

## UNDERSTANDING THE FATE AND BIOACCUMULATION OF CYCLIC VOLATILE METHYL SILOXANES IN ARCTIC LAKES

Krogseth IS<sup>1\*</sup>, Warner NA<sup>1</sup>, Christensen GN<sup>2</sup>, Whelan MJ<sup>3</sup>, Breivik K<sup>4,5</sup>, Evenset A<sup>2</sup>, Wasbotten IH<sup>6</sup>

<sup>1</sup>NILU – Norwegian Institute for Air Research, Fram Centre, NO-9296 Tromsø, Norway; <sup>2</sup>Akvaplan-niva, Fram Centre, NO-9296 Tromsø, Norway; <sup>3</sup>Department of Geography, University of Leicester, Leicester, LE1 7RH, United Kingdom; <sup>4</sup>NILU – Norwegian Institute for Air Research, P.O. Box 100, NO-2027 Kjeller, Norway; <sup>5</sup>Department of Chemistry, University of Oslo, P. O. Box 1033, NO-0315 Oslo, Norway; <sup>6</sup>Unilab Analyse AS, Fram Centre, NO-9296 Tromsø, Norway.

### Introduction

Cyclic volatile methyl siloxanes (cVMS) are used extensively in the production of silicone polymers, in personal care products, and in various technical applications. The main environmental emissions are from the use of personal care products, either through volatilization to the atmosphere or through wastewater effluents.<sup>1</sup> There are currently no regulations on the use of cVMS, but the congeners octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) have been subject to recent scrutiny from environmental scientists and regulatory authorities due to their suspected potential for bioaccumulation, persistence, and toxicity.<sup>2-4</sup> The cVMS appear to be less persistent than 'classical' POPs, but they are widely spread throughout the environment, with elevated concentrations being detected in some environmental media.<sup>1</sup> Their potential for persistence and bioaccumulation will depend on environmental, organism, food-chain and/or physiological characteristics, but this is still not fully understood.<sup>5-7</sup>

The physicochemical properties of cVMS are interesting as these chemicals possess unusually high volatility combined with a high hydrophobicity. Once emitted to aquatic systems they will be subject to various environmental processes (e.g. hydrolysis, volatilization, and/or partitioning to organic matter).<sup>6</sup> In lakes that are ice-covered throughout the winter, exchange between the lake and the atmosphere is limited, and volatilization of cVMS may be restricted. This could result in higher dissolved concentrations of cVMS in water due to both restricted volatilization and slower hydrolysis rates at low temperatures, and hence increased cVMS exposure to the entire aquatic ecosystem.

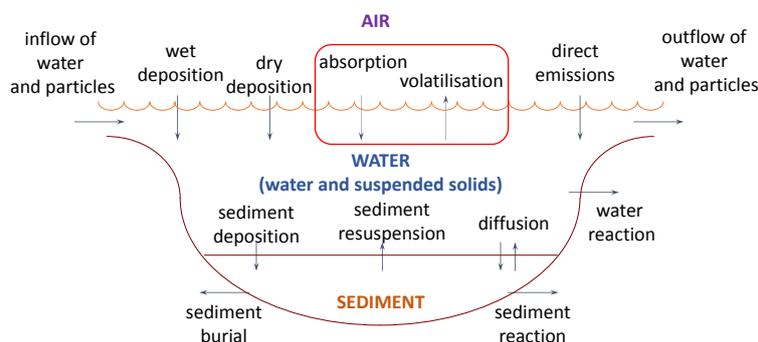
The aim of this study was to investigate the environmental behavior of cVMS in Arctic lakes, with a specific focus on gaining further insight into the influence of environmental characteristics on their persistence and bioaccumulation potential. Lake Storvannet in the municipality of Hammerfest in Northern Norway (70 °N, 23 °E) was chosen as a case study (Figure 1).<sup>8</sup> This is a well-characterized lake that receives variable sewage emissions from leaking pipes and overflow events and that is ice covered from approximately November to May. An integrated approach which combines modeling and monitoring efforts is being applied.



**Figure 1:** The sampling sites in Storvannet (A-D), inflowing (F and G) and outflowing (E) rivers. Direct emissions of sewage occurred earlier at site D. The shaded areas indicate where sewage leaks and overflows are known to occur. The right-hand map shows the location of Hammerfest.

## Materials and methods

Initial model simulations using dynamic multimedia environmental fate and bioaccumulation models were used to explore the behavior of cVMS in the lake system including the effect of ice-cover, and also to plan the timing of the measurement campaigns. The physical environment was represented using a dynamic version of Mackay's QWASI model,<sup>9,10</sup> parameterized for Storvannet (Figure 2). Gaseous exchange of cVMS between air and water was turned off in the model when the air temperature dropped below -2 °C to simulate ice cover in winter. Previously collated physical-chemical properties for cVMS were used as input to the model,<sup>11</sup> as well as a hypothetical constant emission scenario for 60 years. Predicted concentrations of cVMS in the dissolved water phase from the dynamic QWASI model were used as input to the dynamic bioaccumulation model ACC-Human.<sup>12</sup> Only the aquatic module of the model was used, consisting of three trophic levels represented by zooplankton, planktivorous fish, and piscivorous fish.



**Figure 2: Schematic illustration of the compartments and the transport and degradation processes that are included in the Dynamic QWASI model.<sup>9,10</sup> Absorption and volatilisation between air and water (red box) are only simulated in summer to simulate ice cover in winter.**

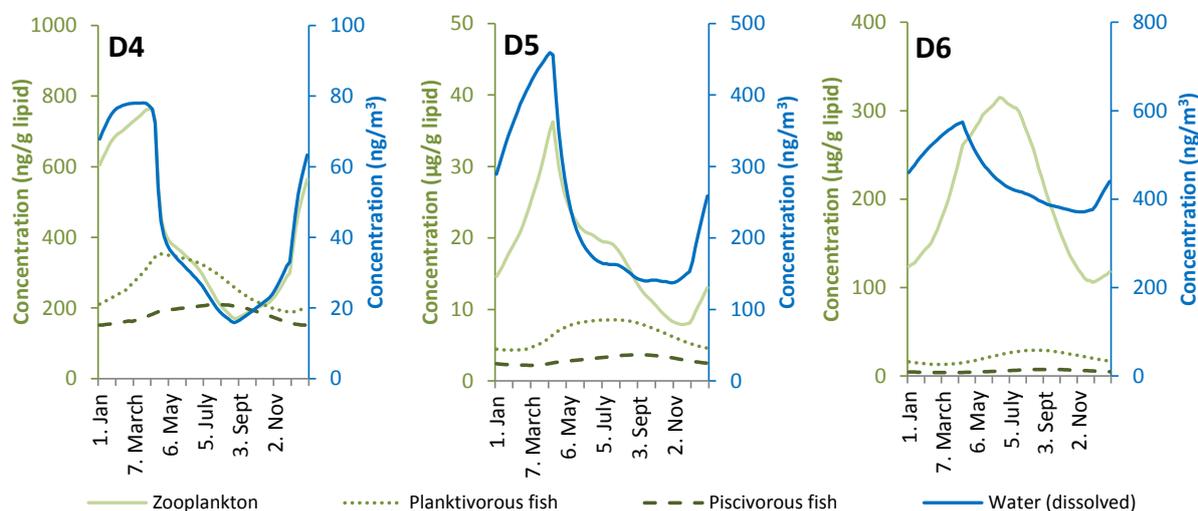
Environmental samples were collected from Storvannet in winter (March/April) 2014, and will also be collected in summer 2014. Water and surface sediment was collected from four sites in the lake. In addition, water was sampled from the two inflowing and one outflowing rivers, a sediment core was obtained from one of the lake sites in the winter season, and sewage samples were collected (Figure 1). Samples were also obtained from several trophic levels in the lake ecosystem, such as zooplankton and benthic fauna, sticklebacks, and stationary trout and char. The water and sewage samples were analyzed for cVMS using an existing static headspace method coupled to gas chromatography with mass spectrometric detection (GC-MS).<sup>13</sup> Sediment and biota were extracted using a modified version of previously established liquid extraction methods, followed by analysis on GC-MS.<sup>14,15</sup> Additional parameters such as organic carbon content in water and sediments, lipid content in biota, and stable isotopes ( $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ ) in sediment and biota were determined. Precautionary steps were taken to minimize background contamination of cVMS in the samples, and field blanks were included for all matrices.<sup>15</sup>

## Results and discussion

The initial model simulations indicated a pronounced seasonality of cVMS concentrations in water (Figure 3). The concentrations were predicted to increase during winter, with a peak at the end of the winter season followed by a rapid decline when the ice breaks up. The lowest concentrations were predicted to be at the end of the summer for D4, in early autumn for D5, and in late autumn for D6. The longer response times for the larger cVMS congeners could possibly be explained by their slower hydrolysis rate constants. The main elimination pathways of cVMS from the water column were predicted to be volatilisation and hydrolysis for D4 and D5, and volatilisation and sediment burial for D6. Only a weak seasonality was predicted for the D4 concentrations in sediment, while no seasonality was predicted for the concentrations of D5 and D6 in sediments.

The seasonality of cVMS concentrations in the water column was predicted to propagate to the food-chain (Figure 3). There was predicted to be a lag-phase in the seasonality between water and biota (D6) or between trophic levels (D4 and D5). This could potentially cause seasonal variations in bioaccumulation of cVMS in this

system. In general, the model predicted lower lipid-normalized cVMS concentrations with higher trophic level. However, in summer, the D4 concentrations were predicted to be higher in planktivorous and piscivorous fish than in zooplankton (Figure 3).



**Figure 2: Predicted concentrations of D4, D5, and D6 in fresh water (dissolved phase, right-hand axis), zooplankton, 5-year old planktivorous fish, and 5-year old piscivorous fish (all on left-hand axis) after 60 years with hypothetical constant emissions.**

Preliminary results from the measurement campaign in Storvannet in winter indicate that D5 and D4 are clearly present in sewage that is emitted to the lake, while D6 was often between limits of detection (LOD) and limits of quantification (LOQ) (Table 1). In the lake water, concentrations of cVMS were below or close to LODs, which indicates that cVMS could be present in the lake, but at levels below detection capabilities. Low detection is likely a result of a system that only receives variable sewage emissions from an area with a relatively low population (approximately 10 000 inhabitants), and methods that are not sensitive enough. D5 and D6 were well above method detection limits (MDL) in surface sediments in the lake, while D4 was not detected (Table 1). This illustrates that cVMS residence time in the water phase is not long, and that their fate in the lake system will be driven by the sediment compartment where concentrations are higher and residence times longer. In the sediment core, there was a clear trend of decreasing D5 concentrations with depth.

**Table 1: Limits of detection (LOD) and quantification (LOQ) for cVMS. LOD and LOQ for water (ng/L) were calculated as the average level in the field blanks plus 3 and 10 times the standard deviation of the level in the field blanks ( $n = 16$ ). Preliminary method detection limits (MDL, ng/g ww) for sediments were calculated based on reference sediment with low concentrations of cVMS that was brought to the field ( $n = 3$ ).<sup>15</sup>**

	Water/sewage (ng/L)		Sediment (ng/g ww)
	LOD	LOQ	MDL
D4	6.5	13.4	3.9
D5	10.4	21.7	0.4
D6	18.8	42.2	1.8

This project is still in an early stage. However, the initial model simulations already provide insight into potential mechanisms that could drive variations in the persistence and bioaccumulation potential of cVMS at high latitudes. Further work will focus on finalizing the measurement data from Lake Storvannet, and comparing these data with the model predictions. Moreover, model simulations with emission estimates and food-chain characteristics that are more specifically parameterized for the study site will be carried out, as well as exploration of model design, assumptions, and sensitivity. This iterative integration of models and measurements will facilitate the development of a holistic and mechanistic explanation of the environmental behavior of cVMS

in Arctic lakes, and provide further insight into the influence of environmental parameters on their environmental persistence and bioaccumulation potential.

#### **Acknowledgements**

We thank the Research Council of Norway (Project no. 222259) and the Fram Centre Flagship “Hazardous substances – effects on ecosystems and human health” for funding, and Hammerfest kommune and Vest-Finnmark jeger og fiskeforening for field assistance.

#### **References:**

1. Wang DG, Norwood W, Alaee M, Byer JD, Brimble S. (2013); *Chemosphere* 93(5): 711-725
2. Brooke D, Crookes M, Gray D, Robertson S. (2009); *Environmental risk assessment report: Decamethylcyclotetrasiloxane*, Environment Agency of England and Wales
3. Brooke D, Crookes M, Gray D, Robertson S. (2009); *Environmental risk assessment report: Octamethylcyclotetrasiloxane*, Environment Agency of England and Wales
4. Brooke D, Crookes M, Gray D, Robertson S. (2009); *Environmental risk assessment report: Dodecamethylcyclohexasiloxane*, Environment Agency of England and Wales
5. McGoldrick DJ, Chan C, Drouillard KG, Keir MJ, Clark MG, Backus SM. (2014); *Environ. Pollut.* 186: 141-148
6. Whelan MJ. (2013); *Chemosphere.* 91(11): 1566-1576
7. Warner NA, Nøst TH, Andrade H, Christensen G. (2014); *Environ. Pollut.* 190: 109-114
8. Christensen GN, Falk AH. (2010); Akvaplan-niva report no. 5175-01
9. Mackay D, Joy M, Paterson SA. (1983); *Chemosphere* 12(7-8): 981-997
10. Breivik K, Bjerkeng B, Wania F, Magnusson J, Helland A, Pacyna JM. (2003); NILU report no. OR 24/2003
11. Whelan MJ, Breivik K. (2013); *Chemosphere* 93(5): 794-804
12. Czub G, McLachlan MS. (2004); *Environ. Toxicol. Chem.* 23(10): 2356-2366
13. Sparham C, Van Egmond R, O'Connor S, Hastie C, Whelan M, Kanda R, Franklin O. (2008); *J. Chromatogr. A* 1212(1-2), 124-129.
14. Warner NA, Evenset A, Christensen G, Gabrielsen, GW, Borgå K, Leknes H. (2010); *Environ. Sci. Technol.* 44(19): 7705-7710
15. Warner NA, Kozerski G, Durham J, Koerner M, Gerhards R, Campbell R, McNett DA. (2013) *Chemosphere* 93(5): 749-756