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NILU report 35/2024

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# NILU report 35/2024

ISBN 978-82-425-3184-1
ISSN 2464-3327

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**Certifications**
NS-EN ISO 9001
NS-EN ISO 14001

**Accreditation**
NS-EN ISO/IEC 17025

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Org.no. 559442-9580
**www.nilu-research.se**

**Title**
Investigating snow deposition of cyclic siloxanes in an Arctic environment

**Norwegian title**
Undersøkelse av snødrevet deponering av sykliske siloksaner i et Arktisk miljø

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**Short summary (English)**
cVMS are high production volume chemicals that are used for a wide range of industrial and domestic applications. Given the high volatility of cVMS, emissions occur mainly to the atmosphere, and cVMS are present in the Arctic atmosphere, e.g. at the Zeppelin Observatory near Ny Ålesund, Svalbard, suggesting potential for long-range atmospheric transport. A study to investigate whether cVMS have the potential to deposit to surface media, and thereby represent a potential risk to the terrestrial or marine environment in polar and Arctic regions was carried out. Overall, cVMS levels in samples of vegetation, soil, sediment and marine biota were low. D4 was detected in most samples at concentrations above LOD, but below LOQ, while D5 and D6 were generally not detected. The low cVMS concentrations in soil, vegetation, sediments, and fish are in line with most current research on cVMS in remote regions, which together suggest that input of cVMS from atmospheric deposition and snow melt is likely not a major contributing source.

**Short summary (Norwegian)**
cVMS er kjemikalier med høyt produksjonsvolum som brukes til et bredt spekter av industrielle og husholdningsapplikasjoner. Gitt den høye flyktigheten til cVMS, skjer utslipp hovedsakelig til atmosfæren, og cVMS er til stede i den arktiske atmosfæren, for eksempel ved Zeppelinobservatoriet nær Ny-Ålesund, Svalbard, noe som antyder potensial for langtransport i atmosfæren. En studie for å undersøke om cVMS har potensial til å avsettes til overflatemedia, og dermed representere en potensiell risiko for det terrestriske eller marine miljøet i polar- og arktiske regioner ble derfor utført. Totalt sett var cVMS-nivåene i prøver av vegetasjon, jord, sediment og marine organismer lave. D4 ble påvist i de fleste prøvene ved konsentrasjoner over LOD, men under LOQ, mens D5 og D6 generelt ikke ble påvist. De lave cVMS-konsentrasjonene i jord, vegetasjon, sedimenter og fisk er i tråd med de fleste tidligere studier på cVMS i avsidesliggende områder, som sammen antyder at tilførsel av cVMS fra atmosfærisk avsetning og snøsmelting sannsynligvis ikke er en stor bidragskilde.

**Keywords**
cVMS, Deposition, Snow

**Number of pages**
22

**Classification**
A-Open

**Project leader**
Maja Nipen

**NILU project number**
O-110035.ops3

**Client/Report prepared for**
Norwegian Environment Agency

**Contract reference**
M-2872/2024

**Signature of the responsible person**
Aasmund Fahre Vik, deputy CEO & CTO

**Date**
09.12.2024



**Citation**
Nipen, M., Hartz, W., Bäcklund, A., Schulze, Christensen, G., D., Løge, O. S., Nikiforov, V., Bohlin Nizzetto, P. (2024). Investigating snow deposition of cyclic siloxanes in an Arctic environment. (NILU report 35/2024). Kjeller: NILU.

# Contents

# Investigating snow deposition of cyclic siloxanes in an Arctic environment

## 1. Background

Cyclic volatile methyl siloxanes (cVMS) are high production volume chemicals which are used in a wide range of applications in personal care products, consumer products, construction, and industrial applications (Horii & Kannan, 2020; Wang et al., 2013).

Given the high volatility of cVMS, emissions largely occur to the atmosphere, where the main removal process is considered to be degradation via OH-radicals to silanols (Brooke et al., 2009a, 2009b, 2009c; McLachlan, 2020). The potential for long-range atmospheric transport of cVMS has been well documented, e.g. via data from monitoring of atmospheric pollutants at the Zeppelin Observatory, Svalbard, where notable concentrations of cVMS have been measured in air (Halvorsen et al., 2023; Halvorsen, 2024; Krogseth et al., 2013). However, for cVMS to represent a risk to remote ecosystems, deposition to surface media needs to occur. Most empirical studies from Arctic/Antarctic regions have shown that levels of cVMS in terrestrial and marine environments are low when there is no direct impact from local sources (Krogseth & Warner, 2020). Moreover, a range of modelling results have shown that cVMS have a limited potential to deposit given their high volatility (Breivik et al., 2022; McLachlan, 2020). However, a study by Sanchís et al. (2015b) showed high levels of cVMS in the aquatic and terrestrial environment in Antarctic areas assumed to be unaffected by local sources. Snow scavenging and deposition of atmospheric cVMS via snow was hypothesised. Unfortunately, no samples of snow or air were analysed to support this hypothesis. It is worth noting that questions have been asked regarding the quality of the study relating to e.g. long-term storage of samples and lacking measures to control for sample contamination (Mackay et al., 2015; Warner et al., 2015). The authors responded to these comments (Sanchís et al., 2015a).

The objective of our study was to further investigate whether cVMS have the potential to undergo atmospheric deposition to surfaces, and thereby represent a potential risk to the terrestrial or marine environment in polar and Arctic/Antarctic regions. The study was centred around the Zeppelin Observatory and surrounding region, where samples from potential recipient compartments of cVMS from snowmelt was collected. In addition, sampling of fresh snow was attempted. Snow is expected to have a larger potential compared to rain for scavenging cVMS from air given i) larger surface area, ii) lower vapor pressure at low temperatures, and iii) higher concentrations of cVMS in the Arctic atmosphere in winter compared to summer. Unfortunately, no usable snow data were possible to achieve due to contamination issues, but the work associated with developing a snow sampling unit and snow sample collection is presented in Appendix 2 of this report. The focus in this report will therefore be on terrestrial and aquatic environmental samples. The results from an expanded study, including sample collection near the settlement at Ny Ålesund and a more remote location is presented in an accompanying report.

# 2. Methods

## 2.1. The study region

This study has been carried out in the region surrounding the atmospheric observatory on Zeppelin Mountain (474 m.o.h.) near Ny-Ålesund, Svalbard (Figure 1, Figure 2). Samples were collected from terrestrial environment (vegetation and soil) near the Zeppelin Observatory. Samples from the aquatic environment (sediment and biota) were collected from Kongsfjorden, in an area assumed to receive run-off from glaciers and from surrounding mountains during snow melt. The sampling site is also assumed to be unaffected by wastewater from the Ny Ålesund settlement as it is located upstream of the Ny Ålesund wastewater outlet according to known fjord circulation patterns (Choi et al., 2020)

*Figure 1 Atmospheric monitoring observatory at Zeppelin. The Ny-Ålesund settlement can be seen in the background (photo NILU).*

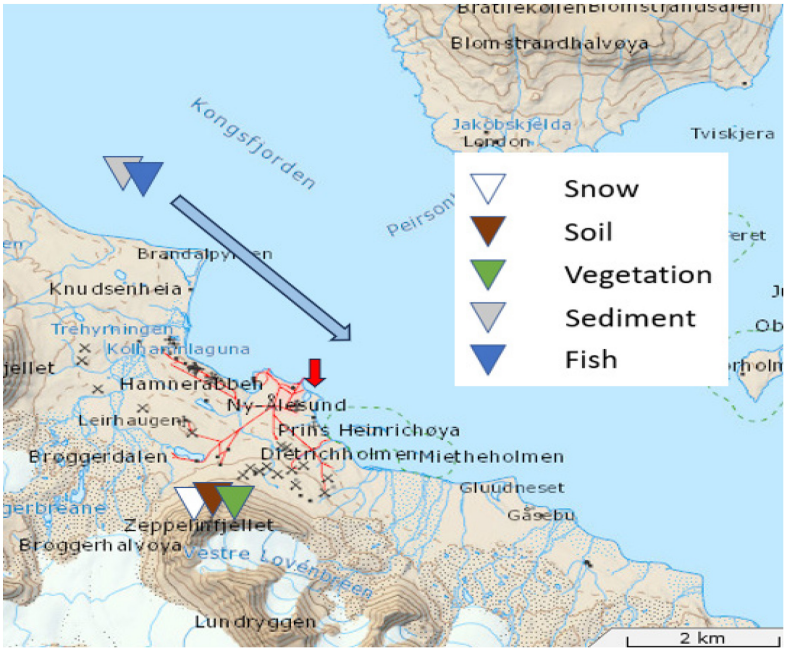


Figure 2 *Map of the study region including locations for sample collection (triangles). Red arrow shows outlet for wastewater from the Ny-Ålesund settlement, light blue arrow shows the general direction of ocean current (Map: Adapted from Norwegian Polar Institute).*

## 2.2. Study design

The sample types included in the study, and the rationale for inclusion is provided below:

- **Soil** (planned: n = 3, actual: n = 4)**:** Soil generally has high fugacity capacity for compounds which are comparable to cVMS, and soil could potentially be a recipient of siloxanes following snowfall and subsequent snowmelt.
- **Vegetation** (planned: n = 3, actual: n = 2)**:** Vegetation such as moss and lichen can potentially function as a passive sampler for atmospheric compounds, and can potentially be a recipient of siloxanes following snowfall and subsequent snowmelt, and thereby representing a source for terrestrial biota.
- **Sediment** (n = 3)**:** cVMS are very hydrophobic and will to a large extent partition to particles and sediments in water. Sediments may therefore represent a sink for cVMS deposited during snowfall following snowmelt.
- **Marine biota** (n = 3)**.** Marine biota in locations receiving snowmelt will potentially also be exposed to cVMS. For this study, muscle from Shorthorn Sculpin (*Myoxocephalus scorpius*), a highly stationary species, was used.
- **A range of field blanks and lab blanks** were included for quality control.

## 2.3. Sample collection

Field work was carried out in September 2023. Soil was collected to a depth of approximately 5 cm from at least four spots within an area of approximately 1 $m^2$ and placed on a piece of aluminium foil. A stainless-steel spoon was used to homogenize the collected soil on the aluminium foil, and a subsample from the collected soil was transferred into a 100 mL sample jar. Larger rocks were avoided during sampling. Given its mountain top location, the soil near the Zeppelin Observatory is rocky and sandy with low content of organic matter. No removal of litter layer was necessary.

In this study, moss or lichen was originally targeted. Near the Zeppelin Observatory however, vegetation is very sparse. Two locations with Saxifraga plants could be found (Figure 3), and enough material for two samples was collected. Vegetation was collected directly into the sample jar using tweezer and scissors. Roots and soil were avoided.

*Figure 3 Examples of Saxifraga, the vegetation sampled for the study (Photos: NILU)*

Sediments were collected in Kongsfjorden approximately 4 – 5 km from the Ny-Ålesund settlement, in an area with assumed limited influence from local sources (Figure 2). Sediments were collected at approximately 100 m depth using a van Veen grab. Samples were collected from the surface layer of sediment in the grab into a 100 mL sample jar using a stainless-steel spoon. Sediment which had been in direct contact with the surface of the grab was avoided. Collected sediments were fine grained.

In this study, Shorthorn Sculpin was targeted to represent aquatic biota. The Shorthorn Sculpin is a relatively stationary benthic species, allowing for the possibility of connecting cVMS concentrations with the sampling location. Fishing was done using nets, and the Shorthorn Sculpin was dissected outdoors immediately after arrival back at the shore. To ensure sufficient material for analysis, Shorthorn Sculpin muscle was chosen. Muscle was placed in 100 mL sample jars.

All samples were stored in a freezer until analysis.

### 2.4. Analysis

The following siloxane compounds were included in the analysis: Octamethylcyclotetrasiloxane (D4, cas no. 556-67-2), Decamethylcyclopentasiloxane (D5, cas no. 541-02-6), and Dodecamethylcyclohexasiloxane (D6, cas no. 540-97-6). All sample preparation in the lab was kept to a minimum in order to avoid loss of cVMS through evaporation. The preparation of recipient compartment samples was carried out at NILU's laboratory in Tromsø as described in previous studies (Heimstad et al., 2023; Ingjerd Sunde Krogseth et al., 2017). Briefly, for soil and sediment, the material was homogenized by stirring with a spoon or spatula, while for biota, sample material was homogenized as fine as possible using Ultra-Turrax stainless steel mixer which was washed between each sample with water, acetone and hexane. Approximately 1.0 ± 0.2 g of material was transferred to a centrifuge tube. Sediment samples were centrifuged to remove excess water. Samples were extracted with hexane and acetonitrile as solvent with ultrasonication, followed by shaker table, and centrifugation. As much as possible of the supernatant was transferred to a 2 ml GC vial and stored at -20 $^{o}$C overnight to precipitate out lipids and other biological material. Recovery standard was added to a sub sample before analysis on GC/MSD.

For soil and sediment, total organic carbon (TOC) was determined by a thermal oxidation/reduction method (SoliTOC cube) at Akvaplan NIVA (Tromsø). Dry weigh of soil and sediment was determined gravimetrically. Lipid content of fish was determined using a gravimetric method at NILUs laboratories at Kjeller.

### 2.5. Quality control measures

Strict quality control measures during field and lab work is essential to achieve reliable results in the analysis of siloxanes (Gerhards et al., 2022; Homem & Ratola, 2020). A range of measures were implemented in this study to minimize bias due to sample contamination or other analytical challenges, such as loss from volatilisation during storage or sample treatment.

In the field, strict QA/QC protocols were followed to minimize possible contamination during collection and handling of samples. These procedures required that anyone taking part in sampling were not using personal care products (e.g. shampoo, deodorant, skin cream, etc.) on the day of sampling. Also, use or handling of any silicone containing materials (lubricants, sealants, etc.) on a day of sampling was avoided.

All equipment used was baked and/or solvent rinsed with high purity acetone or hexane before use. The sample jars used have previously been tested to document that they are gas tight. All sample preparation was carried out in clean room facilities, ensuring a controlled, contaminant-free environment essential for the accurate analysis of cVMS.

Possible field blank matrices with known, low cVMS concentrations and similar properties as soil, vegetation, sediment, and fish were not available at the time of sampling. In order to determine any possible influence of ambient cVMS during fieldwork, storage and transport, 100 mL sample jars containing a few grams of XAD-2 sorbent (ultra clean resin, XAD-2 equivalent) were used as field blanks. In general, XAD-2 like sorbents have a higher potential for sorbing ambient cVMS compared to soil, vegetation, sediment and fish.

In the lab, solvent blanks and XAD-2 blanks (laboratory only) were included along with all samples and field blanks. Given the differences in properties between the field blank matrix and the sample matrices, samples

were only blank corrected based on solvent blanks, not field blanks. The field blanks were blank corrected based on XAD-2 blanks.

LODs and LOQs for potential recipient compartment samples were based on three and ten times the standard deviation of the field blanks. For robustness, all field blanks from the expanded study were used to set the LODs and LOQs (Appendix 1). Furthermore, results were evaluated against field blanks for the individual sample collection.

# 3. Results and discussion

## 3.1. Results from quality control samples

Solvent blanks prepared along with the samples were low and consistent, showing low background from lab facilities and personnel, as well as solvents, equipment, and during instrumental analysis. XAD-2 lab blanks also showed relatively low and consistent concentrations, but somewhat higher compared to solvent blanks for D5 and D5, indicating some additional background from the XAD-2 (Table 1).
The field blanks were less consistent, and generally showed somewhat higher levels compared to XAD-2 lab blanks. This indicates some additional cVMS background during sampling, transport, and/or storage (Table 2). Table 3 shows the average detection limits for the individual matrices.

*Table 1: cVMS level in lab blanks analysed alongside vegetation, soil, sediment, and marine biota samples.*

| Sample Text | Sample weight (g) | D4 (ng) | D5 (ng) | D6 (ng) |
|---|---|---|---|---|
| **Blank 1 XAD-2** | 0.821 | 0.54 | 3.06 | 0,31 |
| **Blank 2 XAD-2** | 0.799 | 0.47 | 2.84 | 0,24 |
| **Blank 3 XAD-2** | 0.780 | 0.42 | 1.69 | 0,21 |
| **Blank 4 solvent** | | 0.27 | 0.71 | 0.21 |
| **Blank 5 solvent** | | 0.30 | 0.74 | 0.23 |
| **Blank 6 solvent** | | 0.29 | 0.74 | 0.22 |

*Table 2: cVMS concentration in field blanks (blank corrected based on XAD-2 blanks).*

| Sample text | Sample code | D4 ng/g | D5 ng/g | D6 ng/g |
|---|---|---|---|---|
| **Field blank marine biota** | 2023-KF-FI-FB | 0.08 | 0.00 | 0.01 |
| **Field blank vegetation** | 2023-ZP-VG-FB-A | 0.11 | 1.01 | 0.12 |
| **Field blank soil** | 2023-ZP-SL-FB-A | 3.93 | 1.38 | 0.56 |

*Table 3: Average detection limits for vegetation, soil, sediment and marine biota*

| | Unit | LOD D4 | LOD D5 | LOD D6 | LOQ D4 | LOQ D5 | LOQ D6 |
|---|---|---|---|---|---|---|---|
| **Vegetation** | ng/g ww | 0.24 | 1.09 | 0.47 | 0.71 | 3.29 | 1.41 |
| **Soil** | ng/g dw | 0.34 | 1.57 | 0.68 | 1.02 | 4.75 | 2.03 |
| **Sediment** | ng/g dw | 0.29 | 1.34 | 0.58 | 0.86 | 4.03 | 1.72 |
| **Fish** | ng/g ww | 0.24 | 1.09 | 0.47 | 0.71 | 3.29 | 1.41 |

### 3.2. Results

Results from cVMS analysis of vegetation, soil, sediment and marine biota from near the Zeppelin Observatory and Kongsfjorden are shown in Table 4. In Figure 4, the measured concentrations are shown along with average LODs and LOQs for the respective matrix.

*Table 4: cVMS results from vegetation, soil, sediment and marine biota (Shorthorn Sculpin) samples (blank corrected based on solvent blanks). Values above LOQ in bold, values below LOQ but above LOD in green italic.*

| Sample type | Sample code | D4 | D5 | D6 | TOC (% dw) | Lipid (%) |
|---|---|---|---|---|---|---|
| **Vegetation (ng/g ww)** | 2023-ZP-VG-NV-A | *0.25* | <1.09 | <0.47 | | |
| | 2023-ZP-VG-NV-B | *0.31* | <1.17 | <0.51 | | |
| **Soil ng/g dw** | 2023-ZP-SL-NV-A | **0.85*** | <1.20 | *0.52** | 0.27 | |
| | 2023-ZP-SL-NV-B | *0.72** | <1.22 | <0.53 | 0.16 | |
| | 2023-ZP-SL-NV-C | *0.64** | <1.17 | <0.50 | 0.17 | |
| | 2023-ZP-SL-NV-D | **1.07*** | <1.32 | <0.57 | 0.13 | |
| **Sediment ng/g dw** | 2023-KF-SD-NV-A | *0.72* | <1.49 | <0.65 | 0.66 | |
| | 2023-KF-SD-NV-B | *0.59* | <1.58 | <0.68 | 0.66 | |
| | 2023-KF-SD-NV-C | *0.49* | <1.55 | <0.67 | 0.64 | |
| **Shorthorn Sculpin (muscle) ng/g ww** | 2023-KF-FI-NV-A | *0.61* | <1.07 | <0.46 | | 0.44 |
| | 2023-KF-FI-NV-B | *0.59* | <1.09 | <0.47 | | 0.47 |
| | 2023-KF-FI-NV-C | *0.77* | <1.23 | <0.53 | | 0.46 |

* Field blank associated with soil samples contained higher cVMS levels compared to the measured values

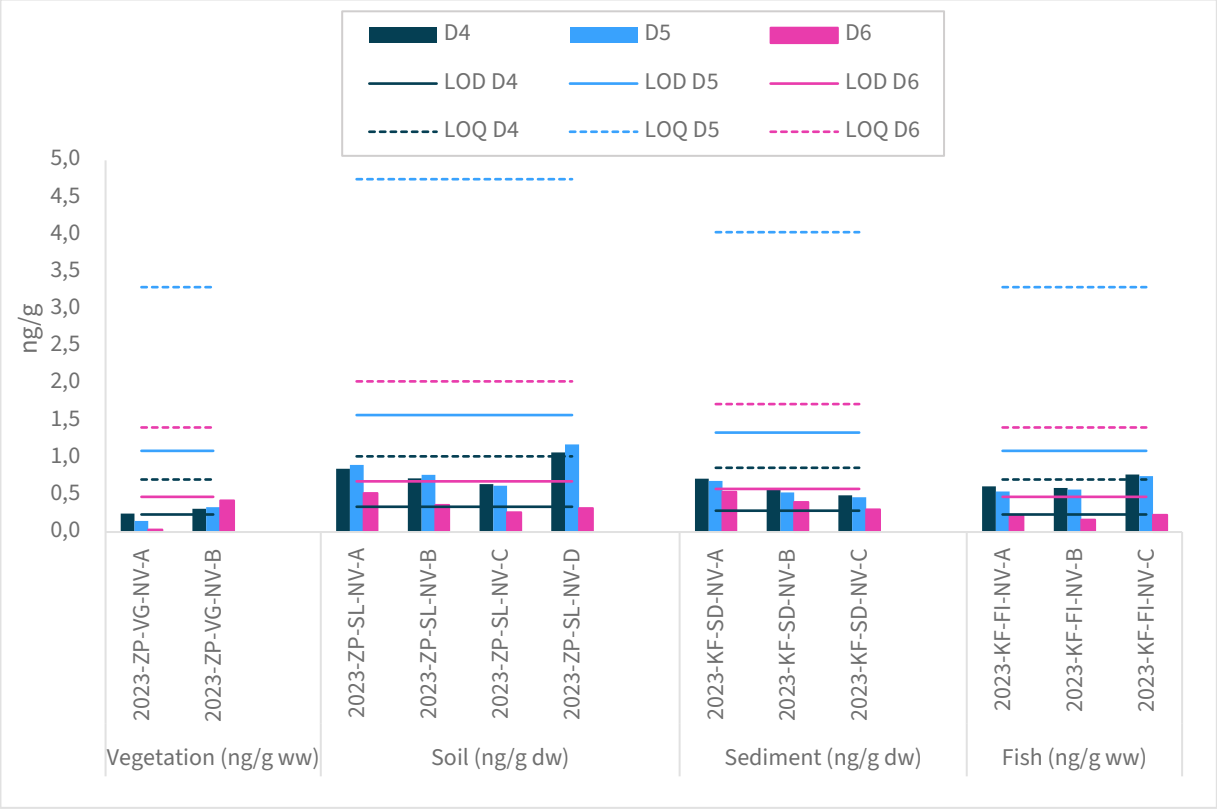


*Figure 4* Measured values, and average LODs and LOQs for the individual sample types.

For vegetation, D4 was detected above LOD but below LOQ in both samples, while D5 and D6 were not detected.

For soil, D4 was detected above LOD in all four samples, and above LOQ in two samples, with concentrations of 0.85 and 1.07 ng/g dw. D6 was detected above LOD but below LOQ in one soil sample, while D5 was not detected. It should be noted that the field blank associated with the soil samples showed higher concentrations of D4 compared to the soil samples, and comparable concentrations of D6 (Table 2). These concentrations should therefore be interpreted with caution. TOC levels in the soil samples for this study were low, ranging from 0.13 to 0.27 %.

In sediments, D4 was detected above LOD but below LOQ in all three samples, while D5 and D6 were not detected. TOC levels in the sampled sediments ranged from 0.64 to 0.66 %.

In samples of Shorthorn Sculpin muscle, D4 was detected above LOD but below LOQ in all three samples, while D5 and D6 were not detected. Lipid levels in the muscle were very low, ranging between 0.44 and 0.47 %. Given the low lipid content, we present the results on a wet weight basis, rather than lipid normalised, to avoid the added uncertainty associated with lipid normalisation when lipid content is very low.

Overall, D4 was detected in the majority of vegetation, soil, sediment and marine biota samples at concentrations above LOD but below LOQ, while D5 and D6 were generally not detected. It is worth noting that the measured concentrations of D4 and D5 were comparable (Figure 4), but the detection limits for D4 were lower compared to D5 detection limits (Table 3), a factor which influence the reported results, as concentrations found in this study are in the lower end of what is analytically feasible to measure.

To put our findings into context, we compare with some selected studies. However, cVMS in vegetation and soil has only been reported in a very limited number of studies. Sanchís et al. (2015b) reported concentrations of cVMS in Antarctic vegetation of nd – 21 ng/g dw, nd – 55 ng/g dw and nd – 88 ng/g dw for D4, D5 and D6 respectively. In Antarctic soil, Sanchís et al. (2015b) reported concentrations of nd – 24 ng/g dw, nd – 110 ng/g dw and nd – 42 ng/g dw for D4, D5 and D6 respectively, and TOC levels ranging from <0.1 to 2.6 %. As far as we are aware, no additional studies on soil or vegetation from Arctic or Antarctic regions have been conducted. Heimstad et al. (2023) looked for cVMS in soil and vegetation in an urban area in Norway, but neither D4, D5 or D6 were detected (LODs ranging from 0.42 to 2.04 ng/g dw). Our findings are more consistent with the findings of Heimstad et al. (2023) conducted in an urban area, compared to the findings by Sanchís et al. (2015b) from Antarctica. The uncertainty of the results in the study by Sanchís et al. (2015b) due to the lack of relevant field blanks program should be emphasised, as field blanks are crucial for the interpretation of results, particularly from remote regions.

cVMS in fish and sediments has been reported in other studies from Arctic regions. cVMS has been previously reported in Shorthorn Sculpin liver from two Svalbard fjords by Warner et al. (2010). In a remote fjord (Liefdefjorden) they found nd – 11 ng/g lw D5, and nd – 10 ng/g lw D6 in shorthorn sculpin liver. D4 was not detected. In Adventfjorden, which receives wastewater from Longyearbyen, they found 54 – 2 150 ng/g lw D5 and nd – 31 ng/g lw D6 in Shorthorn Sculpin liver. D4 was not detected. cVMS have also been studied in liver from Atlantic cod (*Gadus morhua*) from two locations in Isfjorden, Svalbard. D4 concentrations had an approximate range of 1.5 – 3.0 ng/g ww, D5 had an approximate range of 3.0 – 10 ng/g ww, and D6 had an approximate range of 1.0 – 4.0 ng/g ww (Schøyen et al., 2024). It should be noted that the studies in question investigated cVMS in Shorthorn Sculpin and Atlantic Cod liver samples, rather than muscle. As cVMS are lipophilic it is not unlikely that cVMS will be preferentially distributed to the liver, particularly in lean fish like the Shorthorn Sculpin. In the study by Warner et al. (2010), D4, D5 and D6 were not detected in sediments from Liefdefjorden and Kongsfjorden, the latter being the same fjord as included in the current study. In sediments from Adventfjorden, they found 0.7 – 2.1 ng/g dw D5, while D4 and D6 were not detected. TOC levels from Kongsfjorden sediments reported by Warner et al. (2010) are consistent with the TOC levels in the current study. In two studies from Hammerfest, cVMS in an urban lake which receives wastewater was investigated (Ingjerd S Krogseth et al., 2017; Ingjerd Sunde Krogseth et al., 2017). They found nd – 2 586 ng/g lw D4, 383 – 24 375 ng/g lw D5, and nd – 952 ng/g lw D6 in liver and muscle from stationary Arctic Char (*Salvelinus alpinus*). In the same lake, they found 4 - 16 ng/g dw D4, 73 – 328 ng/g dw D5 and 17 – 75 ng/g dw D6 in sediments. The results from the current study fits well with previous findings on cVMS in fish and sediments from Svalbard and other Arctic regions, where cVMS concentrations are below detectable levels or low at locations not directly affected by local sources (Krogseth & Warner, 2020).

## 4. Concluding remarks

The hypothesis stating that deposition of cVMS via snow is a driver for high concentrations of cVMS in terrestrial and aquatic media in Arctic/Antarctic regions was introduced by Sanchís et al. (2015b) based on their Antarctic study. Their findings could not be confirmed by studying similar matrices in the Northern Hemisphere in the current study. This despite that air concentrations of cVMS are predicted to be higher in the Northern Hemisphere compared to the Southern Hemisphere, and that the climate conditions in terms of annual average temperature (-1 and -2 ℃, respectively) and annual precipitation (37.4 and 35 mm, respectively) are similar between Svalbard (current study) and Livingston Island, where the study by Sanchís et al. (2015b) was carried out.

In this study, we detected D4 above LOD (but generally below LOQ) in vegetation, soil, fish, and sediment, while D5 and D6 generally were below LOD in all matrices. This is not the pattern we would expect to find if snow scavenging was a driver for cVMS concentrations in this region. On the contrary, we would expect D6 to be more prominent, as D6 has the higher potential to be scavenged by snow (Xu & Vogel, 2021).

The snow sample processing unit developed for cVMS analysis was unable to provide meaningful data to determine the actual content of cVMS in snow from the Zeppelin Mountain, given comparatively high field blank contamination levels. Nonetheless, all cVMS showed good results from spike recovery tests, despite several potential mechanisms for losses during processing the snow samples (for example during melting the sample or extraction). However, further method development to reduce contamination associated with sampling, extraction, transport and/or storage is essential before further snow sampling at background Arctic/Antarctic locations. Further work is being conducted to improve the performance of the unit, and further testing is proposed in an urban area where air concentrations are much higher. This will likely increase the potential to find detectable levels of cVMS in snow. This information might in turn contribute to improve our understanding of the potential for snow to scavenge cVMS from the atmosphere.

Our investigation of cVMS content in environmental compartments which may be recipients of cVMS from snow melt, does however contribute to the ongoing debate on the potential for cVMS to undergo long range atmospheric transport and subsequent deposition during snowfall. The non-detectable/low cVMS concentrations in soil, vegetation, sediments, and fish are in line with most current research on cVMS in remote regions, which together suggest that the input of cVMS from atmospheric deposition and snow melt is likely not a major contributing source.

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# Appendix 1

*Table A 1 Metadata marine biota samples*

| Sample code | Species | Location | Date | Length (cm) | Sex |
|---|---|---|---|---|---|
| **2023-KF-FI-NV-A** | Shorthorn Sculpin | Kongsfjorden | 23.09.2023 | 22 | Female |
| **2023-KF-FI-NV-B** | Shorthorn Sculpin | Kongsfjorden | 23.09.2023 | 22 | Female |
| **2023-KF-FI-NV-C** | Shorthorn Sculpin | Kongsfjorden | 23.09.2023 | 20 | Male |

*Table A 2 Solvent blanks, expanded study*

| | D4 (ng) | D5 (ng) | D6 (ng) |
|---|---|---|---|
| **LB 1 solvent** | 0,21 | 13,05 | 44,53 |
| **LB 2 solvent** | 0,075 | 0,316 | 0,246 |
| **LB 3 solvent** | 0,108 | 0,527 | 0,536 |
| **LB 4 solvent** | 0,091 | 0,286 | 0,193 |
| **Blank 4 solvent** | 0,273 | 0,705 | 0,212 |
| **Blank 5 solvent** | 0,303 | 0,743 | 0,228 |
| **Blank 6 solvent** | 0,285 | 0,741 | 0,217 |
| **Blank 4 soil solvent** | 0,387 | 1,505 | 0,97 |
| **Blank 5 soil solvent** | 0,215 | 0,516 | 0,459 |
| **Blank 6 soil solvent** | 0,169 | 0,48 | 0,295 |
| **Blank 4 veg solvent** | 0,167 | 0,405 | 0,31 |
| **Blank 5 veg solvent** | 0,227 | 0,788 | 0,918 |
| **Blank 6 veg solvent** | 0,212 | 0,528 | 0,456 |
| **Blank 4 solvent sed** | 0,115 | 0,397 | 0,219 |
| **Blank 5 solvent sed** | 0,094 | 0,49 | 0,399 |
| **Blank 6 solvent sed** | 0,092 | 0,385 | 0,243 |

*Table A 3 XAD2 blanks, expanded study*

| | D4 ng/g | D5 ng/g | D6 ng/g |
|---|---|---|---|
| **FB blind 1 XAD-2** | 0,401 | 1,342 | 0,063 |
| **FB blind 2 XAD-2** | 0,462 | 1,527 | 0,119 |
| **FB blind 3 XAD-2** | 0,390 | 1,372 | 0,608 |
| **FB blind 4 XAD-2** | 0,254 | 1,281 | 0,077 |
| **Blank 1 XAD-2** | 0,303 | 2,835 | 0,114 |
| **Blank 2 XAD-2** | 0,229 | 2,636 | 0,024 |
| **Blank 3 XAD-2** | 0,174 | 1,229 | 0,000 |
| **Blank 1 soil XAD-2** | 0,245 | 1,593 | 0,000 |
| **Blank 2 soil XAD-2** | 2,353 | 3,899 | 1,346 |
| **Blank 1 veg XAD-2** | 0,410 | 1,885 | 0,000 |
| **Blank 2 veg XAD-2** | 0,599 | 3,645 | 0,468 |
| **Blank 3 veg XAD-2** | 0,391 | 2,216 | 0,060 |
| **Blank 1 XAD-2 sed** | 0,637 | 3,240 | 0,166 |
| **Blank 2 XAD-2 sed** | 0,478 | 2,667 | 0,059 |
| **Blank 3 XAD-2 sed** | 0,460 | 2,432 | 0,085 |
| **Blank 3 soil XAD-2** | 7,371 | 9,588 | 12,738 |

*Table A 4 Solvent blank corrected field blanks, expanded study*

| | D4 ng/g | D5 ng/g | D6 ng/g |
|---|---|---|---|
| **2023-N -FI-FB** | 0,460 | 2,149 | 0,712 |
| **2023-RM-FI-FB-A** | 0,611 | 1,385 | 0,037 |
| **2023-KF-FI-FB** | 0,317 | 1,657 | 0,058 |
| **2023-ZP-VG-FB-A** | 0,347 | 3,245 | 0,168 |
| **2023-NÅ-SL-FB-C** | 0,124 | 0,950 | -0,198 |
| **2023-NÅ-SL-FB-E** | 0,226 | 2,375 | -0,239 |
| **2023-RM-SL-FB-A** | 0,241 | 0,847 | -0,268 |
| **2023-RM-SL-FB-B** | 0,207 | 0,823 | -0,201 |
| **2023-NÅ-VG-FB-A** | 0,316 | 2,849 | 0,116 |
| **2023-NÅ-VG-FB-D** | 0,262 | 1,077 | 0,326 |
| **2023-RM-VG-FB-A** | 0,248 | 1,399 | 0,166 |
| **2023-RM-VG-FB-B** | 0,258 | 1,276 | 0,252 |
| **2023-NÅ-SD-FB** | 0,371 | 2,951 | 0,025 |
| **2023-RM-SD-FB-A** | 0,395 | 1,825 | 0,250 |
| **2023-RM-SD-FB-B** | 0,326 | 1,081 | 0,000 |
| **2023-ZP-SL-FB-A** | 4,165 | 3,612 | 0,605 |

*Table A 5 XAD-2 corrected FBs, negative values were assigned zero values, extreme values were not included in LOD and LOQ calculation*

| | D4 ng/g | D5 ng/g | D6 ng/g |
|---|---|---|---|
| **2023-N -FI-FB** | 0,08 | 0,77 | 0,50 |
| **2023-RM-FI-FB-A** | 0,23 | 0,00 | 0,00 |
| **2023-KF-FI-FB** | 0,08 | 0,00 | 0,01 |
| **2023-ZP-VG-FB-A** | 0,11 | 1,01 | 0,12 |
| **2023-NÅ-SL-FB-C** | 0,00 | 0,00 | 0,00 |
| **2023-NÅ-SL-FB-E** | 0,00 | 0,00 | 0,00 |
| **2023-RM-SL-FB-A** | 0,00 | 0,00 | 0,00 |
| **2023-RM-SL-FB-B** | 0,00 | 0,00 | 0,00 |
| **2023-NÅ-VG-FB-A** | 0,00 | 0,27 | 0,00 |
| **2023-NÅ-VG-FB-D** | 0,00 | 0,00 | 0,18 |
| **2023-RM-VG-FB-A** | 0,00 | 0,00 | 0,02 |
| **2023-RM-VG-FB-B** | 0,00 | 0,00 | 0,11 |
| **2023-NÅ-SD-FB** | 0,00 | 0,17 | 0,00 |
| **2023-RM-SD-FB-A** | 0,00 | 0,00 | 0,15 |
| **2023-RM-SD-FB-B** | 0,00 | 0,00 | 0,00 |
| **2023-ZP-SL-FB-A** | 3,93 | 1,38 | 0,56 |
| | | | |
| **Average** | 0,034 | 0,148 | 0,073 |
| **Standard deviation** | 0,067 | 0,315 | 0,133 |
| | | | |
| **LOD** | 0,24 | 1,09 | 0,47 |
| **LOQ** | 0,71 | 3,29 | 1,41 |

# Appendix 2

## Development of a novel snow sample processing unit

cVMS are volatile, hydrophobic and undergo degradation processes in water, properties which make it highly challenging to analyse these compounds in snow. In addition, concentrations in snow in remote areas such as Svalbard could be expected to be low (Xu & Vogel, 2021). As far as we are aware, no one have previously reported on cVMS levels in snow.

### 1. Design of the snow sample processing unit

A new technique was developed for the accurate collection, storage and processing of snow samples for cVMS analysis. The snow sample processing unit is shown in Figure A1. The processing unit consists of a ~35L stainless-steel tank with a ~20 cm top opening which was modified for the purpose. The tank was selected for its relatively large size to accommodate a large amount of snow, while the large opening on the tank ensured that snow could be filled with minimal surface contact to avoid sample contamination. The tank seal is gas-tight in order to contain cVMS which enter the gas phase during the melting stage. The tank was fitted with heating elements on the outside to assist snow melting. $N_2$ gas could be connected via stainless-steel fittings to pressurize the tank. This forced the melted sample through a cylinder containing approximately 100 g XAD-2 sorbent (ultra clean resin, XAD-2 equivalent) and then further into a waste bottle to enable volume measurement. The XAD-2 collected cVMS from the meltwater and from the tank headspace air. The XAD-2 filled cylinder was fitted with an internal stainless-steel mesh which holds the XAD-2 in place, and captures larger particles (>XX µm) from the snow. Smaller particles in the snow are captured by the XAD-2.

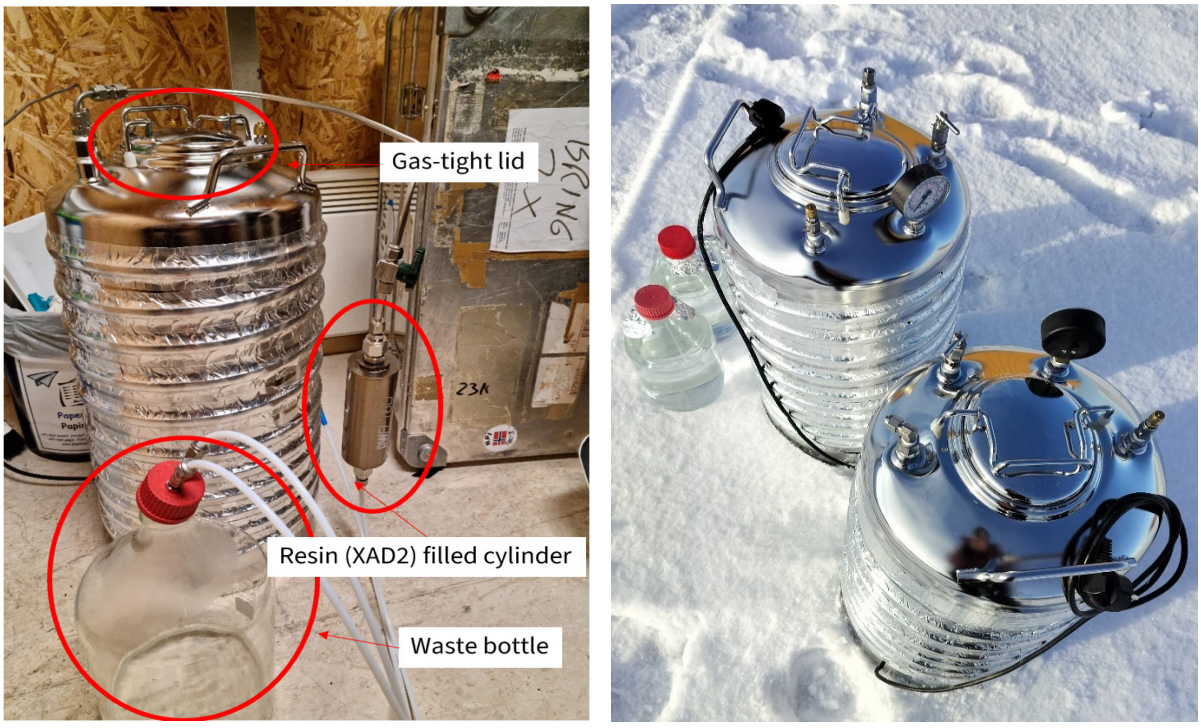


*Figure A 1 Snow sample processing unit (left), and snow sample processing unit tanks in the field (right) (Photos: NILU).*

# 2. Methods

## 2.1. Sampling

The tank, its fittings and the snow sampling shovel were cleaned with high purity acetone before use.

For collection of snow samples, clean tanks which had all openings sealed were brought to the Zeppelin Mountain (Figure A1, right). Bottles of MilliQ water were brought for use as field blank. The bottles for the field blanks were burned before use, and only briefly opened for filling with MilliQ water in the lab, and during transfer to a snow sample processing unit in the field.

Snow was sampled as soon as possible following a snowfall event. Surface snow, to a depth representing the most recent precipitation event, was collected into the tanks using a stainless-steel shovel which was slightly smaller than the tank opening (Figure A2). The opening of the tank was closed gas-tight after the tank had been completely filled with snow. The volume of snow sampled was determined by measuring the area and depth of the sampled snow patch. Snow temperature was recorded using a temperature probe, and the structure of the snow was assessed by visual inspection and recorded by photography.

## *2.2. Sample preparation*

After being brought back to Ny-Ålesund, the tank was pressurised with high purity $N_2$ gas and heated via the external heating element to melt the snow contained inside (Figure A 1). When the snow was completely melted, the sample was pushed through the cylinder containing the XAD-2. Once the melted sample had passed through the XAD-2, the remaining headspace gas and added $N_2$ gas in the tank was passed through the XAD-2. The sampler was then pressurised a further three times and pushed through the XAD-2 cylinder to ensure complete transfer of the original headspace gas through the XAD-2. This ensured that any cVMS contained in air within the snow which was sampled, or cVMS re-volatised to the headspace air during sample melting, was captured by the XAD-2. The XAD-2 filled cylinders were then sealed, stored frozen, and brought back to the lab in Tromsø for cVMS analysis.

Figure A 2 *Collecting snow samples at the Zeppelin Mountain (Photos: NILU).*

### 2.3. Analysis

The XAD-2 was placed in a gas-tight jar along with acetone/hexane (1:1) and $C^{13}$ labelled D4, D5 and D6 for internal standards, and extracted using an orbital shaker. Recovery standard was added to a sub-sample before analysis on GC/MSD, as described in Halvorsen (2024).

### 2.4. Quality control

To determine loss through volatilisation, degradation or breakthrough during processing of snow samples, spike experiments were conducted on snow samples in the field using native cVMS; D4, D5, and D6. To create the spike solutions, 400 ng (high spike level) and 100 ng (low spike level) of D4, D5 and D6 were dissolved in approximately 10 mL of acetone. The spike solutions were brought to the field and added to the snow sample in the processing unit tank immediately after sampling. The tank was subsequently sealed. To be able to distinguish the spiked cVMS from any cVMS present in the snow, parallel snow samples were collected for the spike experiments, where one of the parallels were spiked, and the background cVMS level in snow from the other parallel was subtracted from the results from the spiked snow sample.

Field blanks consisting of approximately 5 L MilliQ water was brought to the Zeppelin Mountain and filled into an identical parallel sampling tank. Handling of the snow field blanks was as similar as possible to actual snow samples. However, for the melting process the treatment differed between snow samples and field blanks. Field blanks were not left with heating on for the same amount of time as snow samples, as we suspected this might lead to degradation and/or volatilization to a larger degree in field blanks compared to samples. During the snow melting process, heating of the sample will act to melt the snow, and not heat the melted sample water, provided there is snow remaining to be melted. For the field blank, sample heating will contribute to heating the water, allowing this to reach much higher temperatures quickly compared to the samples. This in turn might contribute to non-representative cVMS degradation in the field blanks.

In the lab, solvent blanks and XAD-2 lab blanks were included along with snow XAD-2 samples. Samples and field blanks were blank corrected based on XAD-2 lab blanks.

## 3. Results

### 3.1. Quality control samples

Results from spike recovery experiments are shown in Figure A3. At the high spike level, recovery ranged from 60 – 86 %, and at the low spike level recovery ranged from 38 – 64 %. Considering the multiple routes for potential loss during snow sample processing (volatilisation, degradation in meltwater, breakthrough), these recoveries are considered to be good for the high spike level. However, the lower recoveries obtained at the low spike level could suggest that the method is associated with more uncertainty at low cVMS levels.

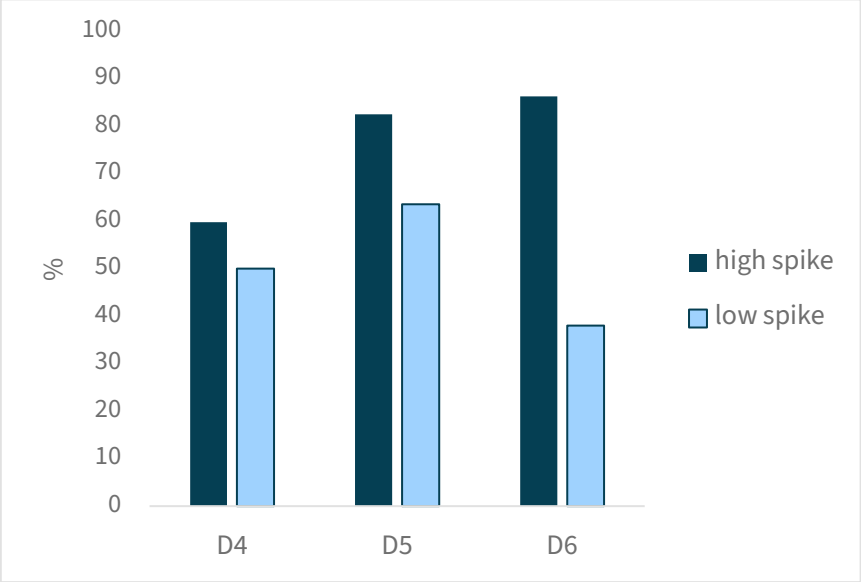


Figure A 3 *Recovery of D4, D5 and D6 from spike experiments using snow samples.*

XAD-2 blanks from the lab contained low levels of cVMS, providing low LODs (D4: 0.03 ng/g XAD-2, D5: 0.2 ng/g XAD-2, D6: 0.1 ng/g XAD-2). Converted to ng/L meltwater based on average amounts of XAD-2 and meltwater this is equivalent to 0.4, 2 and 1 ng/L meltwater for D4, D5 and D6 respectively.

### 3.2. Samples

Unfortunately, the cylinders used for XAD-2 in this study showed some structural malfunctioning as a consequence of excessive heat treatment used to prevent cVMS contamination. This resulted in failure of the thread in the seal of the cylinders, which resulted in the cylinders not being water (or gas) tight. Consequently, high blank contribution in samples were found. The field blanks for snow samples were thus variable and high. Unfortunately, the obtained values are too high in the field blanks to give any meaningful information regarding the content of cVMS in snow at the Zeppelin Mountain.

## 4. Discussion and Conclusion

Despite these challenges, the snow sampler shows promise for future studies. A future study might first aim to measure snow in an urban environment to find detectable levels of cVMS in snow. Combined with parallel air sampling of cVMS, this might enable a better understanding of the potential for snow to scavenge cVMS from the air during snowfall.

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