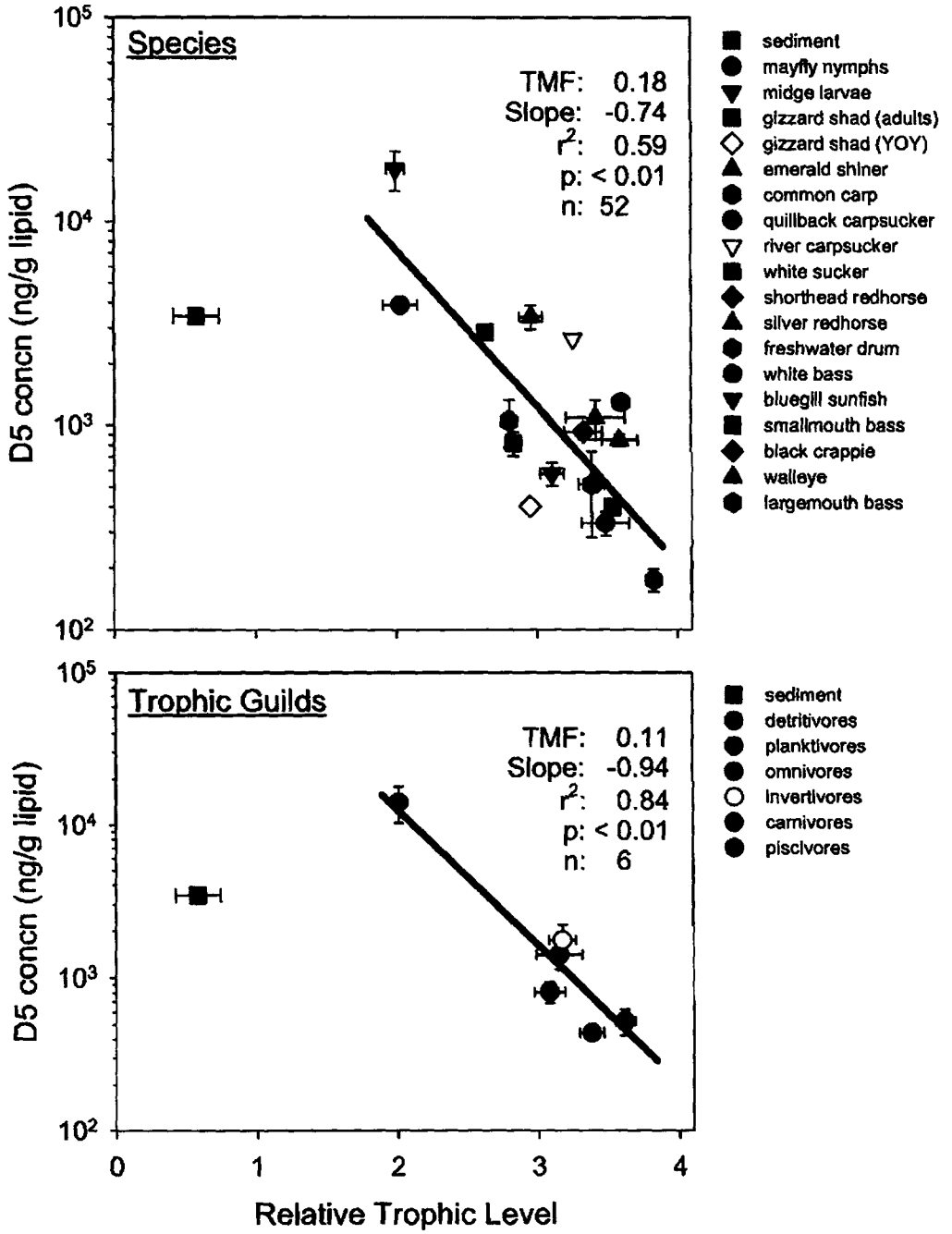

Figure 8. Lipid-normalized whole-body concentrations of D5 and trophic level relationships for the aquatic food web in Lake Pepin. Data represent mean concentrations ± SE (standard error) by individual species or by trophic guild. TMF regression for species was based on all data (n=52 observations across 18 species). TMF regression for trophic guilds was based on mean values (n=6 means across 6 trophic guilds).

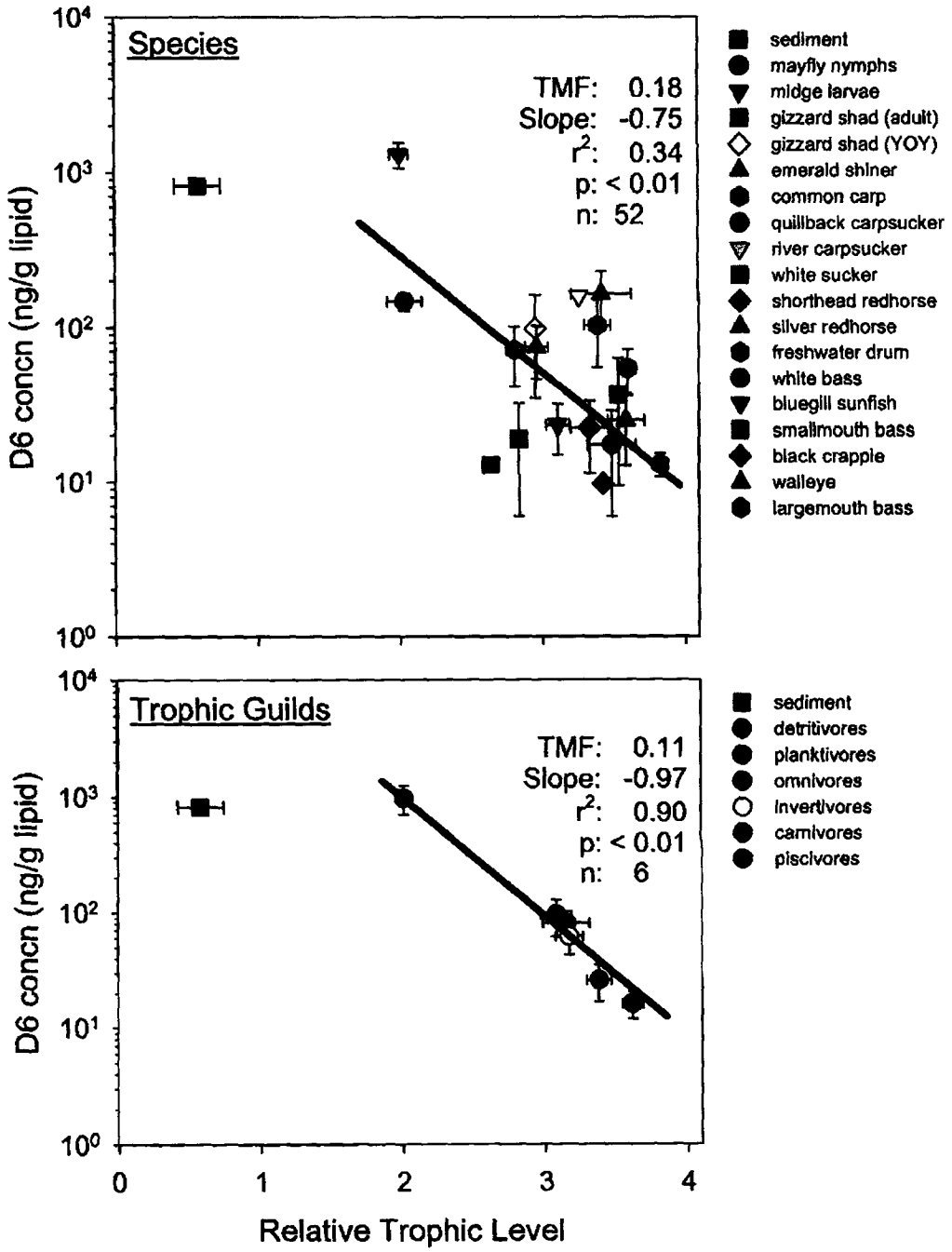

Figure 9. Lipid-normalized whole-body concentrations of D6 and trophic level relationships for the aquatic food web in Lake Pepin. Data represent mean concentrations ± SE (standard error) by individual species or by trophic guild. TMF regression for species was based on all data (n=52 observations across 18 species). TMF regression for trophic guilds was based on mean values (n=6 means across 6 trophic guilds).

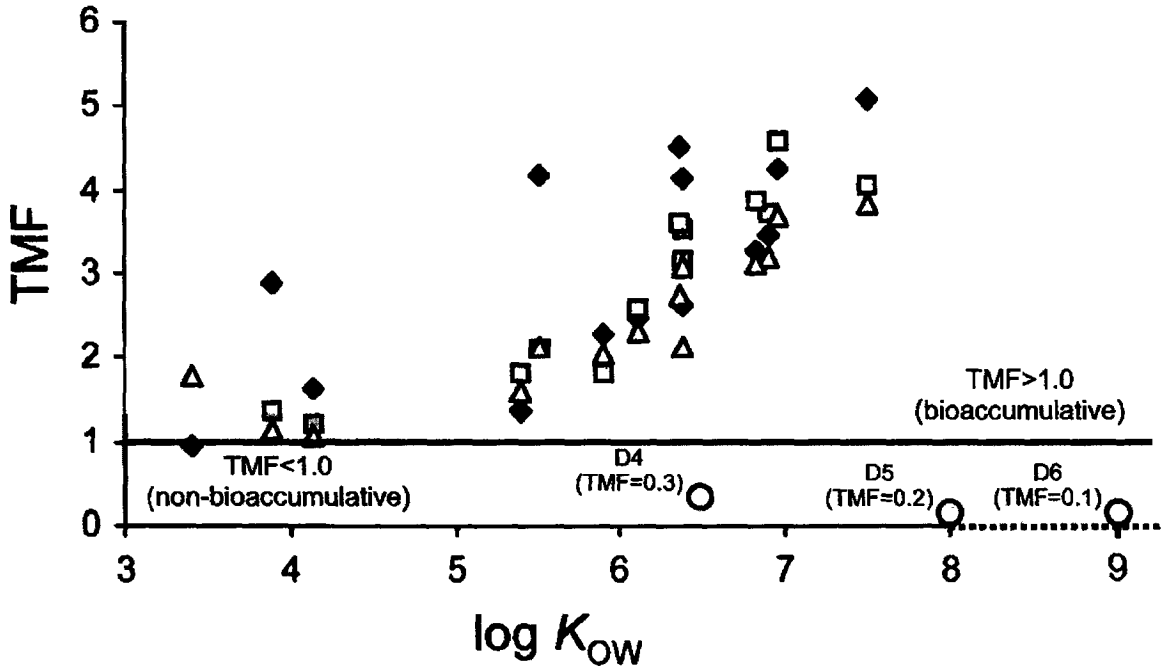

Figure 10. Relationship between the octanol–water partition coefficients (log K_{OW}) and trophic magnification factors (TMFs) for 14 individual polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) averaged across 17 lakes in Canada and the northeastern United States. The original figure (from Houde et. al. 2008) was modified to show the relationship between log K_{OW} and TMF for D4, D5, and D6 in Lake Pepin.

Study Title:	Preliminary Assessment of Cyclic Volatile Methylsiloxane (cVMS) Materials in Surface Sediments, Cores, Zooplankton, and Fish of Lake Opeongo, Ontario, Canada
HES Study No:	10806-108
Test Substances:	Octamethylcyclotetrasiloxane (D_4; CAS No. 556-67-2) Decamethylcyclopentasiloxane (D_5; CAS No. 541-02-6) Dodecamethylcyclohexasiloxane (D_6; CAS No. 540-97-6)
Authors:	David E. Powell
Study Personnel:	Jeremy Durham Darren W. Huff
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Date:	12 January 2010

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ABSTRACT

Evidence indicates that cVMS materials in air may be sufficiently persistent to allow for hemispheric transport and mixing, but the potential to deposit from air appears to be minimal. In order to better understand the fate of cVMS materials released to air, the silicone manufacturers industry associations were invited by Environment Canada to participate in a field monitoring program on Lake Opeongo, which is an oligotrophic lake located in Algonquin Provincial Park in south central Ontario, where source of entry of chemical substances was believed to be dominated by atmospheric deposition. The objective of the study was to conduct a preliminary assessment of concentrations of octamethylcyclotetrasiloxane (D_4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D_5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D_6; CAS No. 540-97-6) in surface sediments, sediment cores, zooplankton, and fish. Lake Opeongo is remotely situated from any significant sources of cVMS materials originating from sewage and runoff but was observed to be a very popular location for canoeing and camping. Use of personal care products during recreational activities could not be definitively excluded as a potentially significant source of cVMS materials to the lake.

Bulk zooplankton, surface sediments (0 to 5 cm), and sediment cores (sectioned into 1-cm thick strata) were collected from Lake Opeongo 02-03 October 2007 with guidance and assistance from Environment Canada. Yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*) were collected 26-31 October 2007 by the Harkness Laboratory of Fisheries Research, located at the southern end of the lake. However, the quality control program that was followed in the field was not sufficient to evaluate the extent of sample contamination that may have occurred during collection of fish. Sediment samples were analyzed for total organic carbon content, for total organic matter content, and for concentrations of D_4, D_5, and D_6. Except for zooplankton, biological samples were analyzed for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$), for whole-body lipid content, and for whole-body concentrations of D_4, D_5, and D_6. Isotopic signatures and lipid content were inadvertently not determined for zooplankton because the samples were consumed during analysis for the cVMS materials.

A highly variable reagent blank response was always present during analysis of samples for D_4, D_5, and D_6, which made quantification of the cVMS materials difficult for all matrices. The source of the background cVMS materials was not identified but represented a systematic contamination that could not be eliminated. Because of the high background contamination and the relatively low concentrations in the samples, absolute masses of the cVMS materials measured in extracts of the surface sediments, sediment cores, and zooplankton were not statistically different from masses measured in the reagent blanks. Concentrations of the cVMS materials in samples from Lake Opeongo were low and clustered about the limits of detection for fish and were below the limits of detection for surface sediments, sediment cores, or zooplankton. Analytical method detection limits expressed on the basis of wet weight across all matrices (sediment, zooplankton, and fish) ranged from 0.47 to 0.90 ng/g ww for D_4, from 1.79 to 3.10 ng/g ww for D_5, and from 0.15 to 0.74 ng/g ww for D_6.

The $\delta^{15}N$ isotopic signatures indicated that the two forage species (perch and cisco) occupied the middle trophic levels (TL ~3.0) and lake trout occupied the highest trophic level (TL ~3.7). Lipid-equivalent concentrations of D_4, D_5, and D_6 were below detection in zooplankton and were highest in the lake trout. Mean predator-prey specific biomagnification factors (BMF) ranged from 1.9 to 2.4 for D_4, from 2.3 to 5.2 for D_5, and from 1.4 to 1.5 for D_6. Non-detection of the cVMS materials in surface sediments, sediment cores, and zooplankton suggested that atmospheric deposition did not appear to represent a significant source of D_4, D_5, and D_6 to Lake Opeongo. The low levels of D_4, D_5, and D_6 that were detected in fish likely originated from personal care products used during recreational activities that were presumably rinsed off the body directly into the water column of the lake. Regardless of source of entry, these preliminary results indicated that concentrations of the cVMS materials in sediments and biota of Lake Opeongo were low and were typically less than or equal to the analytical limits of detection.

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SIGNATURES and APPROVAL

This report consists of 40 pages with 7 tables and 2 figures. The undersigned have read and approved this report.

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INTRODUCTION

Cyclic volatile methylsiloxane materials (cVMS) are widely used in industrial and consumer applications and the wastewater stream represents a major post-use disposal route. Generally, cVMS materials are volatile, have very low water solubility, have intermediate values for K_{OA} (octanol/air partition coefficient), and have very high values for K_{OW} (octanol/water partition coefficient) and K_{AW} (air/water partition coefficient). Because of these partitioning properties, cVMS materials occupy a somewhat unique chemical space and are expected to partition primarily to air during use and after disposal to wastewater. Evidence indicates that cVMS materials in air may be sufficiently persistent to allow for hemispheric transport and mixing, but the potential to deposit from air appears to be minimal.

In order to better understand the fate of cVMS materials released to air, the industry associations were invited by Environment Canada to participate in a field monitoring program on Lake Opeongo, which is an oligotrophic lake located in Algonquin Provincial Park in south central Ontario, where source of entry of chemical substances was believed to be dominated by atmospheric deposition. Lake Opeongo is the largest lake in the Algonquin Provincial Park and is remotely situated from any significant sources of cVMS materials originating from sewage and runoff. Therefore, it was assumed that the only significant source of cVMS materials to Lake Opeongo would have occurred from atmospheric deposition. However, the lake is also a popular location for canoeing and camping and use of personal care products during recreational activities can not be definitively excluded as a potentially significant source of cVMS materials to the lake.

The objective of the study was to conduct a preliminary assessment of concentrations of octamethylcyclotetrasiloxane (D_4; CAS No. 556-67-2), decamethylcyclopentasiloxane (D_5; CAS No. 541-02-6), and dodecamethylcyclohexasiloxane (D_6; CAS No. 540-97-6) in surface sediments, sediment cores, zooplankton, and fish collected from Lake Opeongo. Fish species collected from the lake included small yellow perch (*Perca flavescens*), small cisco (*Coreogonus artedi*), and adult lake trout (*Salvelinus namaycush*). Zooplankton were known to represent a significant fraction in the diet of the forage fish (i.e., small yellow perch and cisco), which were known to be the primary forage species for lake trout in the lake. If it was possible, depending on the concentrations of cVMS measured in the samples, an assessment of the trophic transfer of the cVMS materials in the pelagic food web of Lake Opeongo was to be evaluated, using $\delta^{15}N$ as a continuous variable for assessing relative trophic levels (TL) of the sampled biota.

MATERIALS and METHODS

Study Area

The study area, Lake Opeongo (Fig. 1), has been described in detail elsewhere (Martin and Fry, 1972; Wong et al., 1984; Wong and Nriagu, 1985; Nriagu and Wong, 1986;

Johnson 1989). Lake Opeongo is the largest lake in the Algonquin Provincial Park, located in Ontario, Canada, about 250 km north of Toronto. The oligotrophic lake has a surface area of 58.6 km^2, a maximum depth of 49.4 m, and a mean depth of about 14.6 m. The lake consists of four major basins, each limnologically distinct and joined by shallow restricted channels. Except for recreational camping and canoeing, the lake has a history of very limited human disturbance and is free from potential sources of cVMS materials originating from sewage and runoff. Lake Opeongo is relatively remote such that atmospheric deposition was considered to be the most significant source of contaminants to the lake, which was used as a study area for persistent organic pollutants (POPs) that deposit from the atmosphere (Whittle et al., 2000; Campbell et al., 2003; Muir et al., 2003). It was initially assumed that the only significant source of cVMS materials to Lake Opeongo was from atmospheric deposition.

Sample Collection

Bulk zooplankton, surface sediments, sediment cores, and field quality control (QC) samples were collected from Lake Opeongo 02-03 October 2007 (Fig. 1) with guidance and assistance from the National Water Research Institute, Environment Canada, located in Burlington, Ontario. Yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*) were collected 26-31 October 2007 by personnel at the Harkness Laboratory of Fisheries Research, which is situated at the southern end of the lake. Field QC samples were not collected during fish sampling operations.

Surface Sediments: Surface sediments were collected from 7 locations in the lake using a box core. The locations (Fig. 1) were selected based on the proximity of popular camping sites and other areas of recreational activity to deposition basins in the lake where suspended particles (and associated contaminants) would be focused and deposited. The upper 5-cm of surface sediment was removed from the box core on deck using a pre-cleaned 10-cm i.d. stainless steel core tube, placed into individually labeled polyethylene food storage bags, and stored in the dark in a cooler. Surface sediment samples were transported back to the Harkness Laboratory for processing within 4 hours after collection.

Sediment Cores: Sediment cores were collected from 2 locations in the lake using a box core. The sediment cores were collected from the deepest sediment deposition areas in the south arm and east arm of the lake (Fig. 1). The box core was sub-cored on site using two pre-cleaned 10 cm i.d. polycarbonate tubes. The individual sub-cores were sealed with butyl rubber stoppers and stored in an upright, secured position on deck. Intact sediment cores were transported back to the Harkness Laboratory for processing within 4 hours after collection.

At the Harkness Laboratory, one of the two subcores from each location was extruded and sectioned outdoors (up wind of any buildings) using a hydraulic extruder. The second subcore, which was retained as a backup, was discarded after successful sectioning of the first subcore. To minimize smearing and

contamination, the outer 1-cm of sediment in contact with the sides of the core tube was trimmed and discarded during extrusion and sectioning. Subcores were sectioned into 1-cm thick sections for the entire length of the core. The sediment core from the south arm of the lake was sectioned into 34 strata. The sediment core from the east arm of the lake was sectioned into 40 strata. Extruded strata were placed into individually labeled polyethylene food storage bags, and stored in the dark in a cooler until further processed.

Bulk Zooplankton: Bulk zooplankton was collected using a 100-µm plankton tow (vertical hauls; 35-39 m to surface, depending on location) from two locations in the South Arm of the Lake (Fig. 1). A total of six vertical hauls were made at site LOP-01. A total of 2 hauls were made at site LOP-03 before wind conditions prevented additional casts. While on-site, the bucket contents of each vertical haul was transferred to individually labeled 500-mL wide-mouth glass jars with screw cap lids, stored in the dark in a cooler, and transported back to the Harkness Laboratory for processing within 6 hours after collection.

At the Harkness Laboratory, zooplankton were isolated from the bucket contents using a 100-µm mesh Nitex screen, allowing the water to drain from the sample. The bulk zooplankton sample remaining in the Nitex screen was transferred into a pre-cleaned, 120-mL wide mouth glass jar with Teflon-lined lid and stored in a cooler, in the dark. Because of sample mass limitations, bulk zooplankton from multiple vertical hauls were pooled into a single sample for each site. Bulk zooplankton samples were not sorted to species.

Fish: Yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*) were collected using a graded mesh multifilament nylon gill net. Fish were dip-netted from along side of the boat as the net was retrieved or were removed from the net after it was in the boat. Fish were handled with cotton fish gloves, placed into contaminant-free polyethylene bags, frozen whole and stored in the dark at about -20°C in a conventional freezer at the Harkness Laboratory. Lake trout were stored individually, whereas forage fish (cisco and yellow perch) were pooled and stored as composite samples (n=50 individuals) by species. Fish were transported in frozen condition to Dow Corning Corporation on 23 January 2008 where they were stored at -80°C until further processed.

Sample Processing and Preparation

Bulk zooplankton samples, sediment samples (surface sediments and core strata), and field QC samples were initially processed for extraction and analysis at the Harkness Laboratory on the day that the samples were collected. Samples were homogenized in the individual storage containers, and sub-samples removed for characterization analyses and determination of cVMS concentrations. Sediment samples to be analyzed for water, total organic carbon, and organic matter content were weighed into plastic containers with screw-cap lids. Samples to be analyzed for cVMS materials were weighed into extraction vials and extraction solvents containing internal standards were

added, as described below. Any sample remaining after removing the sub-samples was transferred to pre-cleaned, 120-mL wide mouth glass jars with Teflon-lined lids. All samples were stored in coolers, in the dark, for transport to the National Water Research Institute located in Burlington, Ontario, on 04 October 2007, where the samples were transferred to refrigerated storage at about 4°C in the dark. The samples were shipped under blue ice from the National Water Research Institute on 16 October 2007 to Dow Corning Corporation in Midland, Michigan, where they were received in good condition on 18 October 2007. At Dow Corning, samples were transferred to refrigerated storage at about 4°C in the dark. Sediment samples to be analyzed for water and organic matter content were shipped under blue ice from Dow Corning to the University of Minnesota on 15 November 2007. Samples were received in good condition at the University of Minnesota on 16 November 2007, and placed into refrigerated storage at about 4°C in the dark until processed for analysis.

Individual frozen lake trout, bulk frozen yellow perch (n=50), and bulk frozen cisco (n=50) were provided to Dow Corning Corporation in plastic food bags on 23 January 2008 and were stored at -80°C until further processed. Fish were removed from frozen storage and allowed to come to refrigerated temperature of about 4°C prior to processing. Forage fish (cisco and yellow perch) were processed as composite samples (n=5 impartially selected individual specimens) or as whole individuals. Lake trout were processed as individual whole specimens only. Before processing, thawed fish were measured for fresh weight and total length, scales (cisco and perch) or otoliths (trout) were collected for age determination, and a small piece of skin-free dorsal muscle (about 3 g) was removed from each lake trout from behind the pectoral fin above the lateral line for analysis of stable isotopes. Samples were prepared by cutting up whole, individual fish into small sections using stainless steel knives, with the cut sections being passed three times through a Hobart model 4822 meat grinder having a 13-mm cutting plate. The ground fish was collected into a stainless steel bowl and mixed by hand using a stainless steel spoon after each pass through the grinder. The ground fish was then homogenized by passing through the grinder a fourth time using a 3.2-mm cutting plate. The whole-body fish homogenate was then transferred, depending on size of fish, to a 0.5 to 4-L glass jar with Teflon-lined lid for frozen storage at -20°C.

Characterization of Sediments

Sediment composition and characterization analyses were determined by the Limnological Research Center at the University of Minnesota in Minneapolis. Small aliquots (about 10 g) of each sediment sample in individual plastic containers were shipped under blue ice from Dow Corning to the University of Minnesota by next day air on 15 November 2007. Samples were received in good condition at the University of Minnesota on 16 November 2007, and placed into refrigerated storage at about 4°C in the dark until processed for analysis. Sediment samples (sediment core strata and surface sediment samples) were analyzed by *carbon coulometry* (total carbon, total inorganic carbon, and total organic carbon) and *loss-on-ignition* (total water content and total organic matter content).

Carbon Coulometry Analyses: Organic carbon and carbonate mineral content were determined on freeze-dried and ground samples by coulometric titration (Engleman et al., 1985), using a UIC model 5011 CO_2 coulometer. Results were obtained as total carbon (%TC) and total inorganic carbon (%TIC); with total organic carbon (%TOC) calculated by difference. Percent calcite in the sediment was not calculated because carbonate carbon was not detected in any of the samples.

Loss-on-Ignition Analyses: A small quantity (about 3 cm^3) of sediment from each sample was used to determine sediment composition by analysis of weight loss on ignition of the sample (Heiri et al., 2001). The entire sediment sample was vigorously stirred until homogenized, then sub-sampled with a spatula into a pre-weighed ceramic crucible and weighed again. Samples were oven-dried at 100°C overnight, cooled completely, and weighed to determine water content. Samples were then ignited in a muffle furnace at 550°C for four hours, cooled, and weighed to determine organic matter content. Samples were finally burned at 1000°C for two hours, cooled, and weighed to determine $CaCO_3$ content. The sample mass remaining after the 1000°C burn was considered the "inorganic" content, i.e., silicate minerals, oxides, and silicate algal (diatom) remains.

Characterization of Fish

Fish were analyzed for water content, lipid content and for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) by the Biogeochemistry and Paleoproteomics Laboratory at Michigan State University in East Lansing. Isotopic signatures for trout were determined on skin-free dorsal muscle (lake trout) or whole-body homogenate (cisco and yellow perch). Water and lipid content of all fish were determined on whole-body homogenates. Small aliquots (about 3 g) of each sample in individual plastic containers were transported by car in a cooler containing blue ice from Dow Corning to Michigan State University. Upon arrival samples were immediately placed into refrigerated storage at about 4°C in the dark until processed for analysis.

Water and Lipid Content: Water and lipid content of the fish were determined on whole-body homogenates of individual fish (lake trout) and homogenized composite samples of forage fish (cisco and yellow perch). Water content was determined as weight loss during lyophilization to a constant weight. The remaining lyophilized material was then extracted with chloroform:methanol (87:13) and lipid content determined gravimetrically and expressed on both dry and wet weight basis. The precision (± standard deviation) for this technique, based on replicate analyses of a laboratory standard (rainbow trout, *Oncorhynchus mykiss*), was 0.2 % for water content and 1.25% for lipid content.

Stable Isotope Analysis: Isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) of the forage fish (cisco and yellow perch) were determined on whole-body homogenates of composite samples. Isotopic signatures of the lake trout were

determined on skinless dorsal muscle tissue that was collected from posterior to the pectoral fin above the lateral line of each individual specimen. Samples were lyophilized to a constant weight, extracted with chloroform:methanol (87:13) to remove the lipids, dried in a vacuum oven, and homogenized to a fine powder with a mechanical mill. Samples (about 1.0 mg in tin capsules) were then combusted with O_2 and Cr_2O_2 at about 1030°C in an elemental analyzer (Eurovector). NOx products were reduced with Cu at 650°C. The combustion products N_2, CO_2, and H_2O were separated on a packed column and the $^{15}N/^{14}N$ or $^{13}C/^{12}C$ isotopic ratios determined using an interfaced isotope ratio mass spectrometer (Elementar Americas, Inc). Stable isotope abundances were expressed in per mil notation (δ) as the deviation from standards in parts per thousand (‰) according to the equation:

$$\delta X = \left[\left(\frac{R_{sample}}{R_{standard}} \right) - 1 \right] \times 1000$$

where X is ^{15}N or ^{13}C and R is the abundance ratio of the heavy to light isotope (i.e., $^{15}N/^{14}N$ or $^{13}C/^{12}C$) in the sample (R_{sample}) and the standard ($R_{standard}$). The $R_{standard}$ values were based on atmospheric nitrogen gas for ^{15}N and PeeDee Belemnite (PDB) for ^{13}C. The precision (± standard deviation) for this technique, based on replicate analyses of laboratory standard (Atlantic salmon; *Salmo salar*), was ≤0.2 ‰ for ^{15}N and ^{13}C.

Characterization of Zooplankton

Sub-samples of bulk zooplankton were inadvertently not collected for characterization analyses and the bulk samples were completely consumed during analysis for the cVMS materials. Consequently, isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) and lipid content of the bulk zooplankton were not measured.

Analysis of Cyclic Volatile Methylsiloxane (cVMS) Materials

Surface sediments, fish, and zooplankton were analyzed for cVMS materials (specifically D_4, D_5, and D_6) by Dow Corning Corporation in Midland, Michigan.

Reagents: Hexanes (Optima grade) and acetonitrile (HPLC grade) were obtained from Fisher Scientific and used without further purification for extraction of cVMS materials from sediments. Tetrahydrofuran (THF) anhydrous ≥99.9% was obtained from Sigma-Aldrich and used without further purification for extraction of cVMS materials from zooplankton and fish. Anhydrous magnesium sulfate, also from Fisher Scientific, was used for removing incidental water from all extracts. Isotopically enriched ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6, used as internal standards for the GC-MS determination of cVMS materials in sediment extracts, were synthesized and characterized at Dow Corning Corporation (Midland, MI).

Extraction of Sediments and Bulk Zooplankton: Sediment samples, bulk zooplankton samples, and field QC samples were initially processed for extraction of cVMS materials at the Harkness Laboratory of Fisheries Research. On the day of sample collection, a 6-g sub-sample of wet sediment or a 3- to 6-g sub-sample of bulk zooplankton was weighed into a single-use borosilicate glass vial (28 x 108 mm, ca. 40 mL capacity), followed by addition of 6 mL of acetonitrile. After brief manual agitation, 12 mL of hexanes was added to the vial. The hexanes solvent contained known concentrations of isotopically labeled ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6 to serve as internal standard surrogates. The vial with sample was re-weighed after each solvent addition so that accurate internal standard amounts could be determined. The capped vials were placed on a vortex mixer for 30 min, and the samples then stored in coolers, in the dark, for transport to the National Water Research Institute located in Burlington, Ontario, as previously described. Samples were further processed for cVMS analyses at Dow Corning Corporation. Capped vials were again placed on a vortex mixer for 30 min, followed by brief centrifugation to facilitate separation of the phases. The upper hexane layer was removed to a round-bottom glass tube (20 x 150 mm) containing anhydrous magnesium sulfate (ca. 0.25 g) for drying the extract. A second portion of hexanes without the internal standards was added to the extraction vial. The extraction process was repeated and the hexanes were combined in the glass tube. The extract volume in each tube was reduced in volume to approximately 1-2 mL under a stream of high purity nitrogen in a 25 °C bath. A portion of the resulting concentrated extract was transferred to a crimp-cap vial for GC-MS analysis.

Extraction of Fish: Frozen whole-body homogenates of individual lake trout, cisco, and yellow perch were thawed to 4°C in a refrigerator and stirred before sub-samples were collected for extraction. Sub-samples of each homogenate (about 5 to 8 g) were weighed into single-use borosilicate glass vials (28 x 95 mm, ca. 40 mL capacity) and extracted using a 2:1 solvent-to-sample mass ratio of THF containing known concentrations of isotopically labeled ^{13}C-D_4, ^{13}C-D_5, and ^{13}C-D_6 to serve as internal standard surrogates. The appropriate amount of THF containing the internal standards was added to the glass vials by weight, and the capped vials were placed on a vortex mixer for 30 min. The samples were centrifuged for 5 minutes to separate the solids and the THF extract transferred to a new 40 ml vial. A second portion of THF without the internal standards was added to the first extraction vial, the extraction process repeated, and the extracts combined in the second extraction vial. A portion of the final extract was transferred to a round-bottom glass vial (12 x 33 mm) containing anhydrous magnesium sulfate (ca. 0.25 g) for drying the extract. A portion of the dried extract was transferred to a crimp-cap vial for GC-MS analysis.

Analysis of Extracts: Gas chromatography coupled with mass selective detection (GC-MS) was used to measure the amounts of D_4, D_5, and D_6, and ^{13}C-D_4, ^{13}C-D_5 and ^{13}C-D_6 in the sample extracts. GC-MS analyses of the sample extracts were performed on an Agilent 6890 gas chromatograph interfaced to an Agilent

5973 mass selective detector with an electron impact (EI) ionization source, operated in selected ion monitoring (SIM) mode. For sediment and zooplankton, the GC was configured with a conventional inlet (150 °C) for making splitless injections (0.5 min purge time). For fish, the GC was configured with a conventional inlet (150 °C) for making split injections (5:1 split ratio). The lower inlet temperatures were useful for minimizing the magnitude of instrument-related background, with only modest reduction in sensitivity. For sediment and zooplankton samples, analytes were separated on a HP-5 capillary GC column (5% phenylmethyl silicone, 30 m x 0.25 mm x 0.25 µm df) with helium carrier gas (1 mL/min). Following a 3 min post-injection hold at 50 °C, the column oven temperature was increased to 190 °C over 5.6 min, followed immediately by a second ramp to 250 °C over 1.5 min. Typical retention times were 6.5, 7.6, and 8.7 min, respectively, for D_4, D_5, and D_6. For fish samples, analytes were separated on a DB-WAXetr capillary GC column (polyethylene glycol, 30 m x 0.25 mm x 0.25 µm df) with helium carrier gas (1 mL/min). Following a 3 min post-injection hold at 40 °C, the column oven temperature was increased to 190 °C over 6 min, followed immediately by a second ramp to 210 °C over 0.5 min. Typical retention times were 4.1, 5.7, and 7.0 min, respectively, for D_4, D_5, and D_6. The target ions used for quantitative analysis were: $D_4/^{13}C\text{-}D_4$, *m/z* 281 and 285; $D_5/^{13}C\text{-}D_5$, *m/z* 355 and 360; $D_6/^{13}C\text{-}D_6$, *m/z* 429 and 435. These ions were formed by loss of a single $-CH_3$ group from the parent molecule and had the highest abundance in the EI spectra, excluding the common $[Si(CH_3)_3]^+$ ion at *m/z* 73. Peak area ratios obtained from the resulting single ion chromatograms were used to calibrate response ratio against amount ratio for each compound using standards prepared in hexanes, and covering an approximate concentration range of 2.1 to 2700 ng/mL. The amounts of cVMS materials in each extract were determined from the resulting $1/(\text{peak area})^2$-weighted linear regression calibration functions, from which concentrations in the original sample were calculated.

Quality Control

Cyclic VMS materials are widely used in consumer products and may be present in personal care products, commercial products, and lubricants. Given the significant potential for sample contamination during collection, processing, storage, and analysis for cVMS materials in environmental matrices, a quality control (QC) program was developed and implemented to the extent possible in the field and laboratory (Table 1). However, the QC program for fish was not sufficient to evaluate the extent of sample contamination that may have occurred in the field during collection, handling, shipment, storage, and processing procedures. Because of resource constraints and logistics, field QC samples were only collected for sediment and bulk zooplankton. No field QC samples were obtained during collection of fish by the Harkness Laboratory personnel, who had no prior experience collecting fish for trace-level analysis work. The only quality control that was implemented in the field during collection of fish was that the field crew was instructed to refrain from using personal care products (e.g., sun-block, sun-screen, hand lotion, etc) during sample collection. Hence, the possibility existed

that fish samples may have been contaminated with cVMS materials during collection, storage, and shipment. Because field QC samples were not collected with the fish, the extent of possible contamination could not be evaluated.

To the extent possible, all equipment in direct contact with sediment samples was decontaminated by washing with dishwashing detergent followed by consecutive rinses with deionized water, acetone, and hexane. Sediments in direct contact with equipment that could not be decontaminated before use (i.e., box core, sediment cores, etc.) were not retained. To minimize potential contamination from air, field processing of zooplankton and sediment was conducted outdoors downwind of the lake and upwind from buildings or other potential sources of cVMS materials. To prevent cross-contamination of samples core tubes were used only once and stainless steel instruments used during field processing were rinsed with water during use.

Standard reference materials were not available for D_4, D_5, or D_6 in any matrix. Therefore, laboratory reference materials were prepared by Dow Corning for the sediment and fish matrices. Laboratory reference materials for the bulk zooplankton matrix could not be prepared because sufficient sample masses were not available. The reference material for the sediment matrix was prepared by adding known masses of D_4, D_5, and D_6 to natural sediment having non-detectable concentrations of the cVMS materials. The reference material for the fish matrix was prepared by adding known masses of D_4, D_5, and D_6 to the whole-body homogenate of a rainbow trout (*Oncorhynchus mykiss*) having non-detectable concentrations of the cVMS materials.

Analytical methods were developed and validated using reference materials dosed with isotopically labeled ^{14}C-D_4, ^{14}C-D_5, and ^{14}C-D_6. Concentrations of D_4, D_5, and D_6 in the dosed reference materials were determined by radiometric analysis and by GC-MS analysis. Reference materials dosed with unlabeled D_4, D_5, and D_6 were used to monitor for changes in cVMS concentrations resulting from processing and storage of samples, and day-to-day variability in background and analytical performance.

Reference Sediment: Reference sediment used for the field blanks and reference samples was collected from Sanford Lake, a reservoir created by impoundment of the Tittabawasee River at Sanford, Michigan. Surface sediment (upper 5-10 cm) having a silty clay texture was collected on 29 August 2007. Concentrations of the cVMS materials in the natural Sanford Lake sediments were below detection. Dosed sediment was prepared by adding known quantities of the cVMS materials directly to the natural sediment. Characteristics of the surface sediment collected from Sanford Lake and used as QC samples for this study are shown below:

Characteristic	Value
Classification	Silty Clay
Texture (%, dry wt)	
• Sand	13
• Silt	39

• Clay	48
Solids content (%, wet wt)	29.9
Water content (%, wet wt)	70.1
Total organic carbon (%, dry wt)[1]	3.52
LOI (organic matter content; % dry wt)	12.7
Bulk Density (g cm^{-3} wet sediment)[2]	1.16
cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
• Blank sediment (n=8 replicate analyses)	
○ D_4	0.0 ± 0.2
○ D_5	1.1 ± 0.7
○ D_6	0.5 ± 0.1
• Dosed sediment (n=8 replicate analyses)	
○ D_4	13.1 ± 0.3
○ D_5	13.7 ± 0.6
○ D_6	13.2 ± 0.2

[1] Determined by Walkley Black titration method.
[2] Calculated from loss on ignition, and water content assuming a particle density of 2.6 g cm^{-3} (Håkanson and Jansson, 1983).

Reference Fish: Live rainbow trout (*Oncorhynchus mykiss*) used for the control blanks and reference samples were purchased from Rainbow Ranch Trout Farm, located in Tawas, MI. Concentrations of the cVMS materials in the blank fish were below detection. The dosed fish was prepared by adding known quantities of the cVMS materials directly to the whole-body homogenate of the blank fish. Characteristics of the fish used as QC samples for this study are shown below:

Characteristic	Mean ± sd
Blank fish (n=1 fish; n=6 replicate analyses)	
• cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
○ D_4	0.4 ± 0.1
○ D_5	1.3 ± 0.6
○ D_6	0.3 ± 0.2
Dosed fish (n=1 fish; n=3 replicate analyses)	
• cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
○ D_4	13.3 ± 0.3
○ D_5	13.8 ± 0.4
○ D_6	14.1 ± 0.4
Dosed fish (n=1 fish; n=3 replicate analyses)	
• cVMS concentrations (mean ± 99% CL; ng/g wet wt)	
○ D_4	28.6 ± 1.8
○ D_5	28.8 ± 1.8
○ D_6	30.6 ± 1.9

Detection Levels:
Detection levels as defined by APHA (1999) were used for this study (Table 1). Although the terminology may differ from that provided in more definitive sources (ASTM, 2003; IUPAC, 1995, 2002) the definitions are analogous. Methods for determining detection levels are available in various publications (Analytical Methods Committee, 1987; Taylor, 1987; Kateman and Buydens, 1993; IUPAC, 1995; Berger et al., 1996; Smith, 1997; Eurachem, 1998; APHA, 1999; IUPAC, 2002). Of the different detection levels that were defined, the limit of detection (LOD), the method detection level (MDL), and the limit of quantification (LOQ), are the most valuable for field monitoring. The LOD, MDL, and LOQ are similar in concept to the signal-to-noise ratio, and were defined as:

- LOD: The minimum level of target analyte that can be measured and reported with 99% confidence that the level of analyte is greater than zero. The LOD is based on the ability to distinguish between signal and noise of the instrument and is determined by repetitive analysis of matrix-free blanks.

- MDL: The minimum level of target analyte in a specified matrix that can be measured and reported with 99% confidence that the level of analyte in the matrix is greater than zero. The MDL is a measure of a method's ability to quantify an analyte in a sample matrix and is determined by repetitive analysis of a sample matrix having a small, but measurable amount of analyte (2-5 times the MDL). The MDL will be greater than the LOD because of additional background noise resulting from the sample matrix and variability introduced through processing the sample for analysis.

- LOQ: The minimum level of target analyte in a sample that can be reported with 99% confidence of having an estimation error no greater than 30% when based on a single measurement. The LOQ is the minimum level of target analyte in a sample that can be detected and accurately quantified on a routine basis, and is typically defined as 3.3 times the LOD or, preferably, as 2.5 times the MDL.

Detection limits (DL) were determined as a function of the variance associated with replicate analyses of matrix-free blanks (LOD) and replicate analyses of samples containing small, but measurable amounts of the cVMS materials (MDL, LOQ). The DL (LOD or MDL) at 99% confidence were then defined as:

$$DL = t_{0.99,n-1} \times s_0$$

where $t_{0.99,n-1}$ was the one-tailed t-statistic at 99% confidence for the performed number of sample analyses (degrees of freedom = n-1) and s_0 was the standard deviation for the replicate analyses.

For this study, the LOD was calculated using non-background corrected amounts of D_4, D_5, and D_6 measured in reagent blanks that were carried through the entire analytical procedure. The MDL was calculated using non-background corrected amounts and concentrations of D_4, D_5, and D_6 measured in samples. The MDL for sediment was based on replicate analyses of reference sediment. The MDL for bulk zooplankton was based on replicate analyses of pooled zooplankton samples. The species-specific MDL for fish was based on replicate analyses of an individual lake trout or replicate analyses of pooled cisco and pooled yellow perch.

Background Correction:
A highly variable instrumental blank response was always present for D_4, D_5, and D_6 (Table 2), which made determination of levels of detection and quantification of the cVMS materials difficult for all matrices. The source of the background cVMS materials was not identified but represented a systematic contamination that, presumably, originated from the reagents used to extract the samples, the extraction procedures, and/or the analytical method used to analyze the extracts. The background contamination could be minimized, but not eliminated, by changing the glass injection port liner and rubber septum prior to every analytical run, followed by 5 or more injections of a blank solvent in order to clean the injection port as much as possible. In addition, the phenylmethyl silicone based column (HP-5 capillary GC column) used for analysis of sediment and zooplankton was replaced with a polyethylene glycol based column (DB-WAXetr column) and used for analysis of fish since it was free of siloxane materials.

Measured amounts of cVMS materials in the samples were corrected for background levels of cVMS using results from the reagent blanks. Results for the reagent blanks represented background levels of cVMS materials associated with extraction solvents or lab ware, as well as contamination incurred during handling, treatment (e.g. volume reduction), and analysis of the extracts. Comparison of analytical results for reagent blanks (n=45 reagent blanks analyzed across 8 days) indicated highly significant differences (ANOVA; $p < 0.01$) for D_4, D_5 and D_6 between analytical batches of samples. Because of the variable background, measured amounts of cVMS materials in the samples were corrected for background levels of cVMS using results from reagent blanks that were analyzed on the same day that samples were analyzed. Although background was highly variable for the reagent blanks, the variability associated with analysis of samples was relatively small. As a result, LOD values were highly variable, depending upon analysis date, whereas MDL values were more consistent. Moreover, LOD values for some days were greater than the MDL values.

Because of the high background, and the need to correct for background on a daily basis, concentrations of cVMS materials were "non-detectable" on some days but "detectable" on other days. Consequently, analytical results were considered acceptable only when background levels were less than 5.0 ng (i.e.,

minimal background correction) and limits of detection were less than 2.5 ng. For fish, this combination of acceptance criteria (Table 2) occurred for lake trout that were analyzed on 15-Oct-2008 and for forage fish (cisco and yellow perch) that were analyzed on 15-Oct 2008 (pooled samples) and 27-Apr-2009 (individual samples). The results for forage fish analyzed on 27-Apr-2009 were considered the best acceptable results because individual fish rather than pooled samples were analyzed. Unfortunately, sediment and zooplankton samples analyzed on 25- and 29-October 2007 were consumed and could not be re-analyzed even though background levels and limits of detection were high (Tables 2 and 3).

Units of Measure

For field monitoring, a measurement that is less than a specified detection level (DL) may be: 1) reported as "below detection", 2) reported as zero, 3) reported as less than (<) the value of the DL, 4) reported as some value between zero and the DL, for example one-half the DL, or 5) reported as the actual value (positive or negative), whether or not it is below the DL. The last option, the reporting of the actual value, is the recommended procedure (Clarke, 1998; Frome and Wambach, 2005; Antweiler and Taylor, 2008); otherwise the data is considered to be "censored". For this project, measured concentrations that were less than the MDL but greater than LOD were reported as the measured concentration (i.e., uncensored value). Measured concentrations that were less than the LOD were reported as the LOD divided by the sample weight that was analyzed (i.e., censored value).

Concentrations of D_4, D_5, and D_6 in biota and sediment were measured in wet samples and expressed on the basis of wet weight. Concentrations of D_4, D_5, and D_6 that are 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 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 D_4, D_5, and D_6 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.

Statistical Analyses

Statistical analyses were performed using Minitab® Version 15.1.0 (Minitab 2006) and the Data Analysis Tool Package, as provided with Microsoft Excel 2003 (ver 11.0). A Type I error (α) of 0.05 was used to judge the significance of all statistical tests. Single-factor analysis of variance (ANOVA) was performed to test for differences in mean masses and concentrations (wet weight basis) of cVMS materials measured in reagent blanks, field blanks, and reference samples associated with each analytical batch of field samples (sediment cores, surface sediments, zooplankton, and fish). If the omnibus *F* value indicated significant differences between the mean values, a Tukey

HSD multiple comparisons test (for equal sample sizes) or a Tukey-Kramer multiple comparisons test (for unequal sample sizes) was used to compare individual means (Sheskin, 2000). All cVMS concentration data were converted to lipid weight for calculation of predator-prey specific biomagnification factors.

Predator-prey specific biomagnification factors (BMF values) for cVMS materials in Lake Opeongo fish were calculated by bootstrap analysis using Monte-Carlo simulation. The bootstrap analyses were conducted using Crystal Ball software (ver. 7.3.1). The principal factors of variation were associated with measured lipid content and measured concentrations of the cVMS materials in fish. Principal uncertainty with the BMF calculations was likely associated with trophic level and possible omnivorous feeding by the predator species, but was not evaluated using Monte Carlo simulation because of the complexity of the calculations. Rather, BMF calculations were based on the assumption that the predator species was feeding exclusively on the prey species and BMF values were not adjusted for trophic level position or omnivorous feeding. Input distributions used for the Monte Carlo simulation were chosen on the basis of theoretical considerations because the available data were insufficient to permit distribution fitting. Lognormal distributions were used to represent lipid content and cVMS concentrations in fish because the measured values tended to be clustered near a minimum value (i.e., the detection limits) and environmental data are typically right skewed.

Predator-Prey Specific Biomagnification Factors

Relative trophic levels occupied by biota in the Lake Opeongo aquatic food web were determined by converting $\delta^{15}N$ values to relative trophic level (TL) according to the equation:

$$TL = 3 + \frac{\left(\delta^{15}N_{consumer} - \delta^{15}N_{cisco}\right)}{3.4}$$

where 3 was the assumed trophic level of cisco and 3.4 was the trophic enrichment factor constant for $\delta^{15}N$ (Jardine et al., 2006). Zooplankton were inadvertently not analyzed for $\delta^{15}N$ and could not be used to establish the trophic level baseline.

Predator-prey specific biomagnification factors (BMF) were calculated by dividing mean lipid-equivalent concentrations of the cVMS materials (D_4, D_5, and D_6) in the predator species (C_{pred}; lake trout) by the mean lipid-equivalent concentrations in the prey species (C_{prey}; cisco and yellow perch), using the equation:

$$BMF = \frac{C_{pred}}{C_{prey}}$$

Calculation of BMF was based on the assumption that the predator species was feeding exclusively on the prey species. Biomagnification factors were not adjusted for trophic level position or omnivorous feeding.

RESULTS and DISCUSSION

Analytical results for the QC samples associated with this study are tabulated by individual matrix in Table 4. Mean recovery across all matrices (± 95% CL) of cVMS during analysis of 33 procedural matrix spikes was 97.9 ± 1.9% (range: 80.4% to 103%) for D_4, 103 ± 1.8% (range: 86.7% to 111%) for D_5, and 101 ± 1.3% (range: 91.7% to 106%) for D_6. The mean method precision across fish tissue (sediment and zooplankton not included because concentrations were < LOD), which was estimated from analysis of 12 sets of replicate samples (n=2-7) and expressed as relative standard deviation, was 9.3% (range: 0.5% to 21.9%) for D_4, 14.7% (range: 0.1% to 60.5%) for D_5, and 17.3% (range: 2.1% to 56.0%) for D_6.

Absolute masses of the cVMS materials in extracts of the surface sediments, sediment cores, and zooplankton from Lake Opeongo were not statistically different from masses in the reagent blanks (Table 3). However, absolute masses of D_5 and D_6, but not D_4, were significantly greater in the sediment field blanks compared to the masses of D_5 and D_6 in the reagent blanks. These results demonstrated that D_4, D_5, and D_6 measured in the sample extracts did not originate from the sample matrix. The source of the cVMS materials in the sample extracts was not known but represented a systematic background contamination that, presumably, originated from the reagents used to extract the samples, the extraction procedures, and/or the analytical method used to analyze the extracts. Method detection limits (MDLs, expressed on the basis of wet weight) across all matrices (sediment, zooplankton, and fish) ranged from 0.47 to 0.90 ng/g ww for D_4, from 1.79 to 3.10 ng/g ww for D_5, and from 0.15 to 0.74 ng/g ww for D_6. Comparison of the LODs and MDLs (Table 4) to concentrations in the samples (Table 5) indicated that:

- Background corrected concentrations of D_4, D_5, and D_6 in sediments were less than the LOD and MDL in 81 of 81 samples analyzed (included analysis of 7 surface sediment samples and 74 sediment core strata). Concentrations that were < LOD were estimated to be equal to the LOD divided by the sample mass that was analyzed. Because of the high background during analysis of sediments, some LOD-based estimated concentrations were > MDL, but were treated as being < MDL. Mean background corrected concentrations of D_4, D_5, and D_6 in sediments were less than the LOD and MDL.
- Background corrected concentrations of D_4, D_5, and D_6 in zooplankton were less than the LOD and MDL in 3 of 3 samples analyzed. Concentrations that were < LOD were estimated to be equal to the LOD divided by the sample mass that was analyzed. Because of the high background during analysis of zooplankton, some LOD-based estimated concentrations were > MDL, but were treated as

being < MDL. Mean background corrected concentrations of D_4, D_5, and D_6 in zooplankton were less than the LOD and MDL.

- Background corrected concentrations of D_4 in yellow perch were greater than the MDL for D_4 in 7 of 7 fish analyzed. Mean background corrected concentrations of D_4 in yellow perch were greater than the MDL.
- Background corrected concentrations of D_5 in yellow perch were less than the LOD for D_5 in 1 of 7 fish analyzed and less than the MDL for D_5 in 7 of 7 fish analyzed. Mean background corrected concentrations of D_5 in yellow perch were greater than the LOD but less than the MDL.
- Background corrected concentrations of D_6 in yellow perch were less than the MDL for D_6 in 3 of 7 fish analyzed. Mean background corrected concentrations of D_6 in yellow perch were greater than the MDL.
- Background corrected concentrations of D_4, D_5, and D_6 in cisco were greater than the MDL in 7 of 7 fish analyzed. Mean background corrected concentrations of D_4, D_5, and D_6 in cisco were greater than the MDL.
- Background corrected concentrations of D_4, D_5, and D_6 in lake trout were greater than the MDL in 5 of 5 fish analyzed. Mean background corrected concentrations of D_4, D_5, and D_6 in lake trout were greater than the MDL.

Background corrected concentrations of D_4, D_5, and D_6 were consistently less than the LOD, MDL, and LOQ throughout the entire sediment core profiles for Lake Opeongo (Fig. 2). Similarly, mean concentrations of the cVMS materials in surface sediments and zooplankton were less than the LOD, MDL, and LOQ (Table 5). Except for D_5 in perch, mean concentrations of the cVMS materials were greater than the MDL in fish (perch, cisco and lake trout). Except for D_6 in cisco, mean concentrations of the cVMS materials in cisco and perch were all less than the LOQ. Mean concentrations of D_6 in cisco were greater than the LOQ. Mean concentrations of the cVMS materials in lake trout were all greater than the LOQ. Comparison of concentrations of the cVMS materials across the three species of fish showed that there were no statistically significant differences ($p>0.05$) between concentrations in perch and cisco, but concentrations in trout were significantly greater ($p<0.01$) than concentrations in cisco and perch.

The sampled food web in Lake Opeongo (Table 6) included zooplankton, yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*). However, because lipid content and isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) were not available, zooplankton could not be used to evaluate trophic transfer of the cVMS materials in the sampled food web. Age of the lake trout based on otolith annuli (data not shown) ranged from 7 to 19 years. Ages of the cisco and perch were not determined because the fish were all within the same narrow size class that was considered appropriate for forage species. The $\delta^{13}C$ isotopic signatures indicated that cisco, perch, and lake trout were feeding within the same food chain of the lake. The $\delta^{15}N$ isotopic signatures for fish indicated that the two forage species (perch and cisco) occupied the middle trophic levels (TL ~3.0) and the adult lake trout occupied the highest trophic level (TL ~3.7). Cisco and perch are the primary forage species for adult lake trout in the Lake Opeongo food web (Martin and Fry 1972), which are best

described as the top predator for a class 2 pelagic food chain (Vander Zanden et al 1996, 1999, 2000) consisting of phytoplankton (TL=1), zooplankton (TL=2), cisco (TL=3), and lake trout (TL=4). Lake trout are pelagic piscivores and cisco are pelagic planktivores that feed in the deep, open waters areas of Lake Opeongo and have essentially no association with the sediment compartment. In contrast, yellow perch are omnivores that feed primarily on invertebrates, eggs, and small fish in the shallow water areas of the lake and may have a significant association with the sediment compartment.

Generally, measured concentrations of the cVMS materials in samples from Lake Opeongo (Table 5) were low and clustered about the limits of detection for fish and were below the limits of detection for surface sediments, sediment cores, and zooplankton (Table 4). Background corrected concentrations of the cVMS materials in sediment and zooplankton were estimated as the LOD divided by the sample weight that was analyzed. As such, the reported concentrations represented the upper limits of cVMS concentrations in sediment and zooplankton of Lake Opeongo. Lipid-equivalent concentrations of D_4, D_5, and D_6 (Table 5) were variable across species, were below the limit of detection in zooplankton (the lowest trophic level species), and were the highest in lake trout (the highest trophic level species).

Because cVMS concentrations were approximately the same in perch and cisco, which both occupied the same trophic level (TL ~3) but feed on different organisms in different areas of the lake, cVMS in the forage species likely originated from the water column rather than the sediment. Food web dynamics in Lake Opeongo are pelagic driven (Vander Zanden et al., 1996, 1999, 2000) and influenced very little by the benthic ecosystem, which further supports the hypothesis that cVMS materials in the evaluated food chain did not originate from the sediments. Moreover, the similarity in concentrations between forage fish at the same trophic level but with different diets indicated that accumulation of cVMS materials by the forage fish was likely dominated by uptake across the gill (i.e., respiratory accumulation) rather than uptake from food (i.e., trophic accumulation).

Mean predator-prey specific biomagnification factors (BMF values) and 95% confidence intervals for the trout-cisco relationship were 1.9 for D_4 (95%CI: 1.3 to 2.7), 2.3 for D_5 (95%CI: 1.5 to 3.5), and 1.5 for D_6 (95%CI: 0.9 to 2.2). Mean BMF values for the trout-perch relationship were 2.4 for D_4 (95%CI: 1.6 to 3.3), 5.2 for D_5 (95%CI: 3.0 to 8.6), and 1.4 for D_6 (95%CI: 0.9 to 2.1). Bootstrap analysis indicated a 95 to 100% probability that the estimated BMF values were greater than a value of 1.0 for the three cVMS materials. In contrast to that observed for the forage species, these results suggested that bioaccumulation of cVMS materials by the predator species of Lake Opeongo was influenced by trophic uptake in addition to respiratory uptake.

Sensitivity analysis demonstrated that biological variability had the greatest impact on the estimated BMF values, whereas analytical variability had very little impact. Less than 1% of the total variability associated with the estimated BMF values was related to analytical variability or analysis of samples having concentrations at or near the limits of

detection. Of the total variability associated with the trout-cisco BMF values for D_4, D_5, and D_6, concentrations in trout accounted for 57% to 65%, concentrations in cisco accounted for 7.9% to 11%, and lipid content of the fish (trout and cisco) accounted for 11% to 19%. Of the total variability associated with the estimated trout-perch BMF values for D_4 and D_6, concentrations in trout accounted for 63% to 66%, concentrations in perch accounted for 17% to 26%, and lipid content of the fish (trout and perch) accounted for 2.0% to 15%. Of the total variability associated with the estimated trout-perch BMF values for D_5, concentrations in trout accounted for 45%, concentrations in perch accounted for 45%, and lipid content of the fish (trout and perch) accounted for 2.1% to 7.6%.

Lipid-equivalent concentrations of the cVMS materials in forage fish from Lake Opeongo were a factor of about 3 to 60 times less than concentrations in forage fish in the freshwater food web of Lake Pepin (a temperate eutrophic lake on the Mississippi River) and the marine food web of the outer Oslofjord, Norway (Table 7). In contrast, lipid-equivalent concentrations of the cVMS materials in lake trout from Lake Opeongo were comparable to concentrations in the top predator fish from Lake Pepin and the Outer Oslofjord, and differed by a factor ranging from about 0.3 to 5.1. These results suggested that trophic dynamics and bioaccumulation of cVMS materials in the pelagic-food chain of Lake Opeongo were different than that observed in the benthic food chain in Lake Pepin or the benthipelagic food chain in Oslofjord. However, comparison of results from Lake Opeongo to other ecosystems may not be appropriate because of the following uncertainties associated with the analytical data:

- concentrations of the cVMS materials in Lake Opeongo were typically less than or equal to the analytical limits of detection,
- quantification of the cVMS materials in the Lake Opeongo samples was difficult because of a highly variable and systematic analytical background
- the quality control program for the Lake Opeongo project was not adequate to evaluate the extent of possible sample contamination that may have occurred.

CONCLUSIONS

Lake Opeongo is relatively remote from any potential sources of cVMS materials originating from sewage and runoff. Therefore, it was a reasonable first assumption that the only significant source of cVMS materials to Lake Opeongo would be from atmospheric deposition. However, the potential to deposit from air was expected to be minimal because the cVMS materials have very high air-water partition coefficients (K_{AW} > 490; Brooke el al., 2009 a, b, c). Non-detection of the cVMS materials in surface sediments, sediment cores, and zooplankton demonstrated that emission of D_4, D_5, and D_6 to Lake Opeongo was low and that particulate-associated sources such as sewage treatment and surface runoff did not appear to be significant. While it is possible that the low levels of cVMS materials that were detected in fish may have originated from atmospheric deposition it is believed that the cVMS materials were more likely to have originated from personal care products used during recreational activities on the lake. The lake is a popular location for canoeing and camping and use of personal care products during recreational activities could not be definitively excluded as a potentially

significant source of cVMS materials. In addition, the quality control QC program that was followed during collection of samples was not adequate to evaluate the extent of sample contamination that may have occurred in the field.

Regardless of source of entry, concentrations of cVMS materials in the water column of Lake Opeongo would be very low and, presumably, would exist in the freely dissolved phase because the lake is oligotrophic and has a very low suspended solids load. Laboratory studies have demonstrated that cVMS materials in the dissolved phase may accumulate in fish through bioconcentration processes (i.e., uptake from water across the gill), which may represent the primary mechanism responsible for occurrence of low but detectable levels of the cVMS materials in fish from Lake Opeongo. The observation that predator-prey specific biomagnification factors (BMF) were greater than a value of 1.0 suggested that cVMS materials in the pelagic food web of Lake Opeongo may have accumulated in fish through uptake from water across the gill and uptake from food across the gut.

These preliminary results suggested that bioaccumulation of the cVMS materials may have occurred in the pelagic food web of Lake Opeongo and that accumulation of D_4, D_5, and D_6 by aquatic organisms was controlled by dietary and respiratory uptake. Nonetheless, the quality control program for the study was not adequate to evaluate the extent of sample contamination that may have occurred in the field during collection, handling, shipment, storage, and processing procedures. Therefore, it can not be reliably determined from the results reported for this preliminary assessment if trophic magnification of the cVMS materials may have occurred in the pelagic food web of Lake Opeongo. Without additional monitoring data from Lake Opeongo, these results are not sufficient to have demonstrated that D_4, D_5, and D_6 are bioaccumulative materials of concern in the aquatic environment.

FUTURE WORK

This report evaluated and summarized results for a preliminary assessment of the concentrations of cVMS materials (D_4, D_5, and D_6) in sediments and biota from Lake Opeongo. However, results presented in the report were not considered reliable because:

- concentrations of the cVMS materials were typically less than or equal to the analytical limits of detection,
- quantification of the cVMS materials was difficult for all matrices because of a highly variable and systematic analytical background
- the quality control program for the study was not adequate to evaluate the extent of possible sample contamination that may have occurred.

In order to address these issues, it is intended that additional work will be conducted with Environment Canada and the Harkness Laboratory of Fisheries Research to collect additional samples from the aquatic food web in Lake Opeongo. Samples will be collected following a quality control program designed to minimize and evaluate the extent of contamination that may occur in the field. These samples will be analyzed

under laboratory conditions that have recently been optimized to minimize and better control background contamination in the laboratory. In addition, trophic magnification factors (TMF values), will be calculated for the Lake Opeongo food web. Trophic magnification factors represent the trophic level increase of a chemical substance that is averaged across the food chain rather than a single predator-prey relationship or biomagnification factor (BMF value). Consequently, TMF values are preferable to BMF values for evaluating the potential for a chemical to biomagnify within a well defined food chain. Variability associated with the TMF values will be evaluated by bootstrap analysis using Monte Carlo simulation with Oracle Crystal Ball software. The principal factors of variation and uncertainty to be evaluated will include lipid content, concentration of the cVMS materials in the organism, trophic level, and omnivorous feeding by the predator species. Finally, the additional work on Lake Opeongo will include modeling and mass balance calculations that will be used to estimate the relative magnitude of cVMS emissions to the lake that originate from atmospheric deposition and from recreational activities.

ACKNOWLEDGEMENTS

Samples were collected from Lake Opeongo with guidance and assistance from the National Water Research Institute, Environment Canada, located in Burlington, Ontario and the Harkness Laboratory of Fisheries Research, which is situated at the southern end of the lake. We are especially grateful for the technical guidance and assistance provided by Camilla Teixeira and Michael Keir of the National Water Research Institute, and for the technical guidance, assistance, and accommodations provided by Gary Ridout and staff at the Harkness Laboratory. Derek Muir (National Water Research Institute) arranged ship time for this work and provided comments on an earlier draft of the report. Technical oversight during analysis of samples for water content, lipid content and for isotopic signatures of nitrogen (N; $\delta^{15}N$) and carbon (C; $\delta^{13}C$) was provided by Hasand Gandhi (Biogeochemistry and Paleoproteomics Laboratory, Michigan State University). Technical oversight during characterization of the sediment samples was provided by Amy Myrbo (National Lacustrine Core Repository, Limnological Research Center, University of Minnesota).

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Table 1. Summary of the quality control (QC) procedures implemented during collection and analysis of samples from Lake Opeongo.

QC Sample	Description	Matrices
Detection limits	• Limit of detection (LOD): The minimum level of analyte that can be detected and reported with 99% probability that it is different from a matrix–free blank. Determined by repetitive analysis of reagent blanks. • Method detection limit (MDL): The minimum level of analyte in a sample matrix that can be measured and reported with 99% confidence that the level of analyte in the matrix is greater than zero. Determined by repetitive analysis of samples having a small, but measurable amount of analyte (2-5 times the MDL). • Limit of quantification (LOQ): The minimum level of analyte in a sample matrix that can be reported with 99% confidence of having an estimation error no greater than 30% when based on a single measurement. Defined as 3.3 times the LOD or, preferably, as 2.5 times the MDL.	• sediment • zooplankton • fish
Reagent blanks	Extraction solvents dispensed directly into an empty extraction vial. Used to evaluate contamination from solvents, containers, and analytical operations, for blank-correction of sample data, and for calculation of detection limits (LOD and LOQ).	• sediment • zooplankton • fish
Field blanks	Reference sample having very low or non-detectable concentrations of cVMS materials that was taken into the field and processed like a field sample. Used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples.	• sediment
Laboratory blanks	Reference sample having very low or non-detectable concentrations of cVMS materials that was processed in the laboratory like a field sample. Used to evaluate contamination bias resulting from storage, processing, and analysis of samples.	• sediment • fish
Field replicates	Replicate field samples that were processed, extracted, and analyzed as individual samples. Used to evaluate between-sample variability (precision).	• sediment • zooplankton • fish
Laboratory replicates	Replicate sub-samples of a processed field sample that were extracted and analyzed as individual samples. Used to evaluate within-sample variability, for calculation of detection limits (MDL), and to evaluate analytical precision.	• sediment • zooplankton • fish

Table 1. Continued.

QC Sample	Description	• Matrices
Field spikes	Field samples spiked in the field with known amounts of cVMS materials. Used to evaluate loss of cVMS during collection, processing, transport, storage, and analysis of samples, and to evaluate analytical bias.	• sediment
Laboratory spikes	Processed field samples spiked in the laboratory with known amounts of cVMS materials. Used to evaluate analytical bias.	• zooplankton • fish
Reference Samples	Control samples having known concentrations of cVMS materials (reference samples having very low or non-detectable concentrations of cVMS materials were used for field blanks and laboratory blanks). Used to evaluate contamination or loss of cVMS from samples during collection, transport, processing, storage, and analysis, for calculation of detection limits (MDL), and to evaluate analytical bias and precision.	• sediment • fish
Internal standards	Stable isotopes (^{13}C) of D_4, D_5, and D_6 added to assess and correct for instrument variability.	• sediment • zooplankton • fish

Table 2. Background, limit of detection (LOD), and method detection limit (MDL) for D_4, D_5, and D_6 during analyses of samples collected from Lake Opeongo.

Date of Analysis	Bkg (ng)	LOD[1] (ng)	MDL (ng/g ww)[1,2] Sed	Zoo	Cis	Per	Trt
D_4 Results							
24-Oct-2007	1.73	1.47					
25-Oct-2007	9.28	6.22	1.26				
29-Oct-2007	4.57	3.76	1.03	0.89			
26-Jun-2008	181	357			17.4	16.6	
03-Jul-2008	36.3	6.20			4.21	2.51	
20-Aug-2008	132	24.3					4.24
15-Oct-2008 (Trt)	-5.96	1.69					0.90
15-Oct-2008 (pooled)	-3.01	1.31			0.72	0.30	
27-Apr-2009	1.60	0.51			0.58	0.47	
D_5 Results							
24-Oct-2007	11.1	3.80					
25-Oct-2007	27.2	17.4	2.13				
29-Oct-2007	25.1	17.5	1.31	2.08			
26-Jun-2008	60.3	15.8			4.96	8.08	
03-Jul-2008	67.5	21.0			7.65	3.97	
20-Aug-2008	90.1	21.3					2.61
15-Oct-2008 (Trt)	4.77	1.24					3.10
15-Oct-2008 (pooled)	1.84	0.90			0.40	1.24	
27-Apr-2009	9.45	2.12			1.79	2.36	
D_6 Results							
24-Oct-2007	1.29	0.72					
25-Oct-2007	4.83	3.68	1.06				
29-Oct-2007	4.55	6.64	1.06	0.68			
26-Jun-2008	26.7	8.29			0.79	3.27	
03-Jul-2008	13.5	7.18			1.35	0.60	
20-Aug-2008	15.2	3.44					0.77
15-Oct-2008 (Trt)	1.66	1.93					0.47
15-Oct-2008 (pooled)	0.59	1.39			0.36	0.22	
27-Apr-2009	-2.27	0.26			0.15	0.47	

[1] Detection limits (DL) were defined as a function of the variance associated with replicate analyses of solvent blanks (LOD) and samples (MDL). The DL at 99% confidence was defined as:

$DL = t_{0.99,n-1} \times s_0$ where: $t_{0.99,n-1}$ = the one-tailed t-statistic at 99% confidence for the n replicate analyses

s_0 = the standard deviation for the n replicate analyses

[2] Method detection limits were determined by replicate analyses of sediment (Sed), zooplankton (Zoo), cisco (Cis), yellow perch (Per), and lake trout (Trt).

Table 3. Absolute masses (not corrected for background) of D_4, D_5, and D_6 measured in reagent blanks, field blanks, sediment samples (surface sediments and sediment cores), and zooplankton samples.

	Reagent Blanks	Field Blanks	Sediment	Zooplankton
D_4 Results				
Range (ng):	2.79-13.3	4.21-12.6	2.83-15.8	3.86-5.72
Mean (ng):	6.92	7.72	6.56	4.61
Std. dev. (ng):	2.94	3.14	3.11	0.841
Sample number (n):	16	8	81	4
ANOVA p-value:		0.403		
D_5 Results				
Range (ng):	14.3-38.3	26.5-40.7	20.9-42.4	26.6-32.6
Mean (ng):	26.2	33.8 **	29.2	28.7
Std. dev. (ng):	5.72	5.35	5.39	2.69
Sample number (n):	16	8	81	4
ANOVA p-value:		0.016		
D_6 Results				
Range (ng):	2.08-9.66	6.60-9.94	3.34-7.59	3.55-4.77
Mean (ng):	4.69	7.92 **	4.99	4.07
Std. dev. (ng):	1.74	1.21	1.06	0.519
Sample number (n):	16	8	81	4
ANOVA p-value:		0.001		

** Indicates that the mean measured mass was significantly greater than the mean measured mass in the reagent blanks, based on a Tukey-Kramer multiple comparisons test (Sheskin 2000).

Table 4. Background, levels of detection, precision, and bias associated with quality control accepted analyses of D_4, D_5, and D_6 in samples collected from Lake Opeongo.

Matrix	N[1]	D_4	D_5	D_6
Sediment (analysis date: 25-Oct-2007 and 29-Oct-2007)				
• Background (reagent blanks; ng)	16	6.92	26.2	4.69
• LOD (reagent blanks; ng)	16	7.66	14.9	4.52
• MDL (reference sediment; ng/g wet wt)[2]	8	0.90	2.05	0.74
• LOQ (2.5×MDL)		2.25	5.13	1.85
• Precision				
o reference sediment (mean RSD %)	8	2.3	4.0	1.9
o field replicates (RSD; %)	8	< MDL[3]	< MDL[3]	< MDL[3]
o sample replicates (mean RPD ± sd; %)	8	< MDL[3]	< MDL[3]	< MDL[3]
• Bias				
o field blanks (mean concn ± sd; ng/g ww)	8	0.04 ± 0.25	1.09 ± 0.68	0.47 ± 0.13
o reference sediment (mean recovery ± sd; %)	8	95.7 ± 2.4	105 ± 3.4	99.2 ± 2.4
o field spikes (mean recovery ± sd; %)	8	101 ± 0.5	105 ± 0.5	100 ± 0.5
o sample spikes (mean recovery ± sd; %)	18	98.1 ± 1.2	102 ± 4.9	97.8 ± 1.2
Zooplankton (analysis date: 29-Oct-2007)				
• Background (reagent blanks; ng)	8	4.57	25.1	4.55
• LOD (reagent blanks; ng)	8	3.76	17.5	6.64
• MDL (samples; ng/g wet wt)[2]	4	0.89	2.08	0.68
• LOQ (2.5×MDL)		2.23	5.20	1.70
• Precision				
o field replicates (RSD; %)	3	< MDL[3]	< MDL[3]	< MDL[3]
o sample replicates (mean RSD ± sd; %)	1	< MDL[3]	< MDL[3]	< MDL[3]
• Bias				
o sample spikes (mean recovery ± sd; %)	2	101 ± 0.1	105 ± 0.6	100 ± 0.2

Table 4. Continued.

Matrix	N[1]	D_4	D_5	D_6
Cisco (analysis date: 27-Apr-2009)				
• Background (reagent blanks; ng)	4	1.60	9.45	-2.27
• LOD (reagent blanks; ng)	4	0.51	2.12	0.26
• LLD (control fish; ng/g ww)	6	0.28	2.14	0.51
• MDL (samples; ng/g wet wt)[2]	7	0.58	1.79	0.15
• LOQ (2.5×MDL)		1.45	4.48	0.38
• Precision				
o reference fish (RSD; %)	6	5.8	4.3	4.1
o field replicates (RPD; %)	2	19.7	36.4	11.4
o sample replicates (RSD; %)	7	14.9	16.8	8.9
• Bias				
o control fish (mean concn ± sd; ng/g ww))	6	0.38 ± 0.08	1.34 ± 0.64	0.23 ± 0.15
o reference fish (mean recovery ± sd; %)	6	91.1 ± 9.8	95.9 ± 8.1	98.0 ± 6.2
o sample spikes (mean recovery ± sd; %)	3	100 ± 0.9	103 ± 2.2	104 ± 1.3
Yellow perch (analysis date: 27-Apr-2009)				
• Background (reagent blanks; ng)	4	1.60	9.45	-2.27
• LOD (reagent blanks; ng)	4	0.51	2.12	0.26
• LLD (control fish; ng/g ww)	6	0.28	2.14	0.51
• MDL (samples; ng/g wet wt)[2]	7	0.47	2.36	0.47
• LOQ (2.5×MDL)		1.18	5.90	1.18
• Precision				
o reference fish (RSD; %)	6	5.8	4.3	4.1
o field replicates (RPD; %)	2	23.9	31.9	86.2
o sample replicates (RSD; %)	7	17.2	60.5	30.5
• Bias				
o control fish (mean concn ± sd; ng/g ww))	6	0.38 ± 0.08	1.34 ± 0.64	0.23 ± 0.15
o reference fish (mean recovery ± sd; %)	6	91.1 ± 9.8	95.9 ± 8.1	98.0 ± 6.2
o sample spikes (mean recovery ± sd; %)	3	101 ± 1.6	104 ± 0.6	105 ± 0.8

Table 4. Continued.

Matrix	N[1]	D_4	D_5	D_6
Lake trout (analysis date: 15-Oct-2008)				
• Background (reagent blanks; ng)	3	-5.96	4.77	1.66
• LOD (reagent blanks; ng)	3	1.69	1.24	1.93
• LLD (control fish; ng/g ww)	6	0.28	2.14	0.51
• MDL (samples; ng/g wet wt)[2]	7	0.90	3.10	0.47
• LOQ (2.5×MDL)		2.25	7.75	1.18
• Precision				
o reference fish (RSD; %)	6	5.8	4.3	4.1
o field replicates (RSD; %)	5	33.5	41.8	43.9
o sample replicates (mean RSD ± sd; %)	5	4.5 ± 3.7	3.5 ± 3.0	8.8 ± 4.8
• Bias				
o control fish (mean concn ± sd; ng/g ww))	6	0.38 ± 0.08	1.34 ± 0.64	0.23 ± 0.15
o reference fish (mean recovery ± sd; %)	6	91.1 ± 9.8	95.9 ± 8.1	98.0 ± 6.2
o sample spikes (mean recovery ± sd; %)	3	101 ± 1.1	106 ± 3.9	105 ± 0.6

[1] N is the number of individual samples or sets of sample replicates (2 or more samples) that were analyzed.
[2] The MDL was based on analysis of replicate samples (N=7) containing concentrations of cVMS that were at least equal to the MDL but less than 5 times the MDL. The MDL for fish was based on regression of MDL on mean concentration.
[3] Precision estimates are not reported because measured concentrations were less than the MDL.

Table 5. Concentrations (mean ± SE; standard error) of cVMS materials (D_4, D_5, and D_6) measured in samples analyzed from the Lake Opeongo food web, sorted on increasing trophic level. Bulk zooplankton and surface sediments were collected 02-03 October 2007 with guidance and assistance from Environment Canada. Yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*) were collected 31 October 2007 by personnel at the Harkness Laboratory of Fisheries Research.

			Mean Concn ± SE (ng/g ww)[3]			Mean Concn ± SE (ng/g lipid)[4]		
Species	N[1]	TL[2]	D_4	D_5	D_6	D_4	D_5	D_6
Surface sediment[5]	9		[0.37] ± 0.05	[1.35] ± 0.04	[0.48] ± 0.03	34.4 ± 5.8	124 ± 7.8	44.0 ± 3.0
Zooplankton	3	2.0	[0.43] ± 0.04	[2.02] ± 0.19	[0.77] ± 0.07	10.9 ± 1.1	50.6 ± 4.9	19.1 ± 1.9
Cisco	7	3.0	1.24 ± 0.07	3.40 ± 0.22	0.52 ± 0.02	25.6 ± 1.4	70.3 ± 4.5	10.8 ± 0.4
Yellow perch	7	3.1	0.87 ± 0.06	(1.38) ± 0.29	0.49 ± 0.06	21.0 ± 1.4	33.3 ± 7.1	11.9 ± 1.4
Lake trout	5	3.7	3.77 ± 0.57	12.7 ± 2.37	1.23 ± 0.27	48.7 ± 7.4	166 ± 34.9	16.1 ± 4.3

[1] N is the number of individual samples analyzed. For sediment N was equal to the number of locations where samples were collected (2 sediment cores and 7 surface sediments). For zooplankton N was equal to the number of pooled samples analyzed.

[2] TL is the trophic level occupied by the species, based on the isotopic fractionation of 15N.

[3] Values in [ ] were measured concentrations that were < LOD and are estimated to be equal to the LOD divided by the sample mass that was analyzed. Values in ( ) are concentrations that were < MDL but > LOD, and are reported as the actual measured concentration. Because of the high background during analysis of sediments and zooplankton, some LOD-based estimated concentrations were > MDL, but are reported as being < MDL.

[4] Concentrations for sediment samples were normalized and reported on the basis of total organic carbon (TOC) rather than lipid content.

[5] Sample means and standard errors for surface sediments were based on individual analyses of surface sediment samples (n=7) and mean results for the sediment cores (n=2) averaged across the top 5 strata (i.e., 1-5 cm).

Table 6. Characteristics of samples (mean ± SE; standard error) analyzed from the Lake Opeongo food web, sorted on increasing $\delta^{15}N$. Bulk zooplankton and surface sediments were collected 02-03 October 2007 with guidance and assistance from Environment Canada. Yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*) were collected 31 October 2007 by personnel at the Harkness Laboratory of Fisheries Research.

Species	N[1]	Weight (g)	Length (cm)	Lipid (% ww)[2]	$\delta^{13}C$	$\delta^{15}N$	TL[3]
Surface sediment[4]	9			1.11 ± 0.06			
Zooplankton[5]	3			4.00			2.0
Cisco	7	7.7 ± 0.3	10.6 ± 0.1	4.84 ± 0.67	-26.28 ± 0.01	7.76 ± 0.11	3.0
Yellow perch	7	6.0 ± 0.4	8.6 ± 0.2	4.15 ± 0.19	-25.69 ± 0.02	7.93 ± 0.10	3.1
Lake trout	5	1157 ± 225	48.4 ± 3.4	7.78 ± 0.51	-23.92 ± 0.18	9.87 ± 0.23	3.7 ± 0.1

[1] N is the number of individual samples analyzed. For cisco and yellow perch lipid content and stable isotope fractionation ($\delta^{13}C$ and $\delta^{15}N$) were based on duplicate analyses of a pooled sample of 5 individual specimens.

[2] For sediment samples % total organic carbon (TOC, % ww) was reported rather than lipid content.

[3] TL is the trophic level occupied by the species, based on the isotopic fractionation of ^{15}N.

[4] Sample means and standard errors for surface sediments were based on individual analyses of surface sediment samples (n=7) and mean results for the sediment cores (n=2) averaged across the top 5 strata (i.e., 1-5 cm).

[5] Lipid content of zooplankton was not measured and was assumed to be equal to the value of 4.0 observed for zooplankton in Lake Superior (Muir et al. 2004; Wong et al. 2004). Trophic level of zooplankton was not determined and was assumed to be equal to a value of 2.0.

Table 7. Lipid-equivalent concentrations of cVMS materials in the primary forage fish and top predator fish in freshwater (Lake Opeongo, Canada and Lake Pepin, USA) and marine (Oslofjord, Norway) environments.

	Primary Forage Fish in Study Area					Top Predator Fish in Study Area				
			Concn (ng/g lipid)					Concn (ng/g lipid)		
Study Area	Species	TL[1]	D_4	D_5	D_6	Species	TL	D_4	D_5	D_6
Lake Opeongo	Yellow perch	3.1	21	33	12	Lake trout	3.7	49	166	16
	Cisco	3.0	26	70	11					
Lake Pepin	Gizzard shad	3.0	76	402	99	Walleye	3.6	64	848	25
	Emerald shiner	3.4	98	1087	166	Bass	3.8	78	175	13
Oslofjord (Outer)	Northern shrimp	3.0	10	495	29	Atlantic cod	4.1	17	223	41
	European plaice	3.4	141	1884	261					
Oslofjord (Inner)	Northern shrimp	3.0	100	3723	104	Atlantic cod	4.0	100	2026	138
	European plaice	3.1	414	28136	543					
	Atlantic herring	3.0	115	18379	241					

[1] TL is the trophic level occupied by the species, based on the isotopic fractionation of ^{15}N.

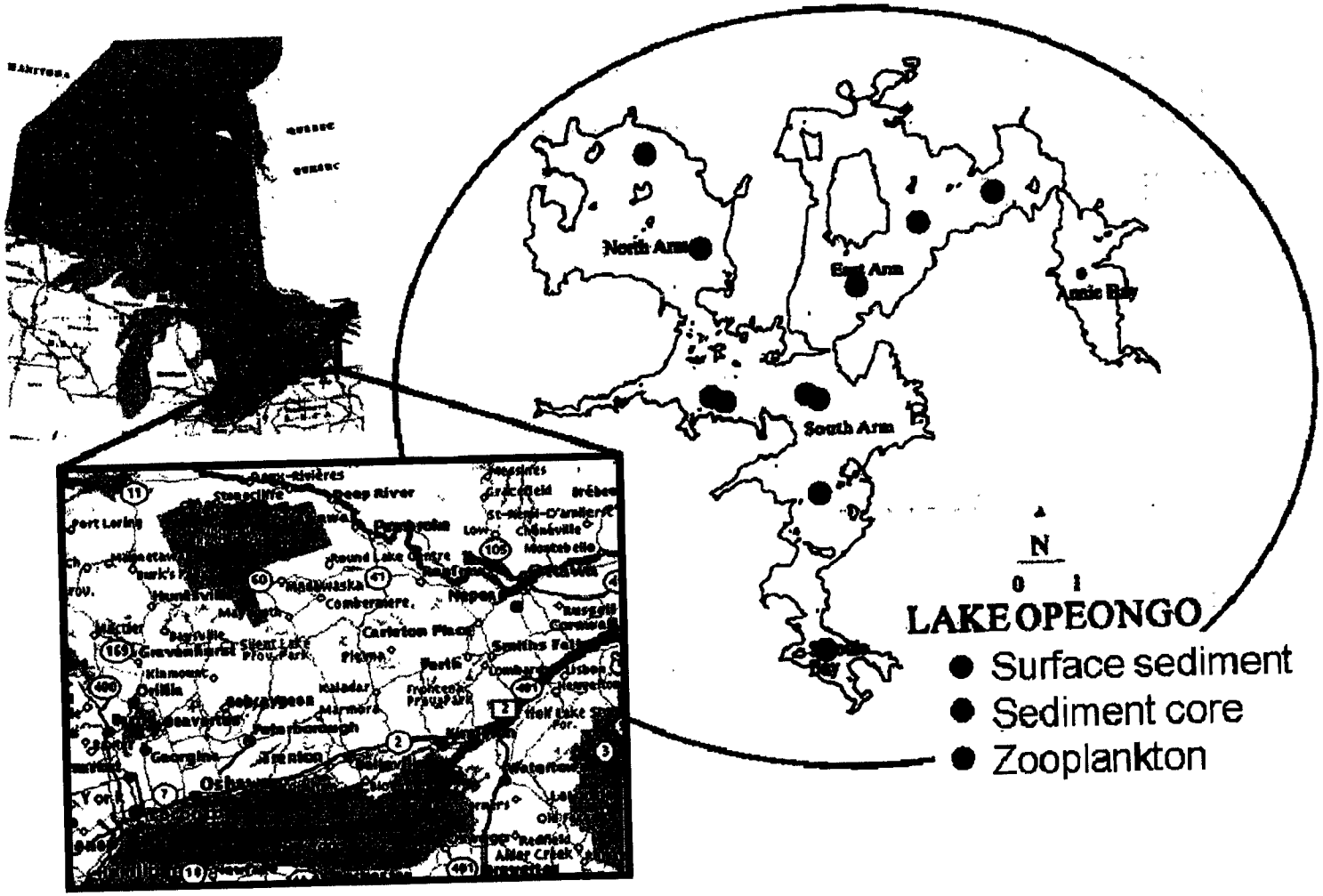

Figure 1. Map of Lake Opeongo showing locations where surface sediments (red circles), sediment cores (blue circles), and zooplankton (green circles) were collected 02-03 October 2007 with guidance and assistance from Environment Canada. Yellow perch (*Perca flavescens*), cisco (*Coreogonus artedi*), and lake trout (*Salvelinus namaycush*) were collected 26-31 October 2007 from the south arm of the lake (exact locations not specified) by the Harkness Laboratory of Fisheries Research, which is located at the southern end of the lake.

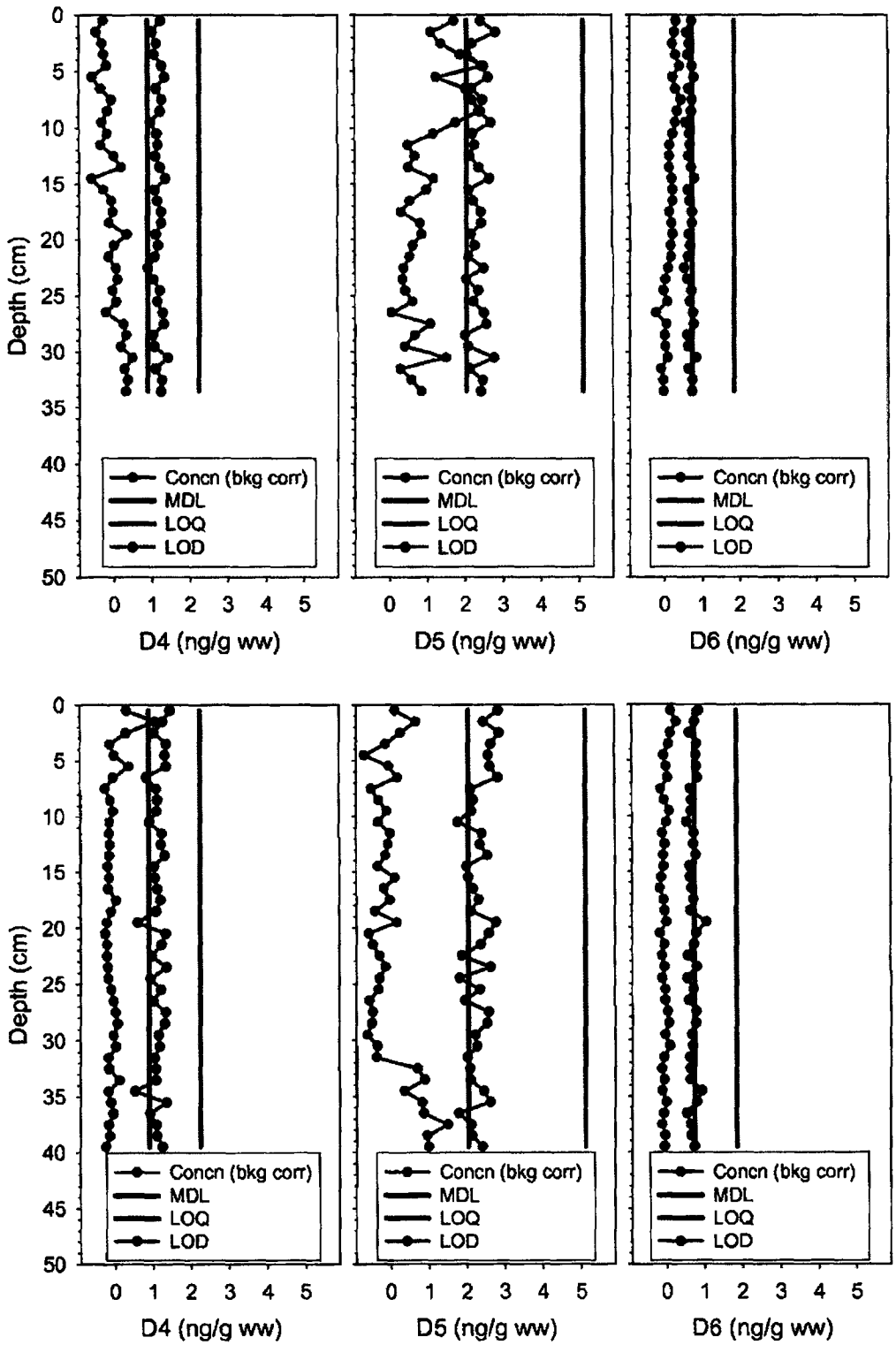

Figure 2. Sediment core profiles for D_4, D_5, and D_6 in Lake Opeongo in comparison to analytical limits of detection. Sediment cores were collected 02-03 October 2007 with guidance and assistance from Environment Canada.