# An inter lab comparison of cyclic siloxanes in codfish collected from the Oslo Fjord

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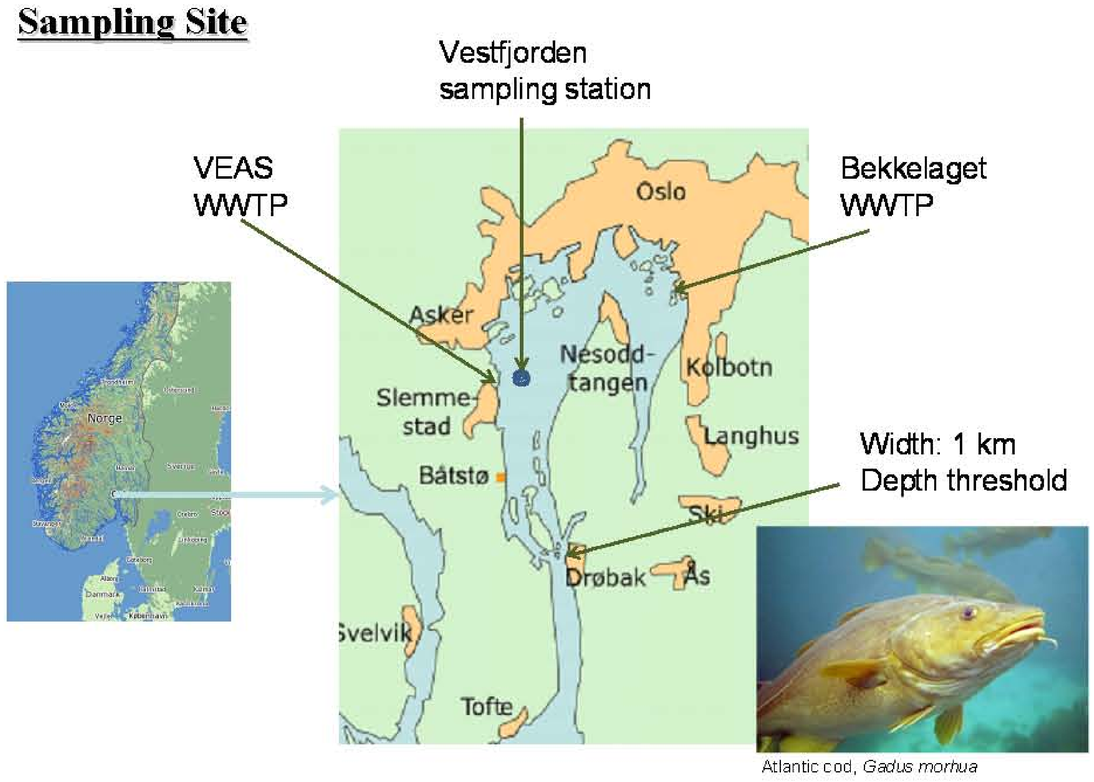
## Introduction

Cyclic volatile methylsiloxanes are high-volume chemicals used in a number of industrial applications and consumer products. They are currently undergoing risk assessment by the European Commission. Detection of cVMS in the Nordic environment have been reported in sediment, biota, WWTP influent and air[1-3]. In order to evaluate the analytical procedures for cVMS for the first time, an analytical comparison of codfish livers was performed across three separate labs: Norwegian Institute for Air Research (NILU), Evonik, and Dow Corning (DCC). Seventeen whole Atlantic cods were collected from the inner Oslofjord by the Norwegian Institute for Water Research (NIVA) and stored frozen. Each Laboratory received five to six whole frozen fish and processed the fish according to each laboratory's protocol. Portions of the liver after dissection and homogenization were divided and sent to all 3 labs for analysis. Each lab used their standard analytical method to analyze the liver homogenates for hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) by GC-MS. The observed concentrations from the 3 analytical laboratories were tabulated and compared for consistency.

## Sampling Site




Atlantic cod, *Gadus morhua*

## Study Design

•Seventeen whole Atlantic cod fish were collected In December 2007 from the inner Oslofjord.

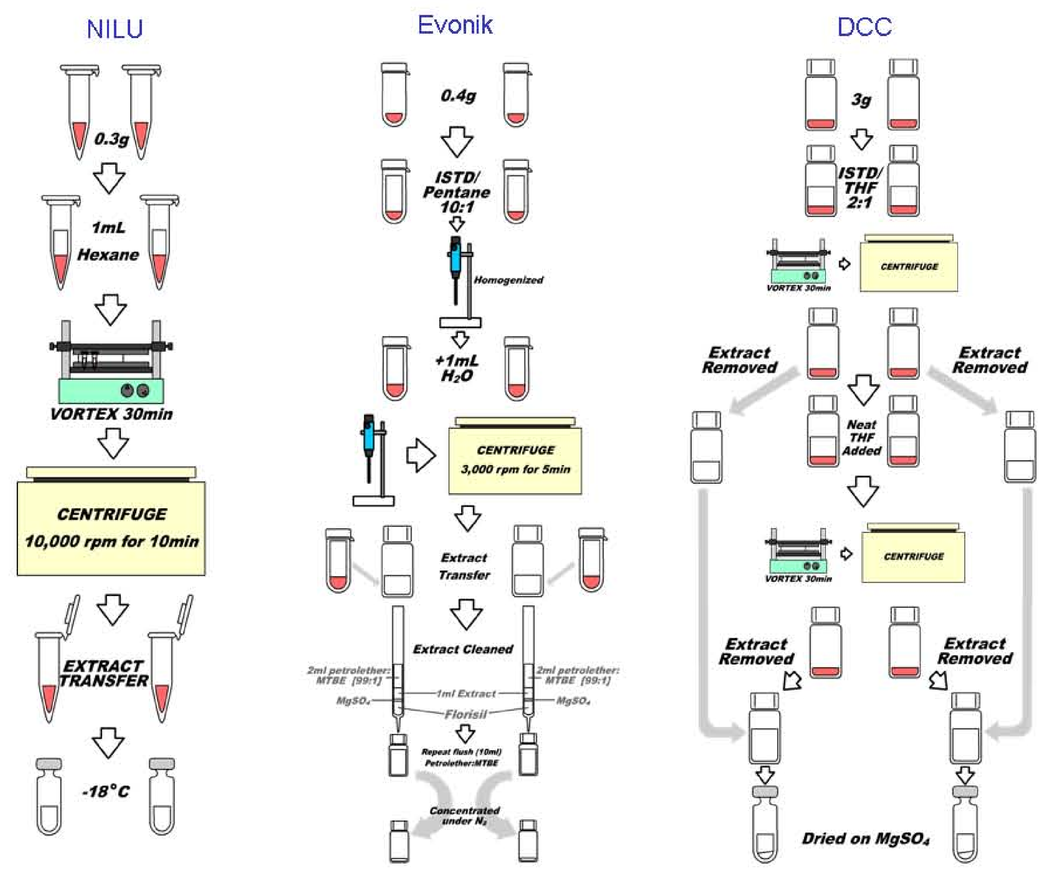
•The samples were divided into three sets using a randomized block design with six blocks: 2 size groups across 3 labs.

•Each laboratory received five to six whole frozen fish and processed the fish (harvesting and homogenization of liver) according to each laboratory's protocol.

•At each laboratory, liver homogenates were divided and portions were sent to the other 2 labs for analysis.

•Each lab used their standard analytical method to extract and analyze the liver homogenates

## Sample preparation and analysis




| Parameter | DCC | Evonik | NILU |
|---|---|---|---|
| Instrument | Agilent 6890 GC | Agilent 6890 GC | Agilent 5890 N GC |
| | Agilent 5973 MSD | Agilent 5973 MSD | Waters Autospec-V Ultima HRMS, R>10 000 |
| Inlet conditions | Splitless | Cool on-column | Splitless |
| | 1 µL | 1 µL | 1 µL |
| | 150 °C | --- | 200 °C |
| Column | Zebron ZB-5 (30 m × 0.25 mm × 0.25 µm) | Agilent DB5-HT (30 m × 0.25 mm × 0.10 µm) | Agilent J&W Ultra-2 (25 m × 0.20 mm × 0.11 µm) |
| Oven start temp | 50 °C (hold 3 min) | 40 °C | 35 °C (hold 3 min) |
| Transfer line | 280 °C | 300 °C | 270 °C |
| Analyte m/z | 207 (D3), 281 (D4), 355 (D5), 429 (D6) | 207 (D3), 281 (D4), 355 (D5), 341 (D6) | 207.0329 (D3), 281.0517 (D4), 355.0705 (D5), 429.0893 (D6) |
| ISTD m/z | 281 (M4Q), 285 ($^{13}$C-D4), 360 ($^{13}$C-D5), 435 ($^{13}$C-D6) | 285 ($^{13}$C-D4), 360 ($^{13}$C-D5), 345 ($^{13}$C-D6) | --- |

## Calculation of Detection Limits

Each laboratory used a separate definition of Limit of Detection:

DCC and Evonik: LOD = 3*SD of Matrix blank response

NILU: LOD = 3* Hexane blank response
(If no blank response: Peak-to-peak S/N 3:1 (MassLynx))

**Method Detection Limit**:

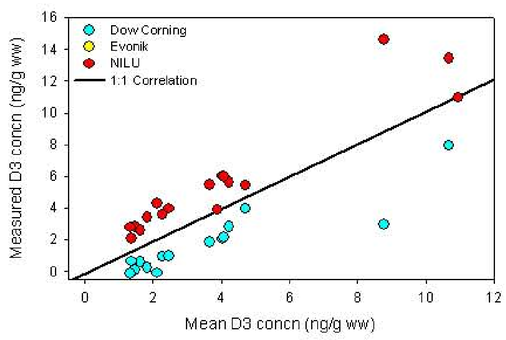
MDL = t * SD of matrix

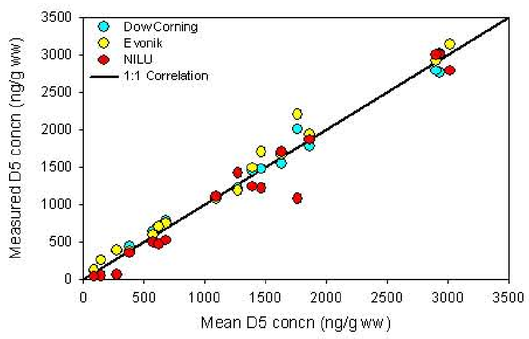
- DCC – non-spiked codfish liver (n = 3)
- Evonik – blank wolffish liver (n = 6)
- NILU – spiked codfish liver (n = 5)

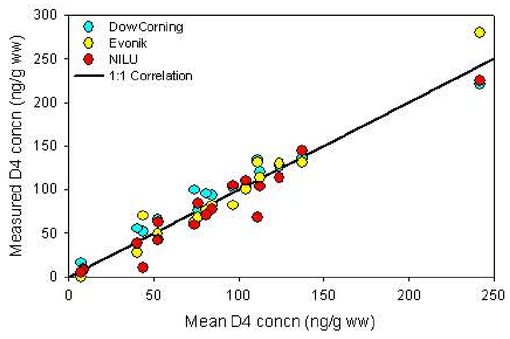
## Summary of cVMS Concentrations

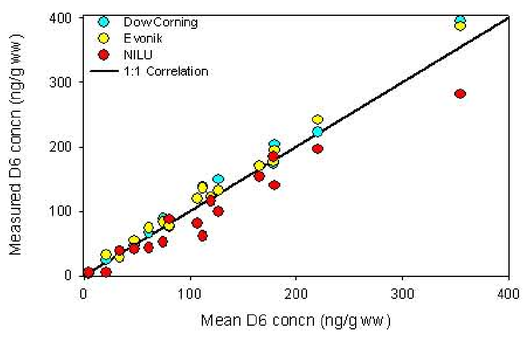
| | | D3 (ng/g ww) | | D4 (ng/g ww) | | | D5 (ng/g ww) | | | D6 (ng/g ww) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fish ID | Processor | DCC | NILU | DCC | Evonik | NILU | DCC | Evonik | NILU | DCC | Evonik | NILU |
| OCF-07 | DCC | 0.1 | 2.9 | 52 | 70 | 10 | 379 | 384 | 62 | 24 | 33 | 5.9 |
| OCF-08 | DCC | 0.9 | 3.6 | 66 | 49 | 42 | 778 | 743 | 520 | 67 | 74 | 44 |
| OCF-10 | DCC | 0.3 | 3.4 | 94 | 82 | 77 | 1477 | 1698 | 1221 | 119 | 120 | 81 |
| OCF-02 | DCC | 2.8 | 5.6 | 128 | 130 | 114 | 3137 | 3141 | 2790 | 396 | 387 | 282 |
| OCF-15 | DCC | -0.1 | 4.3 | 120 | 114 | 104 | 1456 | 1489 | 1238 | 204 | 195 | 140 |
| OCF-13 | DCC | 0.7 | 2.1 | 17 | -0.2 | 5.4 | 111 | 116 | 36 | -6 | 2.2 | 1.6 |
| OCF-09 | Evonik | -0.1 | 2.8 | 55 | 28 | 38 | 433 | 368 | 347 | 47 | 55 | 42 |
| OCF-06 | Evonik | 1.9 | 5.5 | 95 | 77 | 71 | 638 | 591 | 495 | 149 | 132 | 99 |
| OCF-12 | Evonik | 7.9 | 13 | 221 | 280 | 225 | 1785 | 1938 | 1865 | 223 | 242 | 197 |
| OCF-14 | Evonik | 2.2 | 6.0 | 136 | 131 | 145 | 2770 | 3023 | 3007 | 121 | 122 | 116 |
| OCF-11 | Evonik | 3.0 | 15 | 103 | 82 | 105 | 2788 | 2921 | 2999 | 174 | 177 | 184 |
| OCF-01 | NILU | n.a | 3.9 | n.a | 9.0 | 7.9 | n.a | 252 | 40 | n.a | 3.7 | 5.6 |
| OCF-03 | NILU | 2.1 | 6.0 | 100 | 63 | 59 | 707 | 703 | 462 | 89 | 83 | 52 |
| OCF-05 | NILU | 0.6 | 2.6 | 134 | 131 | 68 | 2009 | 2199 | 1078 | 138 | 136 | 62 |
| OCF-04 | NILU | 4.0 | 5.5 | 103 | 100 | 110 | 1212 | 1185 | 1419 | 77 | 78 | 88 |
| OCF-17 | NILU | n.a | 11 | n.a | 43 | 62 | n.a | 1081 | 1106 | n.a | 29 | 39 |
| OCF-16 | NILU | 1.0 | 4.0 | 76 | 68 | 84 | 1542 | 1664 | 1697 | 171 | 170 | 154 |
| **Method Detection Limit (MDL)** | | **7.7** | **3.1** | **3.2** | **7.6** | **4.7** | **23** | **15** | **8.5** | **11** | **6.5** | **10** |

The results shown are uncensored data.



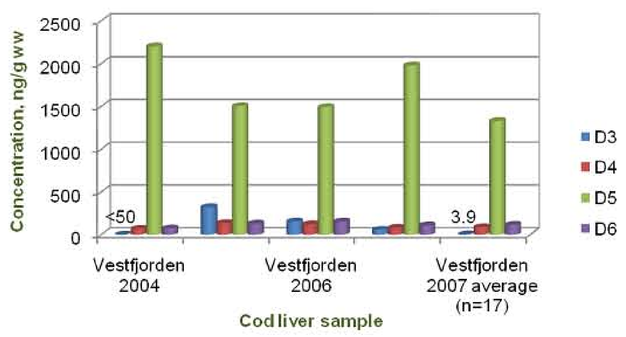

## Conclusions

•While methods for extraction and processing of liver samples were quite different, overall agreement in observed concentrations was relatively good; however there were statistical differences:

- –There was no statistical difference between NILU and Evonik for D4 and D6, but there was a statistical difference for D5
- –There was no statistical difference between DCC and Evonik for D4, D5 and D6
- –There was no statistical difference between NILU and DCC for D4 but there was a statistical difference for D3, D5 and D6
- –No statistical difference between labs in the preparation of the liver homogenates

•There was good agreement with previous Oslo Fjord cod liver results [1,3]

•Methods used in calculation of detection limits were different for all 3 laboratories and a limitation of this study is that a common set of data (matrix and replicates) were not defined up front to allow for a consistent determination of LOD, and MDL, across all 3 labs. This should be considered in future inter-lab comparisons.




1) Nordic cCouncil of Ministers, TemaNord 2005:593, *Siloxanes in the Nordic Environment*, L. Kaj et.al., 2005
2) Swedish Environmental Research nstitute (IVL), Report B1643, *Results from the Swedish Nathonal Screening Programme 2004. Subreport 4: Siloxanes.* L Kaj et.al., 2005
3) Norwegian Pollution Control Authority (SFT), TA-2269/2007. *Siloxanes in the Environment of the Inner Oslofjord.* M. Schlabach et.al, 2007.

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