Assessing the fate and bioaccumulation of cyclic volatile methyl siloxanes (cVMS) in Arctic lakes experiencing seasonal environmental changes

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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]
- This study aims to develop a holistic and mechanistic understanding of these questions by combining multimedia modeling and monitoring.

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?

The Dynamic QWASI & ACC-HUMAN Models

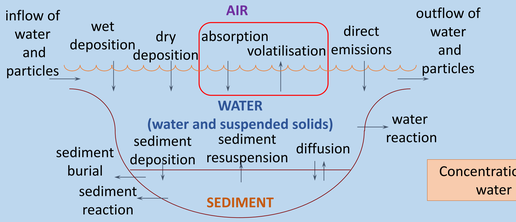

Figure 1: Compartments and transport processes in the Dynamic QWASI model.[5,6] Gaseous air-water exchange was only simulated in the summer season, since these processes are prevented by ice cover in winter. Physico-chemical properties for cVMS[8] and characteristics of Storvannet[4,7] were used as input, and hypothetical constant emissions to water for 60 years were assumed for the initial simulations.

Concentrations in water

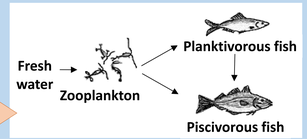

Figure 2: The aquatic module of ACC-HUMAN,[9] used to model the cVMS concentrations in fish.

Initial model simulations

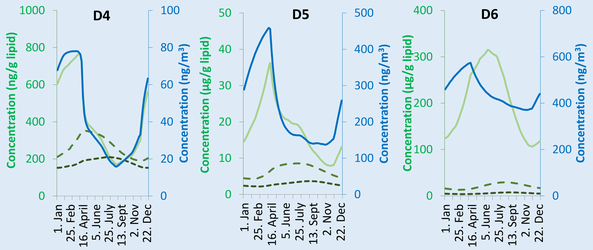

Figure 4: Predicted concentrations of D4, D5, and D6 in fresh water (dissolved phase, right-hand axis), zooplankton, 5-year old planktivorous fish, and 5-year old piscivorous fish (all on left-hand axis). A pronounced seasonality was predicted in concentrations of cVMS in water, with the peak at the end of the winter season and a rapid decrease when the ice breaks up. Concentrations of D6 in water and biota were out of phase, as were concentrations of D4 and D5 between trophic levels. This may cause seasonal variations in bioaccumulation.

Sampling, extraction & analysis

Figure 3: Storvannet is located in Hammerfest (70 °N, 23 °E), a Norwegian town with about 10 000 inhabitants. The lake is ice covered from approximately November to May. Untreated sewage was emitted directly to the lake until 1974 (site D) when it was moved to the harbor (site M).[4] Today, leaking pipes and sewage overflow events result in variable and intermittent emissions to the lake (shaded areas).

Water samples were collected in Storvannet (A-D), inflowing (F and G) and outflowing rivers (E), and in the harbor (M) in March & June 2014. **Sediment** was collected from sites A-D and M and **sewage** at sites E-G. **Fish** was caught in both the lake (Arctic char and Trout) and in the harbor (Atlantic cod). Water samples were analysed with static headspace gas chromatography mass spectrometry (GC-MS),[10] and sediment & biota with liquid extraction with hexane[11,12] followed by analysis on GC-MS. Reference materials (sediment, water, fish) containing low levels of cVMS were used as field blanks.

Measured concentrations

D4 = octamethylcyclotetrasiloxane D5 = decamethylcyclopentasiloxane D6 = dodecamethylcyclohexasiloxane

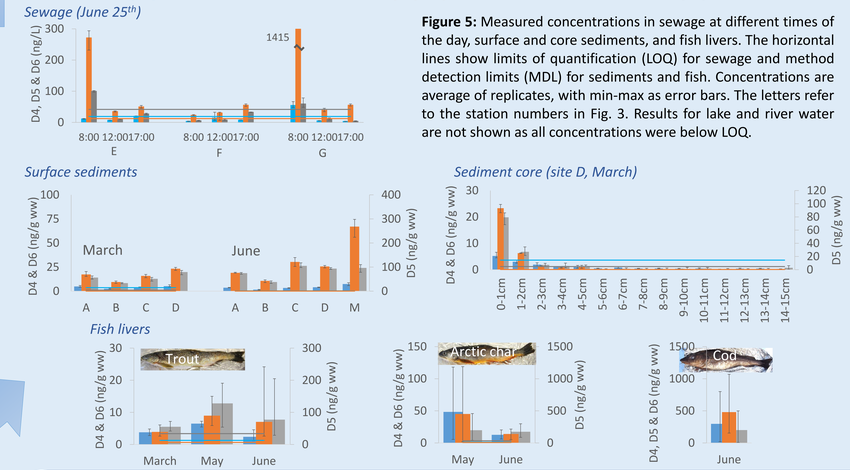

Figure 5: Measured concentrations in sewage at different times of the day, surface and core sediments, and fish livers. The horizontal lines show limits of quantification (LOQ) for sewage and method detection limits (MDL) for sediments and fish. Concentrations are average of replicates, with min-max as error bars. The letters refer to the station numbers in Fig. 3. Results for lake and river water are not shown as all concentrations were below LOQ.

Summary & future work

- cVMS were detected in sewage, but were below LOQs in lake and river water. All cVMS were detected in surface sediment of the lake and the marine harbor. Concentrations decreased rapidly with depth in the sediment core (Fig. 5).
- cVMS were detected in livers from both Trout (*Salmo trutta*) and Arctic char (*Salvelinus alpinus*) from Storvannet, and in Atlantic cod (*Gadus morhua*) from the harbor. Concentrations varied considerably between individual fish, and the highest concentrations were above 1 µg/g ww of D5 in char and cod.
- Temporal variations of cVMS concentrations in Storvannet may be driven more by variable emissions than by seasonality in environmental conditions, complicating the interpretation of results. This stresses the importance of understanding emissions, and will be investigated through model predictions with more realistic emission estimates.
- Model simulations, cVMS measurements, and measurements of physical and chemical sample characteristics (temperatures, content of organic carbon, lipids, $\delta^{15}N$ and $\delta^{13}C$, dating of sediment core) will be combined to gain a mechanistic understanding of the overall behavior, persistence, and bioaccumulation of cVMS in the system.

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.