

Cod: 8.4014

ENVIRONMENTAL BEHAVIOUR OF CYCLIC VOLATILE METHYLSILOXANES IN A HIGH ALTITUDE LAKE: A MODELLED AND MEASURED APPROACH

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Introduction

Cyclic volatile methylsiloxanes (cVMS) are high production chemicals with dominant usage occurring in cosmetic and personal care products. This class of chemicals are emitted to aquatic environments via waste water effluents¹ and have been of research and regulatory focus due to their potential to accumulate in sediment and biological compartments¹, including nearby Arctic communities.^{2,3}

cVMS fate and exposure will be dictated by the characteristics of the impacted environment. Several environmental parameters (temperature, hydraulic residence time, sedimentation rate) play a key role in the overall aquatic persistence.⁴ At higher latitudes, changes in one or several of these parameters (i.e., temperature, ice cover) due to extreme seasonal changes may significantly influence overall persistence of cVMS. Knowledge on how changes in environmental characteristics affect cVMS persistence is of key importance, particularly as restrictions on their usage in personal care products is currently being evaluated in the European Union.⁵

In this study, we describe a holistic evaluation of the environmental fate of cVMS in a high latitude lake experiencing seasonal variations in environmental conditions and intermittent waste water emissions. Lake Storvannet in Northern Norway (70 °N, 23 °E) has received sewage leaks and overflows for decades. The lake is subjected to a strong seasonality with ice-cover for 6 months of the year. Emission events typically occur as combined sewer overflows during the snow melt season and after heavy rainfall. The main objective of the study was to combine measured cVMS concentrations with fugacity-based model simulations to explore both plausible interpretations for observed concentration patterns and the importance of seasonal and temporal variations in the system.

Materials and methods

Concentrations of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) were measured in samples of sewage, lake water, and lake sediment from Storvannet in March and June of 2014, using adapted versions of established analytical procedures for cVMS.³ A version of the QWASI-model previously published by Mackay et al.⁶ was adapted⁴ and parameterized for the dimensions and environmental characteristics of Storvannet. The fate of cVMS in Storvannet was evaluated using a 2-model approach: (i) a steady-state version that assumes constant emissions to the lake and (ii) a dynamic (time-variant) version that takes into account both temporally variable emissions, water-flows, temperatures and ice-cover. In the dynamic model, emissions to the lake were assumed to be three orders of magnitude higher when runoff exceeded 5 mm/day. Ice-cover was taken into account by turning off volatile exchange between air and water when the water temperature dropped below 0 °C. As emissions of cVMS to Storvannet are from unrecorded leaks and overflows, and thus highly uncertain, inverse modelling was employed using the steady-state QWASI-model to predict the rate of emissions required to reproduce the measured concentrations of cVMS in sediment.

Results and discussion

Using the steady-state QWASI model, three different temperature scenarios were evaluated (annual average, summer average, and winter average) to investigate the overall behavior of cVMS within Lake Storvannet. In addition to these scenarios, an additional scenario simulating ice cover (removal of air/water exchange) was evaluated during winter. In both summer and winter scenarios, advection from

the lake was predicted to be the most dominant removal process followed by volatilization. In winter with ice cover scenario, advection was again the dominant removal process, while hydrolysis (for D4) and sediment burial (for D5 and D6) were found to be of greater importance compared to volatilization. These findings can mostly be explained by the low hydraulic residence times within the lake (annual average: 15 days) compared to the rate of the other removal mechanisms, but also by the temperature dependence of predicted partitioning behavior between water and organic carbon for cVMS. Most classical persistent organic pollutants (e.g., polychlorinated biphenyls (PCBs)) have negative enthalpies of phase change between organic carbon and water⁷, favoring a higher partitioning to organic carbon at lower temperatures. Hence, for these compounds a slower degradation in cold climates is strengthened through a smaller fraction present in the dissolved water phase, and they are normally assumed to have a higher overall persistence at lower temperatures. On the other hand, cVMS possess positive enthalpies of phase change between organic carbon and water^{8,9}, thus, favoring greater partitioning from organic carbon to water (lower log K_{oc}) as temperatures decrease (Figure 1). This means that slower rates of hydrolysis at lower temperatures for cVMS is counteracted by a higher fraction in the dissolved water phase, where the cVMS may be removed through both hydrolysis, advection or volatilization. Thus, the predicted overall persistence of cVMS in Storvatn is lower in winter compared to summer due to greater amounts of cVMS present in the water phase where they are more efficiently removed. Ice cover formation on Storvatn predicted greater overall persistence compared to a without ice scenario as volatilization is prevented (Figure 2).

Performance of the steady-state model was evaluated against measured concentrations using an inverse modelling approach. Based on measured cVMS concentrations in sediment (0.21 ± 0.03 , 3.8 ± 1.0 , and 0.85 ± 0.21 $\mu\text{g/g}$ organic carbon for D4, D5 and D6, respectively)³, inverse steady-state modelling resulted in predicted cVMS concentrations in lake water below or around analytical limits of quantification. These findings are not contradictory with measurements as measurements were also below limits of quantification. However, the inverse modelling resulted in unrealistically high emission estimates to the lake when compared to measured cVMS concentrations in sewage. Although this does not invalidate findings of cVMS overall behavior predicted under the steady state scenario (independent of emissions), it highlights that the intermittent emission scenario occurring for Lake Storvatn (e.g. episodic events) is not accurately described by a steady state model. However, by using a hypothetical intermittent emission scenario consistent with combined sewer overflows, the dynamic model could mechanistically rationalize high (and relatively stable) concentrations of cVMS in sediment and low concentrations in the water column (for most of the year) (Figure 3). This illustrates the influence of environmental conditions on the behavior of cVMS and how overall persistence of cVMS will be influenced by physical characteristics of the impacted environment.

Acknowledgements

The authors thank the Research Council of Norway (Project number: 222259) and the Fram Centre “Hazardous Substances – effects on ecosystems and human health” program for financial support of this study. The local anglers and municipality of Hammerfest for sampling assistance, and UniLab Analyse for analysis support.

References

- [1] Wang, D. G., Norwood, W., Alae, M., Byer, J. D., Brimble, S. (2013) *Chemosphere* 93, 711-725.
- [2] Warner, N. A., Evenset, A., Christensen, G. N., Gabrielsen, G. W., Borgå, K., Leknes, H. (2010) *Environ. Sci. Technol.* 44, 7705-7710.
- [3] Krogseth, I. S., Warner, N. A., Christensen, G. N., Whelan, M. J., Breivik, K., Evenset, A., Wasbotten, I. H. (2014) *Organohalogen Compd.* 76, 186-189.
- [4] Whelan, M. J. (2013) *Chemosphere* 91, 1566-1576.
- [5] European Chemicals Agency. (2016) Committee on risk assessment concludes on restricting D4 and D5. http://www.echa.europa.eu/view-article/-/journal_content/title/committee-for-risk-assessment-concludes-on-restricting-d4-and-d5.
- [6] Mackay, D., Joy, M., Paterson, S. A. (1983) *Chemosphere* 12, 981-997.
- [7] Li, N., Wania, F., Lei, Y. D., Daly, G. (2003) *J. Phys. Chem. Ref. Data* 32, 1545-1590
- [8] Xu, S., Kozerski, G., Mackay, D. *Environ. Sci. Technol.* (2014) 48, 11748-11759
- [9] Xu S., and Kozerski, G. E. SETAC Europe, poster WE325, Porto, 2007
- [10] Whelan, M. J., and Breivik K. (2013) *Chemosphere* 93:794-804.

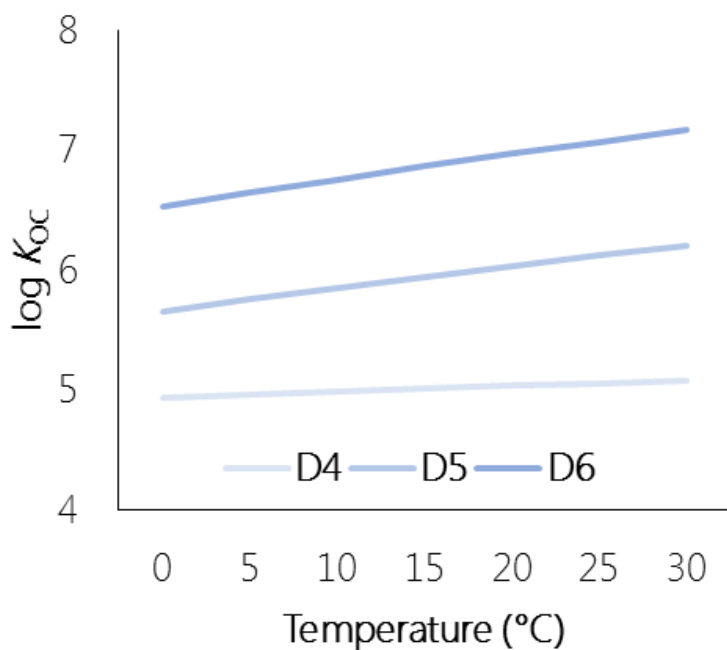


Figure 1. Predicted temperature dependence of organic carbon-water partition coefficient (K_{oc}) for D4, D5 and D6

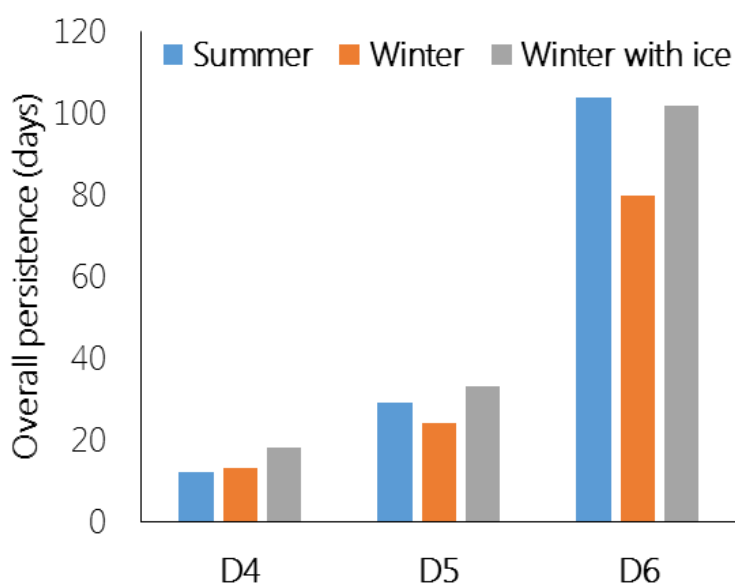


Figure 2. Predicted overall persistence of D4, D5 and D6 in Lake Storvatn under summer, winter, and winter with ice cover conditions

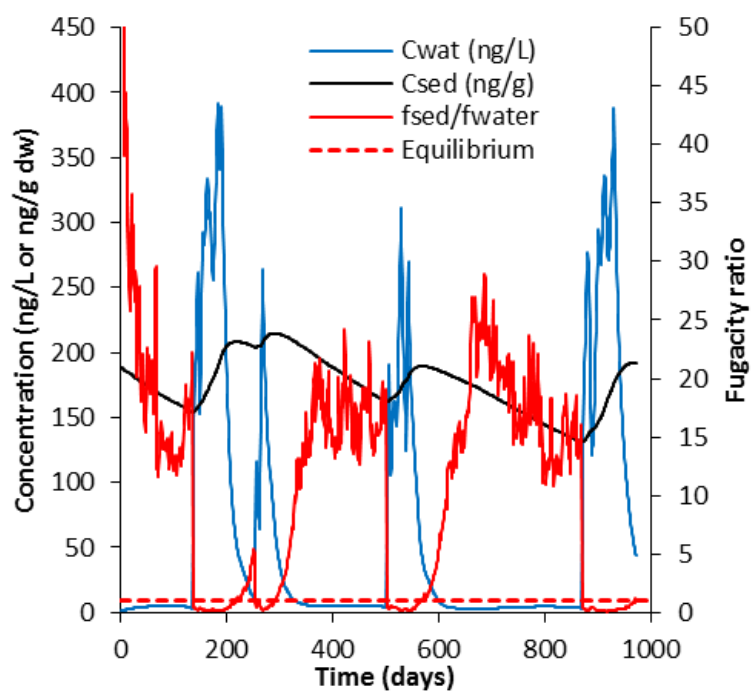


Figure 3. Predicted changes in the concentration of D5 in water (C_{wat}) and sediment (C_{sed}) in Storvannet over a two-year period assuming a hypothetical intermittent emission scenario consistent with combined sewer overflows. Also shown is the fugacity ratio between sediment and water (f_{sed}/f_{water}) which is < 1 during flow events but $\gg 1$ at other times.