Understanding the fate and bioaccumulation of cyclic volatile methyl siloxanes (cVMS) in Arctic lakes

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Key questions

- What is the environmental behavior of cVMS in a lake system which receives variable wastewater emissions?
- Are concentrations and persistence of cVMS in lake systems affected by ice cover?
- How do seasonal changes in the physical environment affect cVMS bioaccumulation in lake ecosystems?

Background & context

- Cyclic volatile methyl siloxanes (cVMS) are used in personal care products and are emitted to aquatic environments through wastewater effluents.[1]
- Bioaccumulation and persistence of cVMS can depend on environmental, organism, and/or food-chain characteristics, but this is not fully understood.[2,3]
- Environmental conditions at high latitudes may slow down removal and degradation processes of cVMS, and hence increase their persistence.
- This study aims to develop a holistic and mechanistic understanding of these questions by combining multimedia modeling and monitoring methods.

Case study: Storvannet

- Storvannet is located in Hammerfest (70 °N, 23 °E), a Norwegian town with about 10 000 inhabitants (Fig. 3).
- Untreated sewage was emitted directly to the lake until 1974.[4] Today, leaking pipes and sewer overflow events result in variable and intermittent emissions to the lake.
- The lake is ice covered from approximately November to May.

The Dynamic QWASI & ACC-Human Models

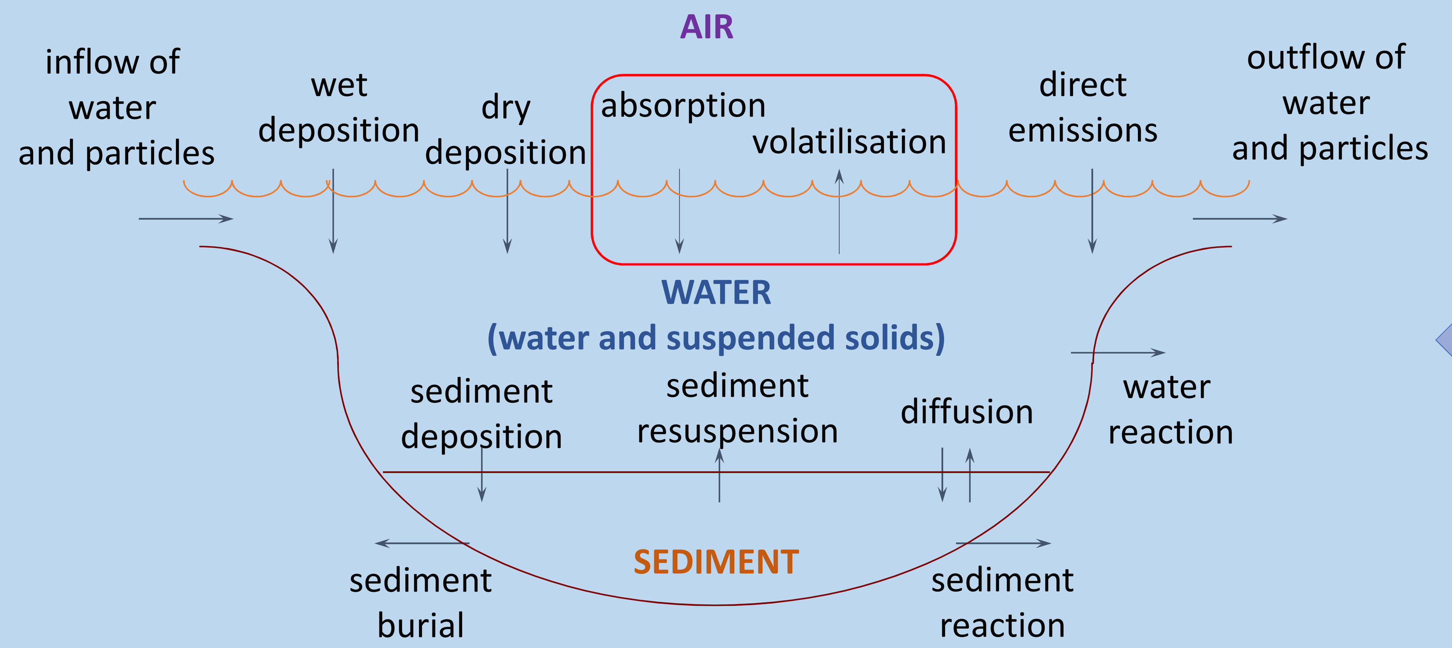

Figure 1: Schematic illustration of compartments and transport processes in the Dynamic QWASI model.[5,6] Absorption and volatilisation are only simulated in the summer season to simulate ice cover in winter.

The physical environment (Dynamic QWASI):

- The Dynamic QWASI model[5,6] (Fig. 1) is parameterized for environmental and climate characteristics of Storvannet.[4,7]
- To simulate ice cover, the model turns off gaseous exchange between air and water when the air temperature is below -2 °C (Fig. 1).
- Physico-chemical properties for cVMS were used as in previous model simulations.[8]
- Initial simulations were run with constant hypothetical emissions to water for 60 years.

Biota (ACC-Human):

- The aquatic module of the dynamic ACC-Human model was used (Fig. 2).[9]
- Predicted water concentrations from the Dynamic QWASI model and physico-chemical properties for cVMS[8] were used as input.

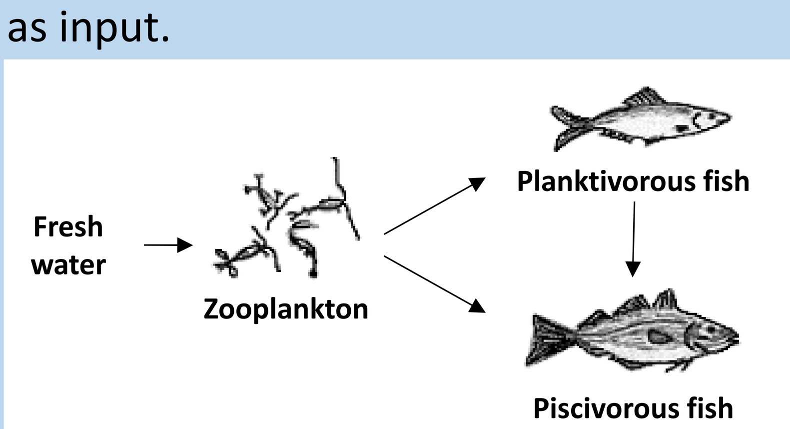

Figure 2: Schematic illustration of the aquatic module in the ACC-Human model.[9]

Sampling, extraction & analysis

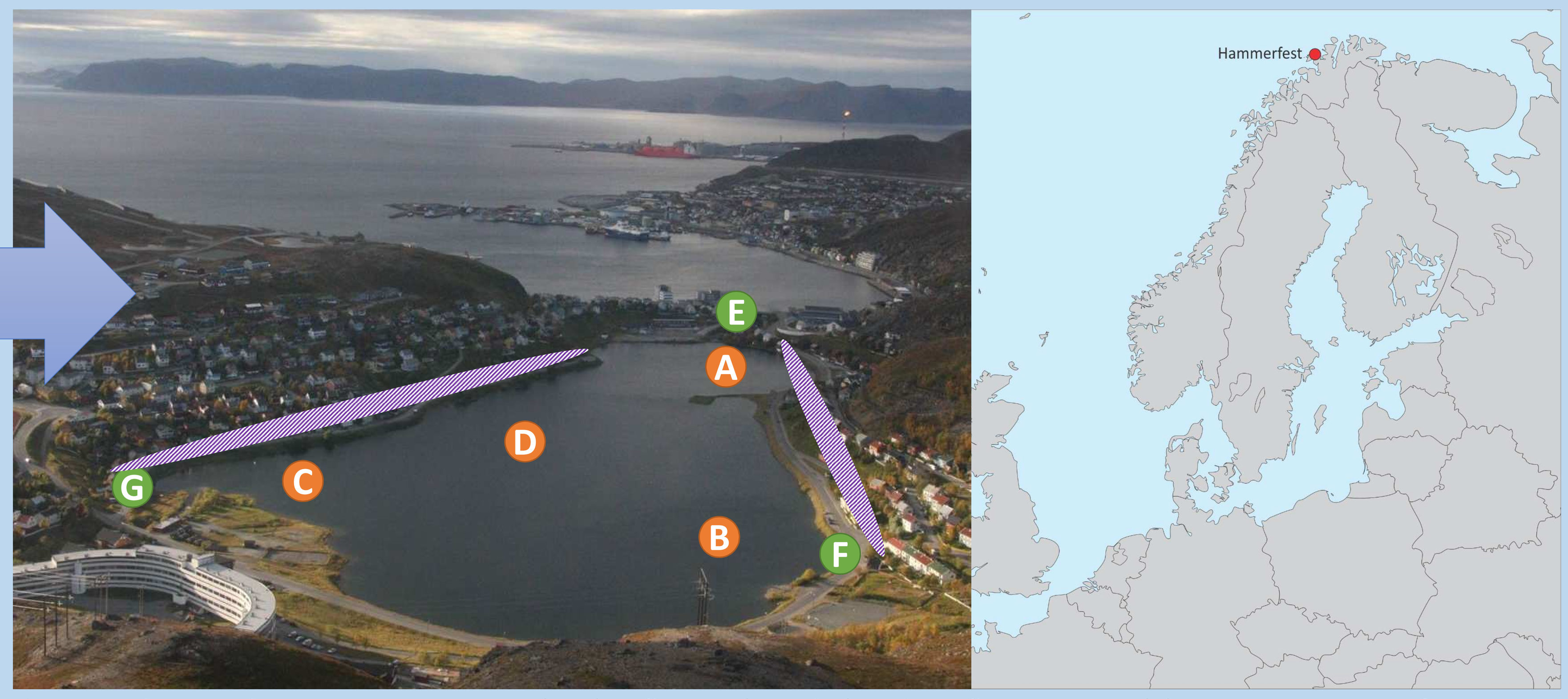

Figure 3: The sampling sites in Storvannet (A-D), inflowing (F and G) and outflowing rivers (E). Direct emissions of sewage occurred earlier at site D. The shaded areas indicate where sewage leaks and overflows are known to occur. The right-hand map shows the location of Hammerfest.

Water:
- 4 lake sites (A-D)
- 1 outflowing river (E)
- 2 inflowing rivers (F&G)
- Sewage

Sediments:
- 3 sites for surface sediments (A-C)
- 1 sediment core (D)

Biota:
- Stationary trout
- Stationary char
- Anadromous char
- Sticklebacks
- Zooplankton (summer only)
- Benthic fauna (summer only)

Water: Static headspace gas chromatography mass spectrometry (GC-MS).[10] ***Sediment & biota***: Liquid extraction with hexane[11,12] and analysis on GC-MS. **Quality control:** Field blanks were analyzed for all matrices. No personal care products were used, and samples were handled in a clean air cabinet (ISO class 5).

Initial model simulations

- A pronounced seasonality was predicted in concentrations of cVMS in water, with the peak at the end of the winter season and a rapid decrease when the ice breaks up (Fig. 5).
- There was a lag-phase in the seasonality between water and biota (D6) or between trophic levels (D4 and D5). This may cause seasonal variation in bioaccumulation potential (Fig. 5).
- The main removal mechanisms from the system were predicted to be volatilization and hydrolysis for D4 and D5, and volatilization and sediment burial for D6.

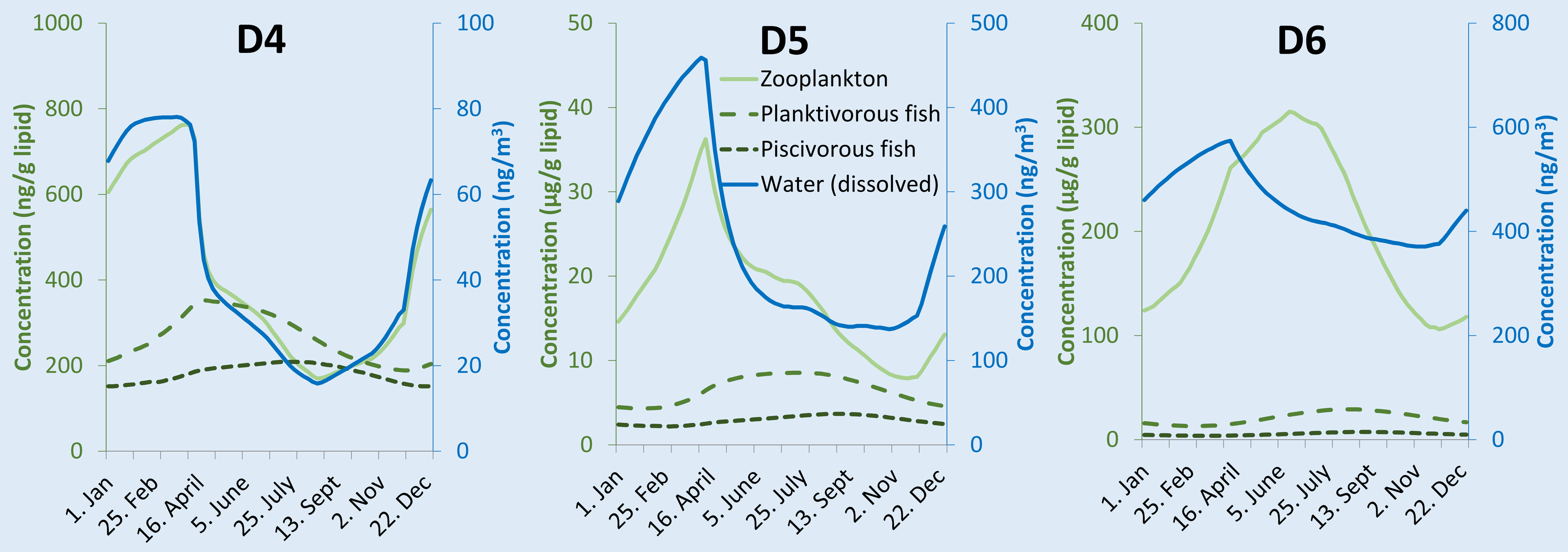

Figure 5: Predicted concentrations of D4, D5, and D6 in fresh water (dissolved phase, right-hand axis), zooplankton, 5-year old planktivorous fish, and 5-year old piscivorous fish (all on left-hand axis) after 60 years with hypothetical constant emissions.
D4 = octamethylcyclotetrasiloxane, D5 = decamethylcyclopentasiloxane,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

Future research

- Winter samples were collected in March/April 2014, and summer samples will be collected in summer 2014. Extraction and analysis of winter samples is underway.
- Additional parameters will also be analyzed (content of lipids/organic carbon, stable isotopes ($\delta^{15}N$ and $\delta^{13}C$), dating of sediment core). The core will provide an historical profile starting prior to cessation of direct sewage emissions to the lake.
- Further development of new and existing extraction and analysis methods for cVMS, if required.
- Exploration of model design, assumptions, and parameters, including sensitivity analysis.
- Evaluation of model predictions and observations in concert to gain a mechanistic understanding of the overall behavior of cVMS in the system, including the influence of environmental conditions on the persistence and bioaccumulation potential of cVMS.

References: [1]Wang, D.G. et al. *Chemosphere* 2013, 93, 711-725. [2]McGoldrick, D.J. et al. *Environ. Pollut.* 2014, 186, 141-148. [3]Whelan, M.J. *Chemosphere* 2013, 91, 1566-1576. [4]Christensen, G.N. and Falk, A.H. 2010, Akvaplan-niva report no. 5175-01. [5]Breivik, K. et al. *Environ. Toxicol. Chem.* 2004, 23, 2386-2395. [6]Mackay, D. et al. *Chemosphere* 1983, 12, 981-997. [7]Norwegian Meteorological Institute, eklima.no, Accessed 4th Sept. 2013. [8]Whelan, M.J. and Breivik, K. *Chemosphere* 2013, 93, 794-804. [9]Czub, G. and McLachlan, M.S. *Environ. Toxicol. Chem.* 2004, 23, 2356-2366. [10]Sparham, C. et al. *J. Chromatogr. A* 2008, 1212, 124-129. [11]Warner, N.A. et al. *Environ. Sci. Technol.* 2010, 44, 7705-7710. [12]Warner, N.A. et al. *Chemosphere* 2013, 93, 749-756. **Acknowledgements:** The Research Council of Norway (Project no. 222259) and the Fram Centre Flagship "Hazardous substances – effects on ecosystems and human health" for funding, Hammerfest kommune and Vest-Finnmark jeger og fiskeforening for field assistance.